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STUDY OF THE EFFECT OF CO_2O_3 AND CUO ADDITIVES ON GROUND ENAMEL OBTAINED IN THE SIO_2–AL_2O_3–NA_2O–K_2O–CAO–B_2O_3–NIO SYSTEM

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Abstract

The purpose of this work is to study the effect of Co_2O_3 and CuO additives on the adhesion of ground coatings obtained in the SiO_2–Al_2O_3–Na_2O–K_2O–CaO–B_2O_3–NiO system. To achieve this goal, glasses were synthesized in the SiO_2–Al_2O_3–Na_2O–K_2O–CaO–B_2O_3–NiO system based on local raw materials with the addition of Co_2O_3 and Cu O. Ground enamels based on these glasses were obtained and their properties were studied. The obtained data show that the most important influence on the adhesion to the steel surface is exerted by copper, nickel and cobalt oxides. The conclusion is made about the predominant effect of copper oxide on the bond strength and about the positive effect of the combined presence of copper and cobalt oxides.

Keywords: *Adheison, ground enamel, enamel coatings, the system*

Introduction

The adhesion of enamel to metal is one of the main characteristics of the metal-enamel system; it determines the stability of the system even before the product enters service. After firing enameled products, a firmly bonded coating is obtained on the metal. The practice of enameling, as well as a large number of research papers, has established the dependence of adhesion strength on a number of factors, such as stresses in the enamel layer, elasticity of enamel and metal, thickness of the enamel layer and other factors (Petzold, A., Peschmann, G., 1990).

The ground creates the best conditions for the adhesion of the coating enamel to the protected surface. The adhesion must be strong enough so that the coating layer cannot be separated from the metal by chemical or mechanical action. The adhesion strength is the force normally directed towards the substrate–enamel interface and necessary for the complete separation of the coating from the substrate over the entire test surface. However, a rupture can occur along one of the interface boundaries (adhesive separation), or along the intermediate layer material and even along the coating or substrate material (cohesive rupture). A mixed nature of the gap is also possible [4]. Therefore, after preliminary preparation of its surface, ground enamel is applied to the product, dried and fired at 850–900 °C, and then the cover enamel is applied in one or more layers with drying and subsequent firing at the same temperature (Bobkova, N. M., Dyatlova, E. N., Kunitskaya, T. S., 1987).

The adhesion of ground glass enamel to steel depends on the duration of contact of the melt with the surface of the substrate, i.e. on the firing time of the enameled product. The increase in adhesion over time has a limit. At a certain point, it stops and the further continuation of the firing becomes harmful. A thick layer of scale is formed under the coating layer which easily breaks off from the steel along with the enamel (Pashchenko, A.A., 1983).

The quality of the enamel coating significantly depends on the adhesion strength to the metal, therefore, it is desirable to enhance the adhesive properties of the ground with metal (Shimizu, T., Jiang, Z.H., Shirasak, M., 1998).

The adhesion strength of enamel to metal depends on several factors, such as the type of metal and enamel, coating thickness, application method, firing conditions, and others (Bragina, L.L., Zubekhin, A.P., 2003).

The strong adhesion of enamel to metal is ensured with adjustments of the thermal coefficient of linear expansion (TCLE) of metal and enamel. The TCLE of the enamel should be less than that of the metal, otherwise there will be a violation of the continuity of the layer. Tensile stresses occur during the cooling of the spread enamel (Kazmina, O.V., Elistratova, A.V., 2022).

To obtain high-quality enamel coatings, ground enamels must meet the following requirements: ensure good adhesion strength of the enamel layer to the metal, decompose iron oxides formed during the firing of ground coatings, contribute to the presence of iron in the melt in the form of divalent ions, have surface tension and viscosity to spread well, moisten oxidized metal and contribute to release of gases, have an insignificant thickness of the burnt coating (Technology of fibrous materials and coatings. 2014).

As a result of the study of multicomponent glass-enamel coatings on stainless steel, the prospects of creating coatings by introducing ions of alkaline earth elements with different ion radius into the borosilicate glass mesh (Novoselova, P.N., Semin, M.A., 2011) are shown.

A study of multicomponent enamels based on borosilicate glasses has been carried out (Ehrt, D., 2013; Topper, B., Möncke, D., Youngman, R.E., Valvi, Ch., Kamitsos, E.I., Christos, P.E. Varsamis, Ch.E.I., 2023).

The study of the dependence of the adhesion strength in the steel – glass enamel coating system on the specifics of the steel oxidation process. Temperature and time conditions of heat treatment is one of the most important factors in enameling, in particular 2C/1F technology. Since the enamel interacts with the metal during firing and forming a boundary zone that provides adhesion, the bond strength of the coating with the metal depends on the composition, structure of this zone and the firing temperature. The bonding process is associated with the formation of a double electric layer at the enamel boundary with an oxide film, not with pure metal. Oxygen plays an important role in the interaction processes, as well as the adhesion oxides included in the enamel, due to which electrochemical reactions occur at the phase interface, during which a transition layer is created that provides strong adhesion of enamel to metal (Soshina, T.O., Muxamadyarova, V.R., 2019; Yatsenko, E.A., 2010).

Based on the results of the study of the field of glass formation in the K_2O-RO-B_2O_3-Al_2O_3-SiO_2-TiO_2-P_2O_5-F system, the synthesis of single-layer glass-crystalline white enamel coatings was carried out. As a result of the research, a technology has been developed for the production of white glass-crystalline enamel coatings on household steel products with improved aesthetic and consumer properties (Klimova L.V., 2017).

The possibility of using glasses based on the basic Na_2O–CaO–TiO_2–SiO_2 system to obtain fluorine-free, non-porous ground coatings has been investigated. The optimal concentration of adhesion oxide (CoO) in the developed enamel compositions has been established. The influence of suspending materials on the characteristics of ground enamel coatings has been determined and their rational amount has been established. The obtained fluorine-free, boron-free ground coatings are recommended for production tests to use them in the enameling of steel products for household purposes (Bely, Ya. I., Kislichnaya, R. I., Nagornaya, T. I., Naumenko, S. Yu., Pavlova, K. V., 2013).

The composition of a complex adhesion promoter has been developed, containing a minimum amount of expensive CoO and NiO oxides and providing the necessary reactivity of the ground melt at a firing temperature of 800–820 °C due to the additional introduction of MnO_2 and Fe_2O_3. The specificity of the processes was revealed and the optimal conditions for the formation of the low–carbon steel system were established – a low-melting two-layer enamel coating of single firing at a temperature of 820 °C based on the developed soil, which contains a complex adhesion promoter in combination with white titanium enamel (Шалигина, О. В., 2006).

Today, to achieve saving it is customary to carry out single-layer enameling method to protect the metal surface from corrosion. However, single – layer enameling is not without drawbacks: The main focus that should be given to the mechanical properties is the adhesion of the glass-enamel coating to the metal, which is ensured by the oxides of Ni and Co. If these oxides are not present in the enamel, it is impossible to ensure adhesion during single-layer enameling. Ni and Co oxides should not be added to the coating enamel, since these oxides have a negative impact on human health. The advantage of double-layer enameling is the possibility of using Ni and Co oxides in the composition of the ground enamel, providing adhesion and using a coating enamel without the participation of these oxides.

Glasses were synthesized in the SiO_2–Al_2O_3–Na_2O–K_2O–CaO–B_2O_3–NiO system. The physical and technical properties of synthesized glasses are determined. Compositions that meet the regulatory requirements for ground enamels have been identified. The possibility of synthesizing ground enamels for household metal products based on local raw materials has been proved (Naimov, Sh.B., Aripova, M. H., 2023).

The purpose of this work is to study the effect of Co_2O_3 and CuO additives on the adhesion of soil coatings obtained in the SiO_2–Al_2O_3–Na_2O–K_2O–CaO–B_2O_3–NiO system.

Materials and Methods

Chemical analysis of the raw materials and synthesized glasses was determined on an energy-dispersive X-ray fluorescence spectrometer Rigaku CG EDXRF (USA).

The structure of the ground coating was studied using a scanning electron microscope JEOL JSM–IT200LA (Japan).

Glass melting was carried out in a gas laboratory furnace in fireclay crucibles with a capacity of 250 ml at a temperature of 1350 °C with exposure for 1 hour. The melt was poured into water and frit granules were obtained.

The temperature coefficient of linear expansion is determined on BK – POL16. Qingdao Chengyu Testing Equipment Co., Ltd.

The ground coating on DC04EK steel was obtained in accordance with the procedure given in (GOST 52569–2018).

The spreadability and adhesion strength of the soil coating to the base were determined in accordance with the methodology given in (GOST 52569–20180.

For the synthesis of glasses in the SiO_2–Al_2O_3–Na_2O–K_2O–CaO–B_2O_3–NiO system, the following raw materials were used: quartz sand from the Samarkand deposit; limestone of the Kashkadarya deposit; clay shale of the Jerdanak deposit (Table 1); technical soda ash GOST 5100–85; o.s.h. boric acid; pure CuO, pure NiO and Co2O3.

To obtain ground enamel, we used the addition of ch.o. grade fireproof clay.

Table 1. *Chemical composition of raw materials*

Raw materials	Mass content of oxides,%											
	SiO_2	Na_2O	K_2O	CaO	Al_2O_3	B_2O_3	MgO	Fe_2O_3	NiO	Co_2O_3	CuO	п.п.п
Quartz sand	92.5	–	1.03	0.271	3.51	–	0.04	0.087	–	–	–	–
Limestone	0.31	–	0.034	53.40	0.23	–	5.03	0.06	–	–	–	40.94
Clay shale	0.676	–	0.04	0.525	96.8	–	–	0.84	–	–	–	1.12

Results

The chemical composition of the synthesized glasses is given in Table 2.

From the obtained data, it can be concluded that copper oxide has a predominant effect on adhesion strength and the positive effect of the combined presence of copper and cobalt oxides. Nickel content also affects the strength of the steel surface – the decrease in the amount of CuO is compensated by an increase in the NiO content (composition No. 3). Thus, we can conclude that the oxides of copper, nickel and cobalt have the most important influence on the amount of adhesion to a steel surface, which to a certain extent coincides with the results obtained by other researchers (Yatsenko, E.A., 2002; Chumakov, A.A., 2019; Yatsenko E.A., Dzyuba E.B., Veropakha N.V., 2012; Ken Chen, Minghui Chen, Fuhui Wang, Shenglong Zhu, 2017; Leila Samiee, Hossein Sarpoolaky, Alireza Mirhabibi, 2007).

Table 2. *Chemical composition of synthesized glass (frit)*

Composition index	Mass content of oxides,%												
	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	TiO_2	P_2O_5	MgO	NiO	Co_2O_3	CuO	Fe_2O_3	B_2O_3
№ 1	43.4	8.12	23.5	0.6	7.61	0.05	–	0.118	0.807	0.324	0.974	0.114	14.2
№ 2	44.2	8.95	22.4	0.562	7.67	0.05	–	0.116	0.429	–	0.677	0.12	14.64
№ 3	44.0	7.67	25.5	0.555	8.1	0.05	–	0.113	0.750	–	0.356	0.1	12.73
№ 4	48.2	8.9	22.2	0.653	7.69	0.07	–	0.121	0.815	0.314	0.653	0.135	10.1
№ 5	54.0	4.89	23.9	0.794	7.84	0.141	0.671	0.122	0.704	0.214	–	0.132	6.8
№ 6	52.0	3.73	29.0	0.684	6.21	0.08	0.705	0.659	0.721	0.223	–	0.127	6.5
№ 7	47.9	4.14	23.3	0.851	7.82	0.144	1.31	0.128	0.712	0.168	–	0.11	13.58
№ 8	47.2	4.71	25.9	0.804	5.61	0.115	1.33	0.06	0.671	0.151	–	0.121	13.48
№ 9	42.3	5.53	25.7	0.615	5.64	0.06	0.681	–	0.665	0.202	–	0.113	18.5

To obtain a ground enamel coating, a slip was prepared from finely ground frit, quartz sand and refractory clay. The properties of the resulting ground enamels are given in Table 3.

Table 3. *Properties of ground enamels*

Composition index	Temperature coefficient of linear expansion $\cdot 10^6$, K^{-1}	Spreadability, mm	Strength of adhesion to steel surface
№ 1	120	37	4,5
№ 2	117	30	4,0
№ 3	124	47	4,0
№ 4	115	37	4,5
№ 5	127	37	3,0
№ 6	140	45	3,5
№ 7	122	45	3
№ 8	129	44	2,5
№ 9	127	57	3

It can be noted that the predominant influence on the TCLE is exerted by the total content of oxides of alkali and alkaline earth metals and the total content of silicon and aluminum oxides. As can be seen from the data presented, compositions No. 1–4 and No. 7 meet the requirement for the value of thermal expansion coefficient of GOST 52569–2018. Therefore, we exclude compositions No. 6 and No. 8 from further studies.

Table 4. *Compliance of the resulting ground enamels with the flowability requirements*

Spreadability, mm according to "GOST R52569–2018 FRITTS Technical specifications"	Composition index	Spreadability, mm
Relatively refractory, component, 25–40 mm	№ 1	37
	№ 2	30
	№ 4	37
	№ 5	37
Medium fusibility, component, 35–55 mm	№ 7	45
	№ 3	47
Relatively low-melting, component, 50–70 mm	№ 9	57

It has been established that the synthesized compositions of ground enamel, when compared with the standard requirements correspond to the following groups in terms of spreadability: No. 1, 2, 4 and 5 are relatively refractory; No. 3, No. 6-No. 8 – to medium fusibility; No. 9 – to a relatively low-melting type. The latter result is easily explained by the high content of boron oxide in the composition of the ground enamel.

Figure 1 shows an electron microscopic image of ground enamel composition No. 1 on a steel surface. The intermediate layer that appeared at the contact between the soil and steel, which provided good adhesion, is clearly visible.

Figure 1. *Electron microscopic image of ground enamel composition No. 1 on a steel surface*

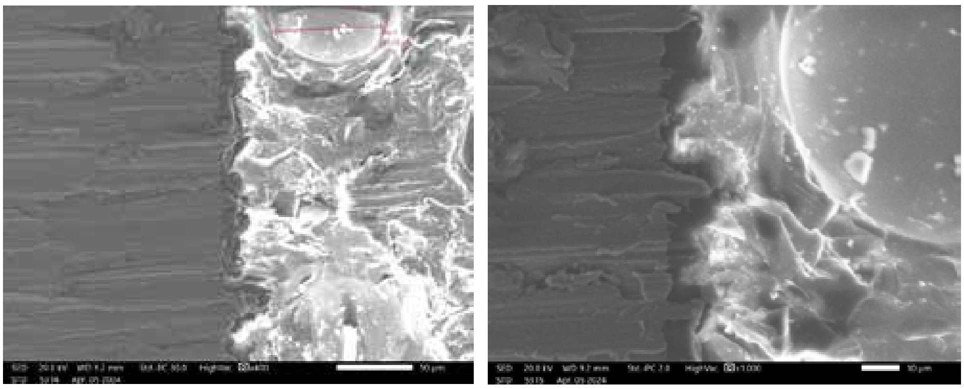
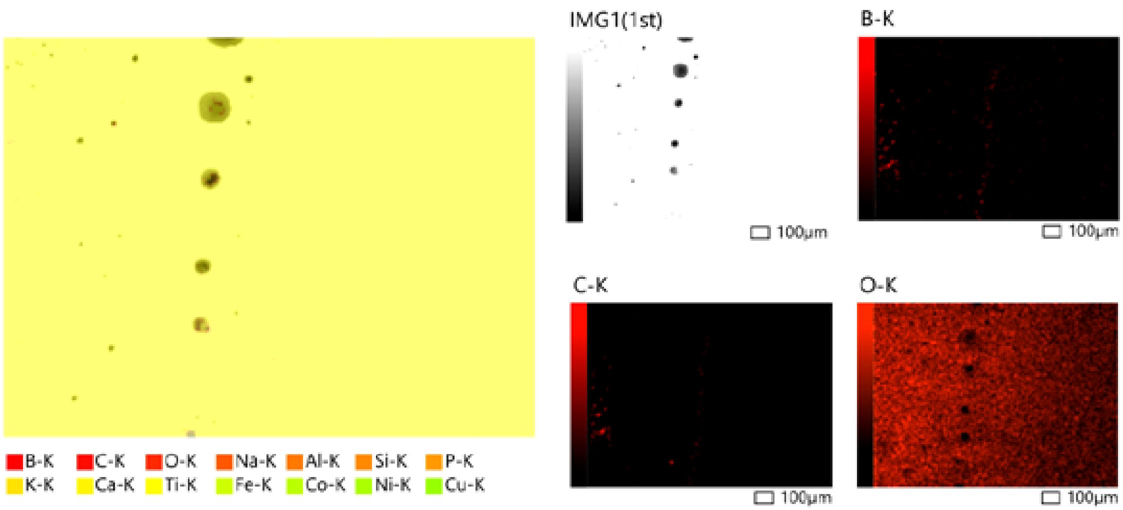
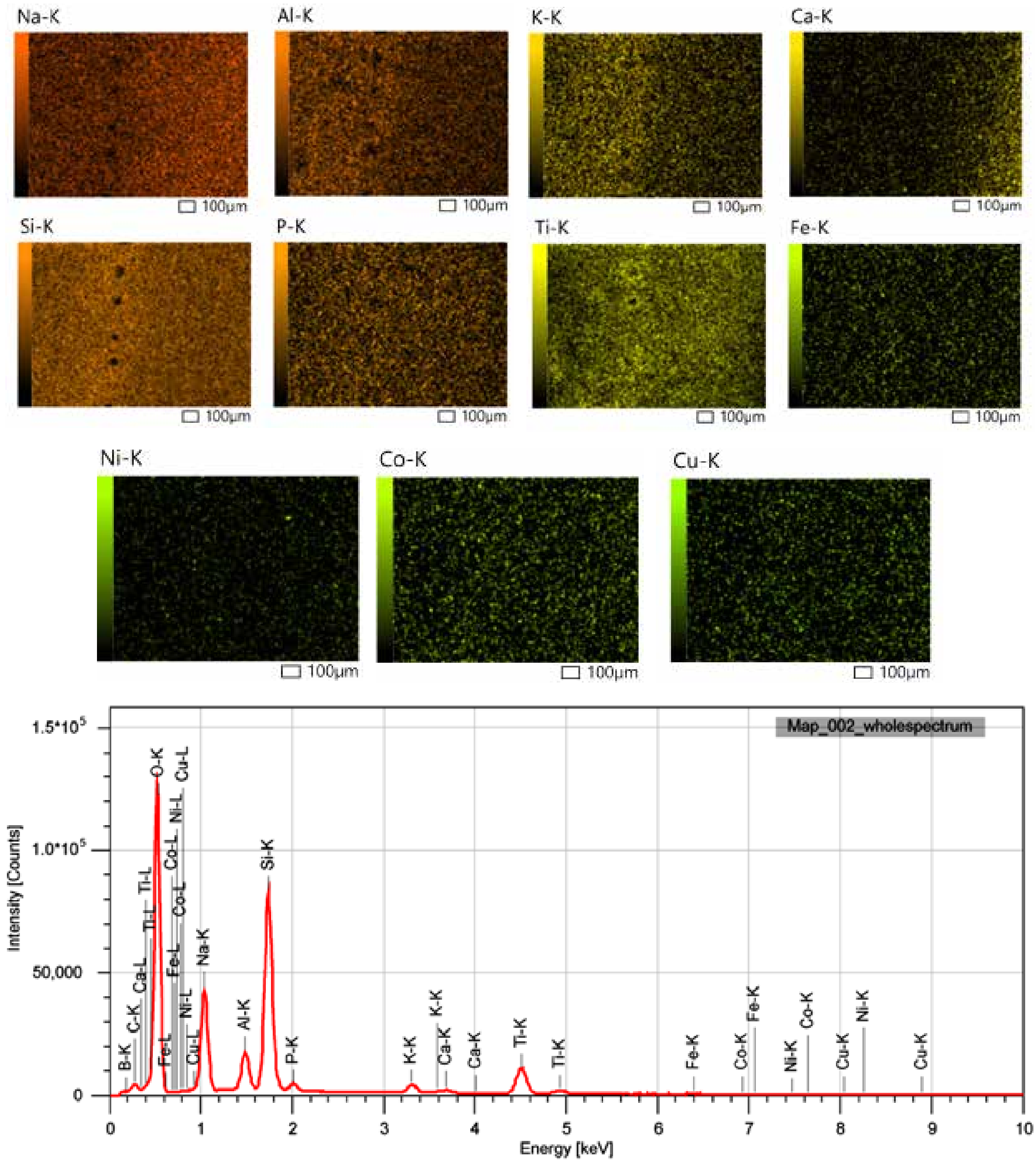


Figure 2 shows the results of EDS analysis of the surface layer of ground enamel

Figure 2. *EDS analysis of the surface layer of ground enamel*





EDS analysis of the soil surface showed that the soil elements are distributed predominantly evenly over the entire surface. The exception is boron, presumably due to enhanced penetration into the coating.

Discussion

The synthesis of glasses in the SiO_2–Al_2O_3–Na_2O–K_2O–CaO–B_2O_3–NiO system based on local raw materials with the addition of Co_2O_3 and CuO and the production of ground enamels based on these glasses showed that copper, nickel and cobalt oxides have the most important influence on the amount of adhesion to a steel surface. It was concluded that copper oxide has a predominant effect on adhesion strength and the positive effect of the combined presence of copper and cobalt oxides.

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