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Functional Corrosion-Resistant Enamel Coatings and Their Adherence Strength

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Functional corrosion-resistant glass enamel coatings make it possible to protect inner surface of oil pipelines in extreme operating conditions. The aim of this study is to propose competitive fluorine-free coatings for energy-effective direct-on enameling technology of pipes. The enamel coatings were applied on the steel surface by the slip method (coatings thickness 450 μm). Their physicochemical and production parameters were defined. The strong adhesion of synthesized enamels to the steel substrate has been achieved by using of the complex adherence promoter, containing optimal quantity of CoO and CuO oxides. The coatings forming mechanism on steel substrate by flexible regime 1 coat–1 firing have been studied. It is established that high level of the coating adhesion is the result of a complex heterogeneous interaction of metal with oxide melt, dissolution and diffusion processes and, as a consequence, intermediate layer formation at the phases boundary during melting (770–780 °C). As a result of conducted research, obtained nonnickel rust-resistant glass enamels have been accepted for production of steel pipes with enameled surface.

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1. Introduction

Nowadays, glass enamel-based materials have been considered as the most promising candidate for protecting of inner surface of steel pipelines from severe corrosion effects in service and being widely used in oil industry. These materials are extremely durable, at least 40–50 years for pipes at a temperature of exploitation up to 100 °C. Furthermore, the enamel protective coatings prevent from paraffin-oil gel deposits on the pipe walls.

The enamel protective coatings can be produced by various methods that typically rely on the use of system of coats of two layers — primer and cover, which vary in composition and functional characteristics and which were accomplished by regime 2C/2F (2 coats–2 firings) [1, 2].

However, industrial large-scale production often requires economical techniques. A new process of direct enameling of pipes is one of such possibilities. Using the latest single-layer enameling technology (1 coat–1 firing) can minimize the consumption of raw material and energy resources due to the decreased number of coating layers and firings [1–3].

This distinctive method is a viable, cost-effective solution to maintaining the integrity of your pipelines.

The present results suggest the new compositions of nonnickel low-melting one-coat glass enamels with addition of special complex adherence promoter to form a bonding phase. Nickel-free compositions can be of great interest for environmentally friendly applications, because nickel oxide is one of the basic oxides of adhesion along with cobalt oxide.

The present paper is focused on evaluation of enamel adherence to the steel surface as one of the most important parameters determining practical application of obtained materials.

2. Experimental

The chemical composition of developed frits brand single-layer enamel (SL) is as follows (mass%): $\Sigma(SiO_2 + B_2O_3)$ 50.4–60.9; $\Sigma(ZrO_2 + TiO_2)$ 6.5–9.0; Al_2O_3 2.5–4.0; $\Sigma(SrO + CaO + MgO)$ 9.3–12.9; Σ $(Na_2O + K_2O)$ 18.4–21.2; adherence activator $\Sigma(Co_2O_3 + CuO)$ 1.1–2.1 [4].

The batches were obtained by mixing the industrial grade quartz, zircon, titanium dioxide, borax, alumina, chalk, strontium, magnesium carbonates, potassium and soda as raw materials. These ecological vitreous materials do not contain harmful compounds and fluorine and, consequently, all the glass components are non-toxic, related to the environment.

In order to improve the adhesion we used the complex adherence activator, containing optimal quantity of adherence agents — cobalt and copper oxides. Subsequently, the batches were placed into chamotte crucibles and melted in an air atmosphere electric furnace, applying the following heating cycle: from room temperature to 1250 °C, with a soaking time of 1.5 h at the maximum temperature of 1250 °C. The melted glasses were quenched in water in order to obtain the frits. The glass

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transition temperature, T_g, of these glasses was 510 °C, determined by the differential thermal analysis at a heating rate of 10 °C/min.

In the work the synthesis of coatings was performed by the slip-firing technology on pipe samples of steel 9ХГС with external diameter 80–426 mm, wall thickness 2–10 mm and length up to 2.6 m. In order to be able to build up the surface for enameling procedure according to our needs it is necessary to have it clean in the beginning. This job is done by shot blasting.

The slips were prepared by milling of the frits in a ball mill with adding of 5% clay, 0.75% electrolytes and fine-grained filler (marshalite (SiO_2) and other) in the amount of 15–18%.

The enamels of brand SL with optimal firing temperature of 760–770 °C are easy to manufacture; they form in wide temperature range (80°) in 15–20 min. The firing of enamels was carried out by inductive method.

Coatings quality was estimated both by visual inspection and the method of assessing the strength properties and thermal stability with simultaneous control of covering continuity. Scanning electron microscopy using a JEOL JSM 6380-LV instrument was used to observe the coatings morphology.

Corrosion resistance of enameled samples has been tested according to ASTM C650.

The coatings forming mechanism on steel substrate and the role of adherence agents were discussed basing on X-ray diffraction and metallographic analyses.

3. Results and discussion

We have developed single layer-type coatings 450 μm thick. The sample appears mostly glassy, shows good homogeneous morphology, continuity and luster, as demonstrated by Fig. 1.

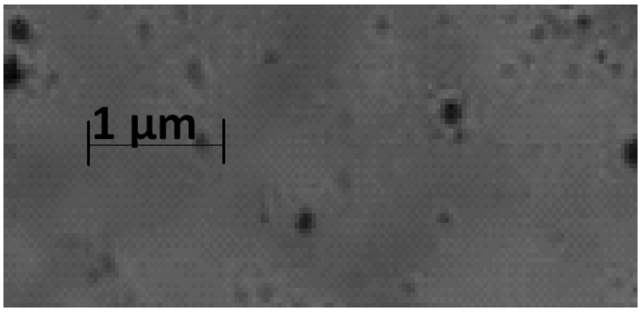

Fig. 1. Scanning electron microscopy analysis of the structure of SL-3 enamel.

Generally, the color of the enamel coating is blue. The synthesized enamels provide good assimilation of mineral fillers, such as high purity quartz, in the amount of 15–18%.

One of the most important parameters determining the quality and practical application of one-coat vitreous enamels is strong adhesion of coatings to the steel surface. The usage of developed by us complex adherence activator provides a firm grip in the system "enamel coating–metal substrate".

We can conclude from measuring series in accordance with European Norms EN 10209 that the best adherence strength of enamels (1–2 grades) is observed when the content of adherence promoter components (Co_2O_3 + CuO) is in an amount 1.8–2 wt% (Fig. 2). The strong adhesion is presented in the case e.g. of 15 SL-3 glass coating, containing (mass%): $\Sigma(SiO_2 + B_2O_3)$ 58; $\Sigma(ZrO_2 + TiO_2)$ 7.6; Al_2O_3 2.5; $\Sigma(SrO + CaO + MgO)$ 9.9; $\Sigma(Na_2O + K_2O)$ 20.2; $\Sigma(Co_2O_3 + CuO)$ 1.8; index — 15 means addition of 15% marshalite to the milled frit.

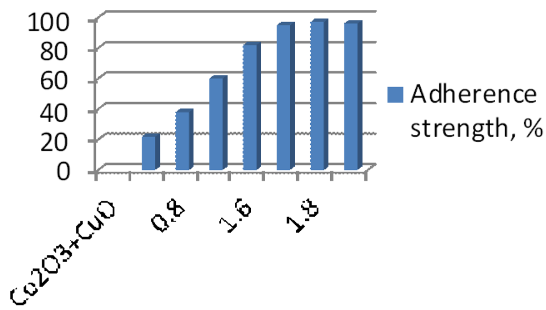

Fig. 2. Effect of promoter oxides on adherence strength of enamel 15 SL-3 to steel.

In fact, this optimal concentration of adherence agents increases the reaction activity of copper containing melts on steel, helps to improve the conditions of wetting, and allows active interaction in the contact zone.

The metallographic study of the interface boundary established that during firing as a result of the heterogeneous interaction on the "steel–enamel" contact surface and diffusion processes, there is formed a transitive inter phase layer approximately 20–22 μm thick (Fig. 3).

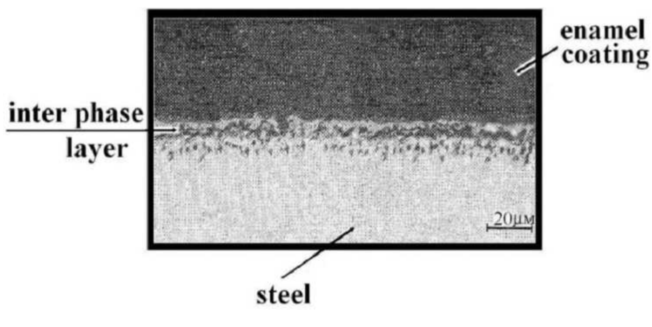

Fig. 3. Fracture of specimen with a single-layer coating fired at 770 °C.

The post-test examination of the specimens comprised X-ray diffraction (XRD). As it was shown by XRD analysis the transition phases of ferrites and iron oxides were detected as the main phases. In this case, adherence activator forms enamel bonds with iron oxides (steel constituents), mainly Fe_2O_3, and forms $CoFe_2O_4$ and

$CuFe_2O_4$ spinel, according to the relation:

$$CuO + Fe_2O_3 = CuFe_2O_4\,,$$

$$CoO + Fe_2O_3 = CoFe_2O_4\,.$$

Spinel ferrites have the structure of the mineral spinel with the general formula AB_2O_4, where A and B describe, respectively, bi- and three-valent metals.

According to XRD analyses of the intermediate layer adjacent to the steel the dominant components were spinel compounds, hematite (Fe_2O_3) and magnetite (Fe_3O_4). Iron oxides dissolved in the glass melt and thereby could also favor adhesion.

The formation of inter phase layer can produce strong grip in the system “enamel coating–steel”, that achieve superior corrosion and mechanical properties of enameled pipes. The chemical resistance of the enamel deposited on the steel is shown in Table.

TABLE

Chemical test according to ASTM C650.

Corrosive medium	Concentration [%]	Time interval [h]	T [°C]	Chemical resistance [mg/cm^2]
HCl	20	48	15–21	0.002–0.003
H_2SO_4	3	16	100	0.02–0.04
NaOH	5	0.5	60	0.06–0.07

According to the calculations the obtained silicate–enamel coating reduces the corrosion rate of steel in 3–4 orders of magnitude.

4. Conclusions

The present results confirm the synthesized enamels can be directly applied on the inner surface of steel pipes. The strong adherence of enamel to metal substrate is due to the formation of transitive layer as a result of complex heterogeneous interaction on the “steel–enamel” contact surface. A combination of enhanced adhesion of one-coat glass enamels with good corrosion resistance provides high performance and economic efficiency of direct-on enameling technology of pipes.

References

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