Influence of fluorine-containing additive on flowability of a glass enamel coating for steel pipelines

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The article considers the problem of pipeline protection against corrosion, which is the main cause of accidents during their operation. It is noted that the optimal method for protection against internal corrosion and asphalt-resin-paraffin deposits is the use of glass enamel coatings, which have increased smoothness and chemical resistance in comparison with other types of coatings. It is shown that in order to ensure the smoothness of the coating, it is necessary to ensure its high flowability, the effect of various fluorine-containing additives on the flowability indices is studied. Cryolite (Na_3AlF_6) was chosen as the optimal fluorine-containing additive, since it has the lowest fluorine losses when introduced into the charge, which makes it more environmentally friendly in comparison with sodium fluorosilicate and fluorspar. The work describes in details the process of obtaining glass enamel frits with different cryolite content (from 0 to 10 % in 2 % increments). The methods for preparing raw materials, melting glass mass and granulating frits are given. Studies of the flowability of the obtained compositions at a temperature 860 °C were conducted. The optimal cryolite content providing the best flowability indices has been established. It has been shown that addition of cryolite helps to reduce the melting point and to improve the flow properties of glass enamel. It has been revealed that the excessive cryolite content (10 %) leads to formation of complex crystalline structures and to decrease of the melt mobility. The mechanism of the action of fluorine compounds affecting the viscosity and surface tension of enamel, as well as their effect on the structure of the silicon-oxygen network, has been analyzed. The microstructures of the developed glass enamel coatings have been examined at a magnification of 50×. The results of the study have great practical importance for the development of glass enamel coating compositions with improved technological characteristics. The obtained data can be used to create effective protective coatings for steel pipelines of various purposes.
Key words: pipeline, frit, glass enamel coating, fluorine compounds, flowability, adhesion strength, cryolite.
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Introduction

Steel pipelines in Russian Federation are among the important components of the national power engineering structure. Steel pipes are widely used for mounting of pipelines for transportation of technical, drinking and mineral water as well as solutions of acids, salts and alkalis, oil, has and other substances for long distances. These substances provide corrosion effect on metal of pipelines [1]. At present time, length of pipelines constitutes about 250,000 km, while one fifth part of pipes (55,000 km) is used for transportation of oil and oil products [2].

Carbon steels St3, St20 and 09G2S are used for production of the main pipelines, because they are characterized by high strength and good weldability [3]. However, these steel grades are subjected to corrosion – the destruction process of metallic pipes, which takes place inside metal due to chemical reactions between pipe material and transported substances. This process can be caused by various factors, such as humidity, chemical components, temperature variations and other operating conditions, which can lead to deterioration of the pipeline state, thinning of its walls, forming of deposits and even holes that can finalize in leakages and accidents. Thereby it is important to control permanently the state of pipelines, to conduct the measures for their corrosion protection and (if required) to provide repair, maintenance and replacement of damaged sections. According to the technical literature data, there are about 80,000 accidents annually with pipelines in Russia, and 50 % of them were connected with metal corrosion destruction [4, 5].

External and internal corrosion are classified for pipelines; their causes are identified as atmospheric phenomena, ground waters or aggressive medium, which is transported inside the main pipelines. External corrosion is caused by atmospheric, soil ground and other environmental factors. Ground waters of humid soil (for coast pipelines) or sea water (for marine pipelines) can be such environment. Such methods as cathode, sacrificial or anode protection can be used to oppose such corrosion [6–9]. In the case of internal corrosion, water with sodium chloride (NaCl), hydrogen sulphide (H_2S) and carbon dioxide (CO_2) are considered and transporting medium; their effect can lead to active corrosion of steel surface. This process presents the serious danger for integrity of pipelines and their efficient operation. To protect steel components from internal corrosion, corrosion inhibitors are used, as well as metallic, organic and inorganic coatings [10–14].

Asphalt-resin-paraffin deposits can appear during operation of steel pipelines for oil products; they constitute a complicated hydrocarbon mixtures containing of solid methane hydrocarbons [15]. They are deposited st internal surfaces of steel pipelines, with decreasing their carrying capacity and increasing the risk of clogging and other negative consequences. Surface roughness of pipes is considered as the areas of forming of paraffin deposits, which increases owing to corrosion destruction of steel surface. To prevent forming of these deposits, inhibitors can be used, as well as smooth protective coatings applied at the internal surface of an oil pipeline [16]. Inorganic glass enamel coatings are among the most effective remedies for this purpose.

Steel enameling presents a composition combining steel strength and high chemical stability of glass enamel coating to aggressive media. Enamel is characterized by universal properties, such as increased corrosion resistance to solutions of acids, salts and alkalis at the high temperatures; stability of operating properties during 10 year and more; complete absence of susceptibility to ageing; mirror smoothness of a surface providing low friction coefficients and absence of adhesion of high-viscous polymeric substances and solid paraffin deposits of oil products; light cleaning; increased wear resistance etc. [17]. Owing to the wide range of operating temperatures from +350 °C to –60 °C, such coatings ideally correspond for protection of steel pipes, which are used in extremal Far North and Central Asia climatic regions in Russian Federation and China.

When choosing the optimal chemical composition of a glass enamel coating for pipelines, flowability on the surface of steel base is considered as one of the main parameters. This indicator determines enamel ability to be uniformly distributed on metal surface during calcination. According to the requirements of the GOST 52569-2018 "Ftits. Technical specifications", flowability of enamel frits for coatings of steel pipelines should exceed 38 mm.

Importance of flowability is determined by the factors of viscosity and surface tension of enamel melts, their regulation can be provided by varying of frit chemical composition. So, increase of the amount of alkali oxides, boron anhydride and fluorine-containing compounds will lead to decrease of viscosity, while increase of content of silicon, aluminium, magnesium and calcium oxides will finalize in viscosity rise [18].

Fluorine compounds are widely used in enamel application industry, because they are considered as efficient fluxing agents, which have the effect on enamel melt viscosity, decreasing mobility of cations with variable valence. When fabricating a glass enamel frit, the following raw materials can be used for introduction of fluorides: cryolite (Na_3AlF_6), fluorine silicate sodium (Na_2SiF_6) and calcium fluoride (CaF_2).

It should be noted that at present time we have lack of information about the effect of various concentrations of fluorine-containing additives of flowability of a glass enamel coating. Thus the aim of this research is a study of influence of fluorine-containing additives on flowability of a glass enamel coating for steel pipelines.

Experimental methods

To obtain the optimal glass enamel coating (GEC), taking into account the data from technical literature, the alumo-boron-silicate system $RO–R_2O–B_2O_3–Al_2O_3–SiO_2–TiO_2$ was chosen as the most suitable for the technology of single-layer enameling of steel pipelines. Based on this system, the authors previously developed the composition of the of single-layer enamel frit [19], it is presented in the **Table 1**.

Cryolite (Na_3AlF_6) was chosen as fluorine-containing additive, because it is characterized by minimal fluorine losses during introduction in charge composition; it makes cryolite more ecologically safe additive in comparison with fluorine silicate sodium and calcium fluoride. So, charge compositions with introduction of cryolite (Na_3AlF_6) in the amount 0–10 % with 2 % step were developed on the base of glass enamel chemical composition.

The charges for preparing of glass enamels included the following raw material components: quartzite sand from Tashlinskoe deposit (Ulyanovsk region, Russia), boric acid, feldspar from Vishnevogorskoe deposit (Chelyabinsk region, Russia), calcinated soda, potassium carbonate, lithium carbonate, titanium oxide, manganese oxide, iron oxide, cobalt oxide, copper oxide, limestone, nickel oxide and cryolite.

To prepare the charges, the components were ground and weighed by technical scales DL-1002 and mixed in porcelaneous drums of a ball mill. Fusion of charges was carried out in the high-temperature elevating furnace TK.4.1600.E.DM.1F with molybdenum disilicide heaters at the temperature 1400 °C with holding during 60 min.

Degree of fusion penetration was determined via the method of "thread sample". For this purpose a bar made of stainless steel 12Kh18N10T was dipped into melt and then a thread was thrown out of it. Absence of bubbles, knots and smooth shining surface of this thread testified on charge fusion penetration and its complete transition to glass-kind state.

Table 1. Chemical composition of the glass enamel coating

GEC	Content of oxides, % (mass.)														Total
	SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	Li_2O	TiO_2	MnO_2	Fe_2O_3	Co_3O_4	CuO	CaO	NiO	F, excess	
	52.0–56.0	12.0–14.0	2.5–3.5	13.0–16.0	1.0–2.0	1.0–2.0	3.5–4.5	1.0–2.0	0.3–0.6	0.7–1.2	0.5–1.0	2.5–3.5	0.3–0.6	1.8–2.3	101.8–102.3

Cooling and granulation of fluid melt was carried out via the "wet" method, according to the GOST R 52569–2018 "Frits. Technical specifications"; then a frit was dried in a drying box at the temperature not exceeding 100 °C until reaching humidity not more than 3 %.

To examine flowability of worked frits, two samples with each composition and with mass 2 g were pressed of ground powder. This operation was conducted with adding of 5–6 drops of water using a cylinder metallic form with size 10×15 mm according to the GOST R 50045-92 "Glass-kind enamels. Determination of fluidity parameters. Testing for flowability". Then the obtained samples were dried in a drying box at the temperature 105 °C during 10 min and placed at steel plates with size 110×110 mm made of steel St20. The surface of these plates was previously subjected to chemical treatment (degreasing, rinsing, pickling, rinsing, neutralization and drying) in order to delete various surface contaminations (such as grease, scale, mud etc.).

The plates with these samples were afterwards placed on the special platform made of thin-sheet heat-resistant steel (see **Fig. 1**) in electric muffle furnace (TK.8.1300.N.1.F), which was preliminary heated up to 860 °C. This platform allows transition of the plate with samples from horizontal state to inclined state (with the angle 45°); then it was held during 1 min in horizontal state and 2 min in the inclined state.

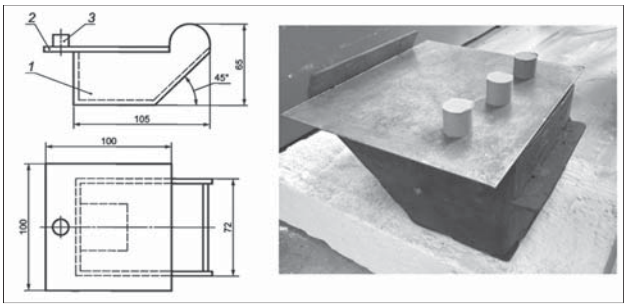

Fig. 1. The unit for flowability determination: *1* – platform; *2* – plate; 3 – sample with examined composition

After extraction from the furnace and cooling of the plates, maximal dimensions of flowability area of fused samples were measured using electronic slide caliper.

To provide evaluation of qualitative parameters of glass enamel coatings on steel, water slip suspensions with humidity 40 % was prepared on the base of obtained frits. Then these suspensions were applied via the wet method on metallic samples made of steel St20, the coating thickness was 200–300 µm. Consequently, the samples were dried at the temperature 105–110 °C during 10–15 min and roasted in electric muffle furnace, which was preliminary heated up to 860 °C, during 3–4 min. Presence of defects in coatings was examined using metallographic microscope Micromed POLAR with 50x magnification.

Experimental part

Flowability of glass enamel coatings

The values of maximal dimensions of flowing area for fused samples was obtained as a result of flowability examination for synthesized compositions of glass enamels, depending on the amount of modifying fluorine-containing additive (**Fig. 2**).

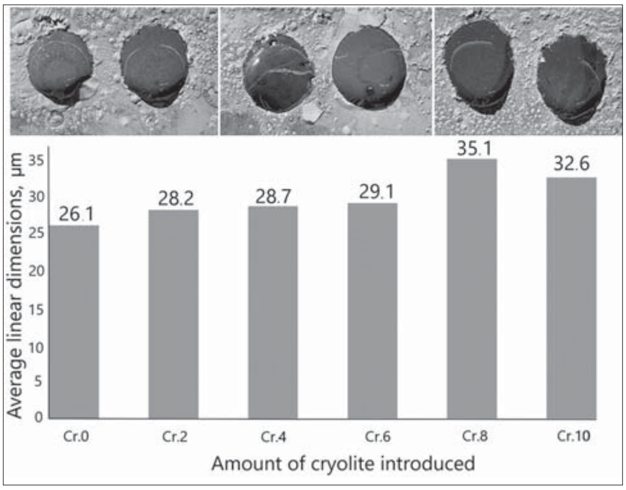

Fig. 2. Flowability for the developed compositions of frits: Cryolite content – Cr.0 – 0 %; Cr.2 – 2 %; Cr.4 – 4 %; Cr.6 – 6 %; Cr.8 – 8 %; Cr.10 – 10 %

As it can be seen from the Fig. 2, cryolite adding in the amounts 2, 4, 6 and 8 % leads to increase of glass enamel melt flowability due to its fluxing effect. When introducing the excessive cryolite amount (10 %), more complicated crystal structures with glass enamel components are forming; they become more stable and more mobile in a melt, what provides decrease of flowability.

The mechanism of incorporation of fluorine ions in a silicon-oxygen net and loosening of glass-formed amorphous structure is presented in the **Fig. 3**.

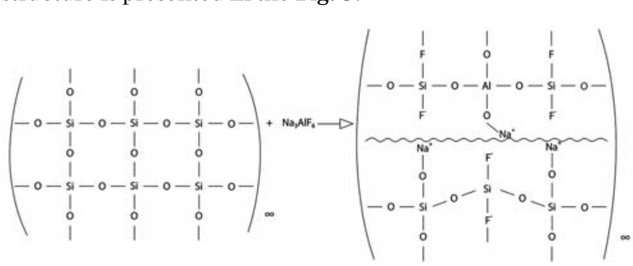

Fig. 3. Interaction between cryolite and silicon-oxygen structure of glass enamel

Analysis of the mechanism of cryolite introduction in of amorphous glass-formed structure at the high temperatures displayed that cryolite, being a complex compound, adds also Na^+ cations and $[AlO_4]$- groups (in addition to F^- anions) in glass structure; these components are built in a silicon-oxygen net, destructing Si-O links. Fluorine has an unique property providing substantial effect on glass flowability, and it is the difference with other modifying elements (such as oxygen, sodium, potassium etc.). This difference id stipulated by the fact that fluorine is the most electric negative element among halogens, what allows it to form very strong covalent links. Its small atomic radius also provides high flowability in glass structure [20].

When increasing the cryolite amount to 10 % and more, ions of alkali metals are encircled by fluorine ions with forming of fluoride crystals of alkali metals; it is unacceptable in the case of obtaining glass enamel coatings in amorphous structure [18].

Microstructure of the steel St20 and glass enamel coatings

Microstructure of steel surface has influence on the pipeline flowing capacity and susceptibility to asphalt-resin-paraffin deposits, which is increasing with enlargement of the surface relief roughness; thereby the optical analysis of steel St20 surface was conducted (the results can be seen in the ***Fig. 4***).

Analysis of the surface microstructure of the steel St20 showed that it is characterized by heterogeneity and essential roughness. It is connected with crystallization features and forming of metal grains during steel cooling, with forming of crystals with irregular form and various dimensions. Such heterogeneity and surface roughness can lead to intensification of corrosion owing to creation of additional places for accumulation of moisture and aggressive media. Thereby application of uniform and smooth glass enamel coating with high melt flowability indicator on this steel base will eliminate and overlap all its heterogeneities.

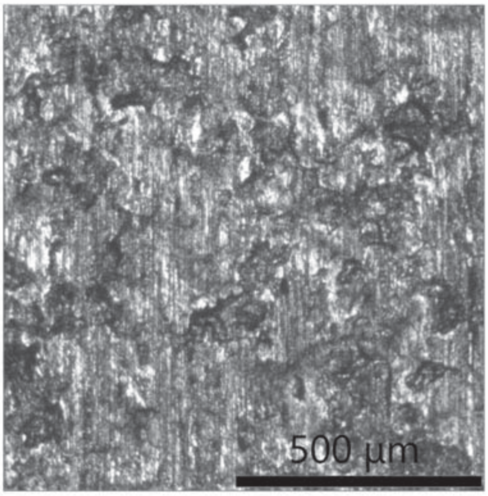

Fig. 4. Microstructure of the steel St20

Melt flowability of enamel coating plays an important role in forming of its microstructure, in homogeneity of its distribution along steel surface during roasting and in forming of defects. So, surface microstructure of enamel coatings was examined (see **Fig. 5**).

It is seen from the Fig. 4 that insufficient flowability (Cr.0, Cr.2, Cr.4, Cr.6 and Cr.10) leads to the problems with coating quality, which are caused be forming gas bubbles and non-uniform distribution of glass enamel along the surface. Ideally smooth coating layer without any defects is observed for the case of maximal flowability of composition Cr.8. All craters and surface unevenness are completely fused, creating smooth homogeneous surface with uniform thickness along complete square of a steel sample. Such coating is characterized by high adhesion with a base and excellent operating properties.

Conclusion

It was established during the research that flowability of single-layer glass enamel coatings for steel pipelines plays an important role for providing absence of defects and coating homogeneity; according to the requirements of the GOST 52569–2018 it should exceed 38 mm. Influence of fluorine-containing additive on flowability of glass enamel coating for steel pipelines was examined and it was revealed that its optimal (introduced in the form of cryolite) is equal to 8 %, what provides flowability 35.1 mm for glass enamel at the temperature 860 °C.

The results of microstructure examination for the obtained compositions displayed that the composition with 8 % of cryolite as a modifying additive is the most optimal, without any visible defects.

Based on the conducted investigations, we can conclude that the developed composition of single-layer glass enamel for steel pipelines is as follows (%): SiO_2 – 54.0, B_2O_3 – 13.5, Al_2O_3 – 3.0, Na_2O –15.0, K_2O –1.5, Li_2O – 1.5, TiO_2 – 4.2, MnO_2 – 1.5, Fe_2O_3 – 0.5, Co_3O_4 – 1.0, CuO – 0.8, CaO – 3.0, NiO – 0.8, Na_3AlF_6 – 8.0 %. This composition is considered as the optimal. Influence of other components on flowability will be examined in the following researches, in order to increase flowability.

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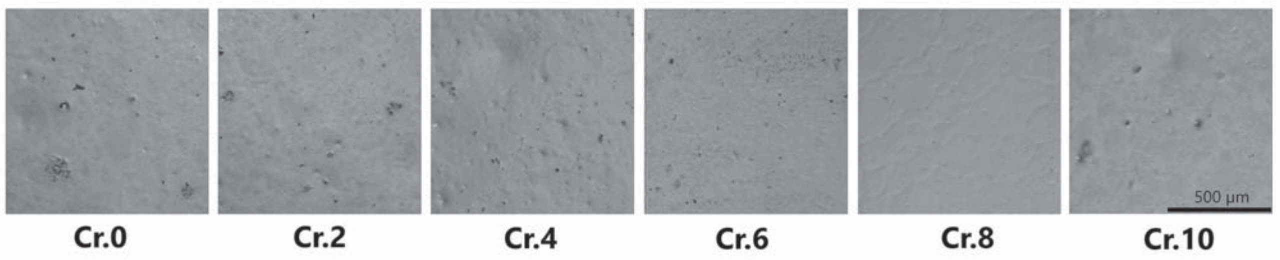

Fig 5. Surface microstructure of enamel coatings

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