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Synthesis and Investigation of White Glass-Ceramic Enamel Coatings for Steel Products

A. V. Ryabova, E. A. Yatsenko, L. V. Klimova*, E. V. Filatova, and A. Yu. Velichko
Platov South-Russian State Technical University (NPI), Novocherkassk, Rostov oblast, 346428 Russia
**e-mail: lyudmila.clim@yandex.ru*
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Abstract—The results of the synthesis and study of white glass-ceramic enamel coatings for the protection of steel products based on R_2O–RO–B_2O_3–Al_2O_3–SiO_2–TiO_2–P_2O_5–F^- system are considered. A number of glass-enamel compositions is developed. The crystallization features are revealed for white covercoat glass-ceramic enamel coatings; and the conditions preventing the anatase-to-rutile modification transition are determined. The influence of dopants upon the crystallization of white enamels is stuedied. The whiteness and spectrophotometric characteristics of the shadings are determined for white enamels using the spectrophotometric method and the RGB color model. It is proved that the synthesized covercoat glass-enamel coatings for steel products meet all the requirements of the technical specifications of the Russian State Standard GOST R 52569-2006 Frits.

Keywords: glass-ceramic materials, white enamel coatings, protective coatings for steel, titanium dioxide, crystallization, synthesis of glass enamels, dopants, determining of white color shadings, spectrophotometric method

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INTRODUCTION

The extension of the application of white crystalline glass enamel coatings in the steel industry requires further improving their technological parameters and operating characteristics via the formation of a specific structure that substantially depends on the chemical composition of the initial glass matrix.

Glass-ceramic white coatings on steel products should be characterized by a high level of aesthetic and consumer characteristics, such as brightness and whiteness, which determines the requirements with respect to the refractive index of enamel frits (n = 1.5) and the type and content of the suppressors in them ($n_{anatase}$ = 2.55; n_{rutile} = 2.70), as well as the physicochemical properties that determine their fritting temperature.

The technology of manufacturing and applying white titanium enamels and other enamels are significantly different from each other and obtaining a quality glass-ceramic coating to a considerable extent depends both on the chemical and phase composition of the glass, and on the maintenance of the technological requirements [1, 2]. However, not all the white enamels on the product appear really white. Most often the products are obtained either having a bluish shading, or having a yellowish shading, whereas the whiteness index of the diffuse reflection coefficient (DRC) is quite high (83%).

The experience of modern manufacturers in releasing enameled steel products shows that in order to protect the internal and external surfaces the manufacturers most widely use titanium containing a covercoat glass-ceramic enamel with a high degree of suppression. This type of white enamel is notable for its high degree of whiteness due to the fact that the suppressing phase of titanium dioxide is present in it mainly in the form of fine anatase crystals. From classical papers in the field of enameling [1, 2], it is known that the crystallization of anatase rather than the rutile (a more stable modification of TiO_2) requires a decrease in its solubility in the enamel melt by maintaining certain proportions between the main oxides, such as $Na_2O : K_2O$ = from 2 : 1 to 3 : 1 and $Al_2O_3 : P_2O_5$ = 1 : 1.

However, all the practical and scientific experience shows that maintaining all of these proportions in the synthesis of white enamel does not ensure the complete stabilization of titanium dioxide in the anatase form. It either transforms into rutile or forms the crystals grown to a significant size (greater than 0.2 μm), which results in the white coating exhibiting a characteristic yellowish shadow.

The purpose of this work consisted in studying the impact of different factors (chemical composition, ratio between the components, and the types and size of the crystalline particles) on the formation of white glass-ceramic enamel coatings and their color shading, as well as on providing the conditions under which the crystals of titanium dioxide can stabilize forming the anatase modification, to prevent the excessive growth of the crystals and further transition into rutile [2].

EXPERIMENTAL

The mechanisms of the processes occurring in the formation of white glass-ceramic coatings and the phase composition of the final steel–enamel system were studied using a set of physicochemical methods such as microscopy and XRD phase analysis, whereas the whiteness of the coatings was evaluated using spectrophotometry and via the registration of diffuse reflectance spectra.

To determine the diffuse reflection coefficients, we used an FB-2 whiteness meter. The intensity of the light beam reflected from the sample surface in such devices is measured by means of selenium photocells, whereas the indications were read using a microampermeter. Structurally, in the heads of the sensor the light beam from the source is incident on the tested surface at an angle of 45°. When measuring the whiteness photocell is normal to the surface or at an angle of 45° for measuring brightness. The disadvantage of such devices consists in the absence of a correcting filter adjusting the sensitivity of the selenium photocell to the human eye sensitivity. The device does not take into account the color shading of the coating.

In this work, we studied the microstructure of the glass-ceramic enamel coatings using a Qanta 200 scanning electron microscope and performed the XRD phase analysis using an ARL XTRA Thermo Fisher Scientific X-ray diffractometer (X-ray fluorescent one), in the form of CuK_α radiation. The XRD patterns were registered for the surface of the enameled steel samples having a size of 10 × 10 mm.

The spectrophotometric studies have been performed using a DTP22 X-RiteColorDigitalSwatchbook system according to the RGB color scheme. The X-RiteDTP22 DigitalSwatchbook system allows one to aim a manual spectrophotometer at a color sample and to see the color on a computer screen. The measured spectral color data were stored in a digital form, and color collections were gathered in the palettes that can be transferred to other graphics programs. The obtained data were then tabled.

The RGB (red, green, blue) is an additive color model that describes the color synthesis method for color reproduction. Any color in this scale is presented by the three components (red–green–blue) on a particular color plane as vector c, whose length determines the brightness and the angular position is responsible for the color. The color scale allows one to fulfill the main task, i.e., to calculate analytically the results originating from the interaction of the color vectors.

The whiteness of enamel coatings containing titanium is affected by the character of the crystallization process, which depends primarily on the chemical composition of the matrix glass. Due to the short duration of the formation of the crystalline phase in the studied coatings, a special role should be played by the prehistory of the initial glass. In choosing the glass compositions as the basis of white coatings with different color shadings, we needed to reveal the area of glass formation in the R_2O–RO–B_2O_3–Al_2O_3–SiO_2–TiO_2–P_2O_5–F^- system and the compositions there to meet the requirements for their properties. Their characteristics are a white color after calcination at a temperature not exceeding 820°C and a wide range of burning temperature ranging from 750 to 820°C.

In this regard, the tasks of this work consisted in studies on the influence of the chemical composition of titanium-containing glass in the R_2O–RO–B_2O_3–Al_2O_3–SiO_2–TiO_2–P_2O_5–F^- system on the whiteness index of white glass-ceramic enamel coatings and the shadings inherent to them; studies on the influence of dopants on the crystallization process; and studies on the conditions under which titanium dioxide can be stabilized to form an anatase crystalline modification, which prevents both excessive crystal growth and further transition into rutile.

In order to obtain white titanium-containing enamels, in the manufactured glass, the content of the basic oxides SiO_2, B_2O_3, and TiO_2 was varied, whereas the total amount of the oxides in the glass was 73 wt %. The choice of the type and quantity of other components R_2O, RO, Al_2O_3, P_2O_5, and F_2 was based on the analysis of the data in the literature. Their content remained constant for each glass composition, wt %: K_2O—2.63, Na_2O—13.50, MgO—1.48, CaO—0.12, Al_2O_3—4.53, P_2O_5—3.94, and F_2 (over 100%)—2.36, which amounted to 27 wt % in total.

Table 1 shows the chemical compositions of 21 glass matrices for white glass-ceramic enamel coatings.

As the basic charge material, we considered the readily available traditional raw materials used in the technologies of enameling. For the preparation of the charge, we used both minerals and reagent-grade, special purity, and analytical grade chemical reagents mixed in porcelain drums. As source materials for the preparation of mixtures, we used analytical grade Na_2CO_3, Li_2CO_3, KNO_3, H_3BO_3, and MgO; and special purity TiO_2, silica sand, feldspar from the Vyshnevogorsk deposit; as well as reagent grade Na_3AlF_6, Na_3PO_4, and $(NH_4)_2MoO_4$. Fluorine (F^-) was introduced to the charge injected in excess over 100% using reagent-grade sodium fluorosilicate (Na_3AlF_6).The glass was manufactured using alundum crucibles in a Silit electric furnace chamber at 1250–1300°C with 30 min exposure. The ready molten glass was exposed to wet granulation via pouring into water. All the glass was

Table 1. Compositions of glass matrices for white glass-ceramic enamel coating

Composition number	Content of components, wt %									
	SiO_2	Al_2O_3	B_2O_3	MgO	Na_2O	P_2O_5	CaO	TiO_2	K_2O	F_2 above 100%
1	39.00	4.53	19.00	1.48	13.50	3.94	0.12	15.00	2.63	2.36
2	40.00	4.53	18.00	1.48	13.50	3.94	0.12	15.00	2.63	2.36
3	41.00	4.53	17.00	1.48	13.50	3.94	0.12	15.00	2.63	2.36
4	42.00	4.53	16.00	1.48	13.50	3.94	0.12	15.00	2.63	2.36
5	43.00	4.53	15.00	1.48	13.50	3.94	0.12	15.00	2.63	2.36
6	44.00	4.53	14.00	1.48	13.50	3.94	0.12	15.00	2.63	2.36
7	39.00	4.53	18.00	1.48	13.50	3.94	0.12	16.00	2.63	2.36
8	40.00	4.53	17.00	1.48	13.50	3.94	0.12	16.00	2.63	2.36
9	41.00	4.53	16.00	1.48	13.50	3.94	0.12	16.00	2.63	2.36
10	42.00	4.53	15.00	1.48	13.50	3.94	0.12	16.00	2.63	2.36
11	43.00	4.53	14.00	1.48	13.50	3.94	0.12	16.00	2.63	2.36
12	39.00	4.53	17.00	1.48	13.50	3.94	0.12	17.00	2.63	2.36
13	40.00	4.53	16.00	1.48	13.50	3.94	0.12	17.00	2.63	2.36
14	41.00	4.53	15.00	1.48	13.50	3.94	0.12	17.00	2.63	2.36
15	42.00	4.53	14.00	1.48	13.50	3.94	0.12	17.00	2.63	2.36
16	39.00	4.53	16.00	1.48	13.50	3.94	0.12	18.00	2.63	2.36
17	40.00	4.53	15.00	1.48	13.50	3.94	0.12	18.00	2.63	2.36
18	41.00	4.53	14.00	1.48	13.50	3.94	0.12	18.00	2.63	2.36
19	39.00	4.53	15.00	1.48	13.50	3.94	0.12	19.00	2.63	2.36
20	40.00	4.53	14.00	1.48	13.50	3.94	0.12	19.00	2.63	2.36
21	39.00	4.53	14.00	1.48	13.50	3.94	0.12	20.00	2.63	2.36

well-cooked, had either a white or cream shading, and there was no crystallization in it.

Further, the frits were ground in a porcelain mortar to pass through a sieve No. 006. The resulting powder was applied onto steel samples with a size of 60 × 60 mm preliminary coated with a ground enamel. The obtained steel samples with deposited enamel were calcined at 800–820°C in an electric muffle furnace for 3 minutes. This holding time provides a complete melting of the enamel coating with a thickness of 0.30–0.35 mm, and the optimal intensity of the crystallization process. The evaluation of the appearance of samples showed that the coatings had no visible defects and exhibited a good brightness and continuity.

RESULTS AND DISCUSSION

In order to estimate the whiteness of the synthesized glass-ceramic coatings, further we performed studies to determine their DRC. The results are shown in Table 2.

The analysis of the results of the measurements have allowed us to reveal that all the synthesized coatings in the R_2O–RO–B_2O_3–Al_2O_3–SiO_2–TiO_2–P_2O_5–F^- system are characterized by a high DRC, but their shading can be visually attributed to the yellow, gray or blue one, which is not taken into consideration by the Russian Standard GOST R 52569-2006 Frits. Technical specifications. The standard determines only the luminance coefficient that should be at least 75%. The enamel coatings having a blue shading exhibit a lower DRC (72.15–73.99%) than coatings with yellow and gray shadings (DRC 73.21–84.76%). As an optimal composition, we have chosen composition no. 9. It is characterized by a white color with a slight bluish shading and the highest DRC (73.99%) among all the coatings with a bluish shading. In the manufacture of enameled household products in accordance with the aesthetic requirements of consumers, a white enamel coating with a blue shading, rather than with yellow or gray shadings are preferred.

Hence, the method for evaluating the whiteness of the glass-ceramic coating based on diffuse reflectance does not take into account the shading of the white color, and therefore to determine the shading, we proposed the spectrophotometric method using an RGB color measurement model. In accordance with this method, the color shading is characterized by certain light wavelengths and color coordinates. In connec-

Table 2. Diffuse reflection coefficients of white glass-ceramic enamel coatings

Composition number	Color of enamel coating	DRC value, %	Composition number	Color of enamel coating	DRC value, %
1	White-gray	73.71	12	White-gray	74.54
2	White-gray	74.90	13	White-blue	72.34
3	White-blue	72.15	14	White-blue	72.76
4	White-blue	72.77	15	White-gray	73.35
5	White-gray	73.52	16	White-yellow	84.76
6	White-gray	74.05	17	White-yellow	84.06
7	White-gray	73.21	18	White-yellow	83.98
8	White-blue	72.26	19	White-yellow	84.05
9	White-blue	73.99	20	White-yellow	84.07
10	White-blue	73.12	21	White-yellow	83.99
11	White-gray	73.65	–	–	–

Table 3. Spectrophotometric color characteristics

Color standard	Characteristics of color				Coordinates of colors		
	wavelength λ, nm	RGB value			X	Y	Z
		red	green	blue			
White	380–760	255	255	255	0.24	0.25	0.24
White-blue	465–482	230	233	221	0.22	0.29	0.24
White-yellow	575–580	222	229	237	0.22	0.23	0.26
White-gray	380–760	234	231	176	0.23	0.23	0.17

tion with this, reference optical characteristics have been introduced for white enamel coatings with different shadings, whose numerical values are shown in Table 3, and the graphical data are presented in Table 4.

The spectrophotometric characteristics of the color are shown in Tables 3 and 4.

The analysis of the data presented in Tables 3 and 4 based on the dominant wavelength allows one to accurately determine the color shadings of the obtained coatings.

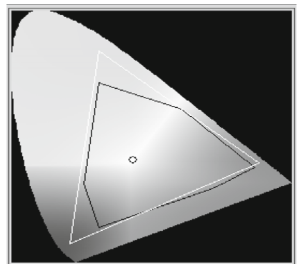
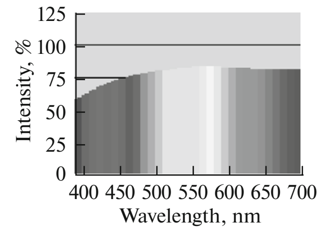
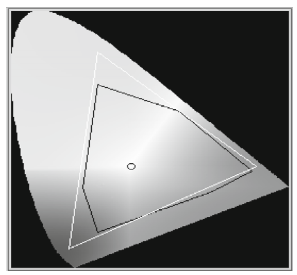
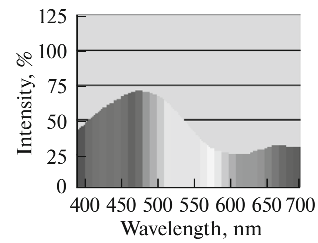
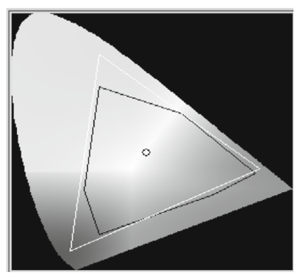
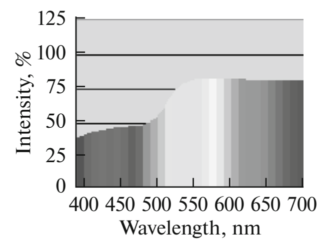
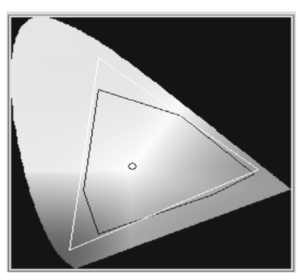
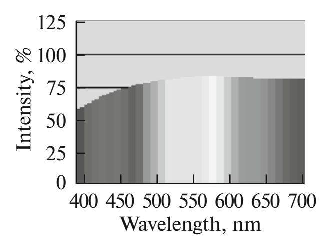
In order to reveal the reasons for obtaining white coatings with different shadings we performed a comparative analysis of the microstructure of the synthesized enamels, which allowed us to reveal that in the course of burning, some compositions (3, 4, 8–10, 13, 14) undergo a uniform bulk crystallization resulting in whiteness with a bluish shading. Compositions 5, 6, 11, and 15 also undergo crystallization; however, their character is uneven, as indicated in the SEM images by the translucent areas, whose presence is responsible for the visually gray shading of the coatings. Compositions 16–21 have a characteristic yellow shading of the surface layer of the enamel coatings, which indicates an anatase-to-rutile transition, beginning from the surface layers of the coatings. Thus, the range corresponding to the optimal compositions of the glass matrices, whose chemical composition provides a uniform fine-grained crystallization, is established. The content (wt %) of the basic oxides there is as follows: 40–42 SiO_2, 16–18 B_2O_3, and 17–19 TiO_2.

Further studies were carried out to provide the conditions corresponding to the stabilization of titanium dioxide crystals with the formation of anatase modification, which could prevent excessive growth of its crystals, as well as their transition to rutile.

The analysis of the literature has allowed us to establish [7] that the introduction of dopants has a significant impact on the glass crystallization process. The introduction of impurity cations to the glass structure and the occurrence of defective sites with nonequivalent bonds could be the cause of both the observed intensification in the formation of the crystalline phases and their stabilization or decay. According to the character of the effect exerted on the crystallization process, the dopants can be divided into two groups: the modifying alkali, alkaline earth metal, and glass-forming oxides (1) and intermediate-type oxides, primarily the oxides of transition elements (2).

However, of the greatest interest, is another aspect of the dopant action; i.e., the introduction of some of them (alkali metal oxides and transition metal oxides) results in a change of the primary metastable phases.

Table 4. Graphic data of spectrophotometry

Sample series	GamutViewer	Spectral curve
White		
White with blue shading		
White with yellow shading		
White with gray shading		

As dopants, we investigated a broad series of oxides of the I–VIII group elements: Li, V, Nb, Ta, W, and Mo. To the optimal composition no. 9, we added different dopants: in compositions 9-1–9-6, we varied one oxide dopant, whereas in compositions 9-7–9-11, we used a combination of a modifier oxide and a transition element oxide. To study the effect of the dopants exerted on the crystallization glass-enamel coatings process, we evaluated the whiteness and color shading for all the compositions (Table 5).

The analysis of the obtained experimental data have allowed us to reveal that the best indicators of the brightness and color characteristics close to the chosen standards are exhibited by compositions 9-1, 9-6, and 9-8, since in the case of using Li_2O and MoO_3 as dopants the DRC increases by 1% on average. At the same timem, it is found that a complex additive containing lithium oxide and molybdenum trioxide is the optimal dopant for manufacturing coatings with a high level of whiteness and blue shading.

In order to reveal the causes of either shading to occur, we performed microstructural studies on the coating compositions; the results are shown in Fig. 1.

The analysis of the SEM images has shown in the course of glass melt liquation regions enriched with titanium dioxide and oxides of alkali elements, and areas with a high content of silica are formed. During the heat treatment of the sample the areas enriched with titanium dioxide and alkali metal oxides undergo crystallization. As a result, the images exhibit dark

Table 5. Effect of different types of dopants on the appearance of enamel coatings

Composition number	Dopant type*	Shading of white enamel	DRC value, %	RGB value		
				red	green	blue
9-1	Li_2O	Blue	72.53	234	231	176
9-2	V_2O_5	Gray-blue	74.96	232	233	175
9-3	Nb_2O_5	Gray-blue	72.15	234	230	176
9-4	Ta_2O_5	Gray-blue	71.77	230	231	176
9-5	WO_3	Gray-blue	73.25	232	231	174
9-6	MoO_3	Blue	72.12	231	232	176
9-7	$Li_2O + V_2O_5$	Gray-blue	73.56	232	231	172
9-8	$Li_2O + MoO_3$	Blue	73.79	230	233	221
9-9	$Li_2O + Ta_2O_5$	Gray-blue	72.73	232	231	176
9-10	$Li_2O + WO_3$	Gray-blue	73.12	234	231	175
9-11	$Li_2O + Nb_2O_5$	Gray-blue	72.65	234	231	176

* Content of dopants less than 1%.

amorphous areas with a high content of silica and crystals formed in the areas with a higher content of titanium dioxide. The comparative analysis of the SEM images showed that white enamel coatings with a preferred blue shading exhibit a mass crystallization of titanium dioxide with the crystal size ranging from 0.1 to 0.2 μm. This explains the presence of the blue shading in the coatings since the suppression mechanism in this case is provided by the diffraction of the light rays. However, the white enamels with gray and

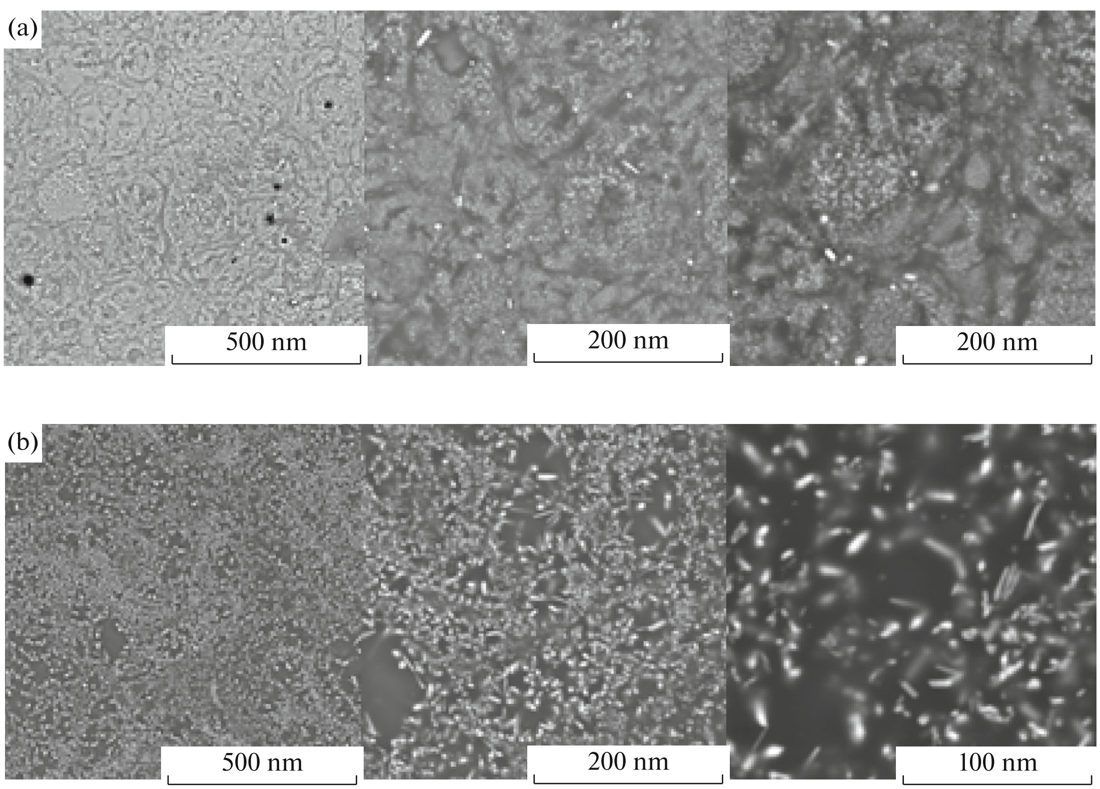


Fig. 1. SEM images of samples: (a) with a blue shading (composition 9; T_{burn} = 820°C, τ = 3 min); (b) with a yellow shading (composition 16; T_{burn} = 820°C, τ = 3 min).

yellow shadings also exhibit the crystallization of titanium dioxide; however, their concentration is considerably smaller, whereas the crystallite size is larger, ranging from 0.7 to 1.0 μm. Therefore, the suppression mechanism in these coatings is determined mainly by the refraction and reflection of light rays and gives them a gray or yellow shading.

In the mechanism for producing white titanium-containing glass-ceramic enamel coatings, an important role is played by the areas of transitions from one modification to another, namely, the transition from the metastable phase of anatase to the stable phase of rutile. As previously stated, this exothermic phase transition occurs irreversibly in the range from 600 to 950°C and depends on the chemical composition and on the temperature of glass matrix heat treatment. Moreover, the anatase-to-rutile conversion level is minimal at the temperature of 600°C and maximal at 725°C and increases with the duration of burning [7].

The analysis of the data in the literature has shown that anatase is the preferred modification in the formation of white coatings; anatase provides uniform crystallization; thus, one of the objectives of this work was to prevent the polymorphic transition from anatase to rutile by stabilizing the anatase form by varying the composition.

The XRD phase analysis was performed to determine the type of titanium dioxide modification contained in the white coatings with different shadings; the results are shown in Fig. 2. The XRD patterns were registered for the surface of the enameled steel samples with the size of 10 × 10 mm.

The comparative analysis of the XRD patterns shown in Fig. 2 has allowed us to reveal that the main phases produced in the course of the heat treatment of the investigated enamel coatings, regardless of the shading is to a greater extent anatase and to a small extent rutile. However, the intensity of the main peak corresponding to the anatase modification is significantly greater in the coatings with blue shading than in the coatings with yellow and gray shadings. This indicates the presence of a significant amount of titanium dioxide in the form of anatase crystals.

Thus, it is found that the introduction of modifier and transition metal oxides ($Li_2O + MoO_3$) as small complex additives affects the properties of the glass matrix, and in particular, the nucleation rate and growth rate of the titanium dioxide crystals. This is caused by the changes in the properties of the glass matrix in the molten state; i.e., the introduction of dopants affects the surface tension there. The introduction of these components, even in small amounts, causes an abrupt decrease in the surface tension and thus positively affects the nucleation rate and the crystal growth rate.

In order to study the transitions between crystalline modifications depending on the burning temperature, we have performed XRD investigations of the enamel

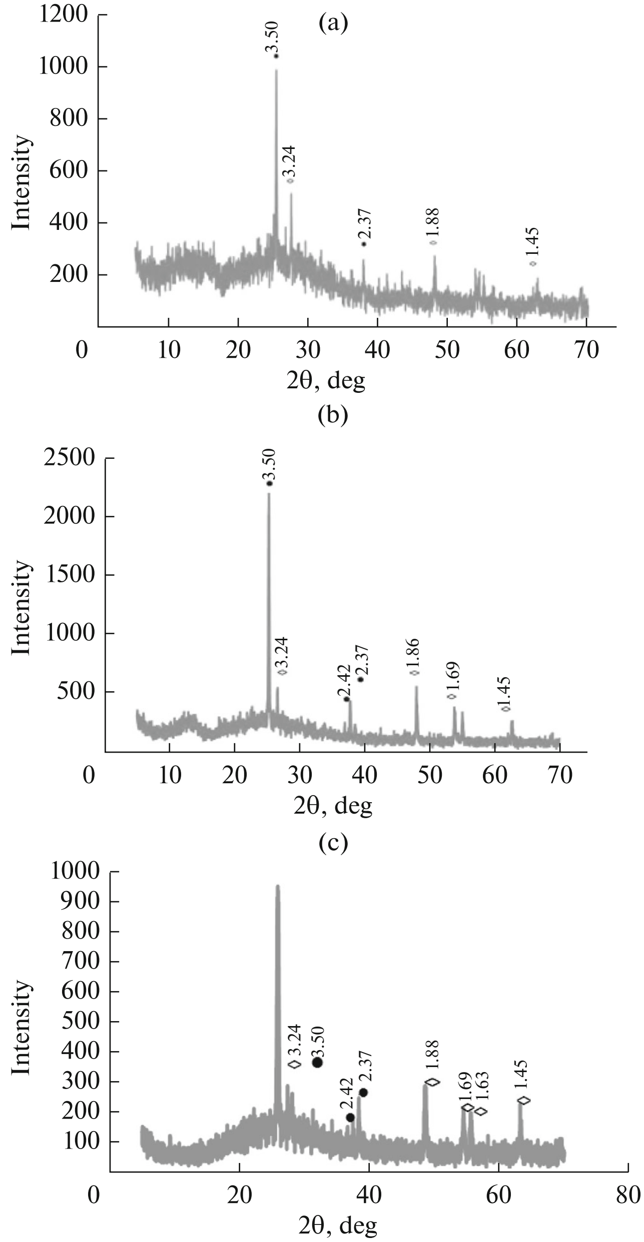


Fig. 2. XRD patterns of experimental glass-ceramic enamel coatings (●—anatase; ◇—rutile): (a) coating with a gray shading (composition 2; T_{burn} = 820°C, τ = 3 min); (b) with a blue shading (composition 9; T_{burn} = 820°C, τ = 3 min); (c) with a yellow shading (composition 16; T_{burn} = 820°C, τ = 3 min).

with the optimal composition burn at the temperatures of 750, 800, and 850°C. The results are shown in Fig. 3.

The comparative analysis of the XRD patterns shown in Fig. 3 have allowed us to reveal that the main phases formed in the course of the heat treatment of the tested enamel coatings at a lower burning temperature amounting to 750°C are both anatase and rutile. The enamel coating is characterized in this case by a

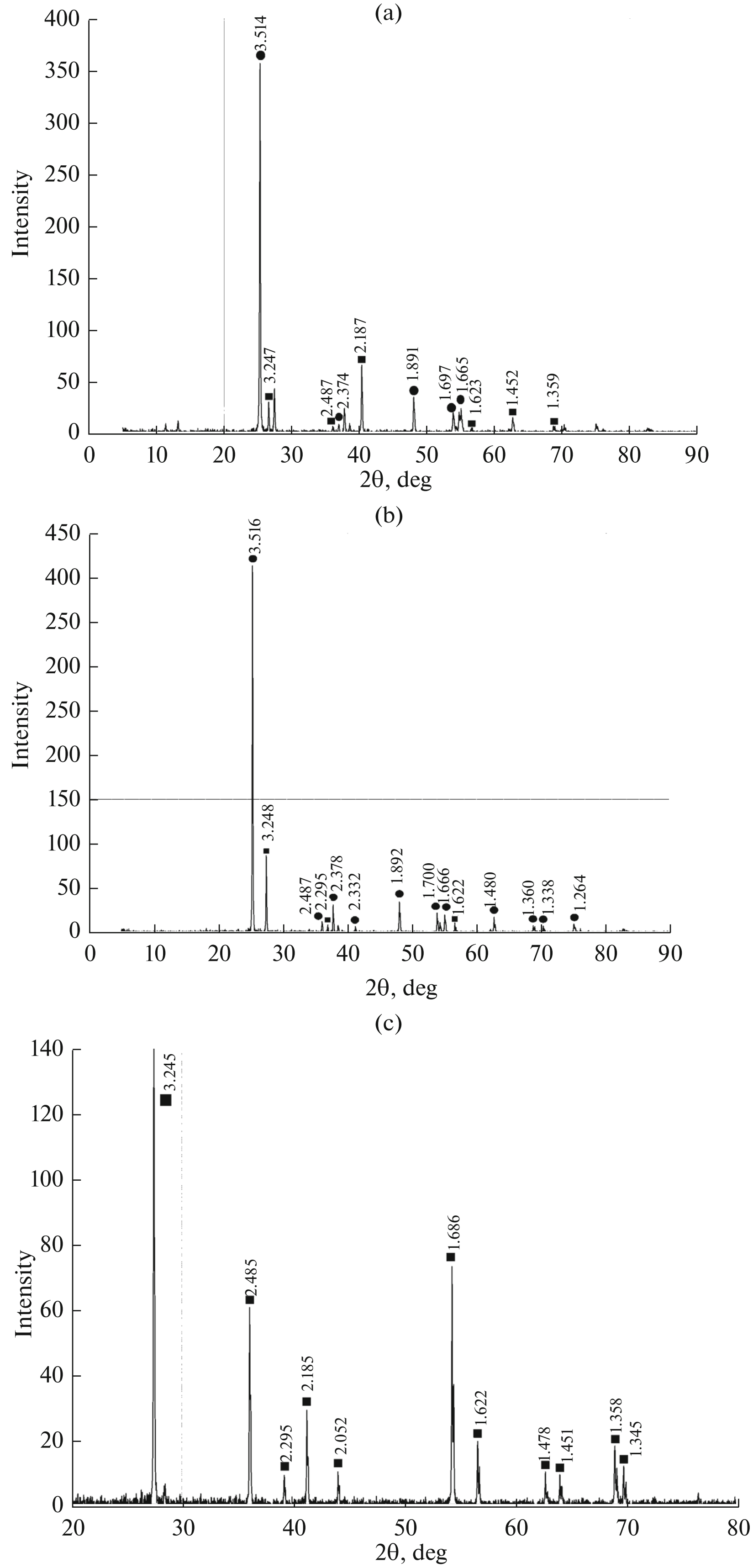


Fig. 3. XRD patterns of white covercoat enamel (composition of 9-8) obtained at different values of burning temperature: (a) $T_{burn} = 700°C$; $\tau = 3$ min; (b) $T_{burn} = 800°C$; $\tau = 3$ min; (c) $T_{burn} = 850°C$; $\tau = 3$ min (●—anatase; ■—rutile).

strong blue shading. At the optimum burning temperature of 800°C the crystalline phase is presented mainly by anatase crystals and the main peak intensity is much greater than that at 750°C, as well as by a small amount of rutile crystals, with the intensity of the peaks corresponding to them being insignificant just as at 750°C. This indicates the fact that the chemical composition of the glass, in particular the introduction of a small amount of modifier and transition metal ions, promotes an intensifying of the titanium dioxide crystallization into anatase at the optimum burning temperature of 800°C and simultaneously inhibits the growth of the rutile crystals. The coating in this case is characterized by a high degree of whiteness and a slightly blue shading. The burning at a higher temperature of 850°C results in the crystallization only of the rutile; moreover, the intensity of all its characteristic peaks is significant and the coating acquires a clearly yellow shading.

Thus, the comparative analysis of the XRD patterns shown in Figs. 2 and 3 has allowed us to reveal that the addition of modifier and transition metal oxides ($Li_2O + MoO_3$) in small amounts promotes the stabilization of titanium dioxide in the anatase form at the optimum burning temperature of 800°C. This in turn provides a high whiteness value (73.79%) and a blue shading, which is preferred in the production of enameled steel household products.

CONCLUSIONS

In the course of this work, white glass-ceramic enamel coatings in the $R_2O–RO–B_2O_3–Al_2O_3–SiO_2–TiO_2–P_2O_5–F^-$ system have been synthesized, and the features of their formation on steel products have been revealed. The effect of the chemical composition of the titanium-containing glass, as well as the effect of the crystallization process, exerted on the whiteness parameter of the white covercoat glass-ceramic enamels and on their characteristic shading has been investigated using a spectrophotometric technique based on an RGB color measurement model. This method has allowed us to specify the shadings of the obtained glass-ceramic enamel white coatings for steel.

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