

Vitreous Enamels for Easy-to-Clean and Catalytic Coatings

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Introduction

At the present time development of the manufacturing of domestic appliances with high level of performance characteristics, particularly gas and electric stoves, ovens, microwaves, roasters etc., remains relevant. Among various technical solutions that provide high degree of reliability, durability, aesthetic qualities of these products, and simultaneously their competitiveness in different market sections one should distinguish the use of vitreous-enamel easy-to-clean and catalytic coatings for low carbon steels [1].

Analysis of multiannual history of innovative developments in the field implemented by specialists from multiple countries allowed to mark out the following steps. The first and the most energy consuming technology of facilitating the cleaning process for ovens came up in 1960s. It involved the use of pyrolytic coatings capable to withstand high temperatures in oven chamber, which allows decomposition of food residues under pyrolysis without damage. Residues are destroyed under pyrolysis without combustion and easily removed from the inner surface of ovens in the form of ash [2]. Then the coatings with catalytic fillers have been developed, that provided the process of oxidative degradation of organic compounds under normal operating temperatures of domestic oven. Fundamental principles of such coatings developed by A. Stiles have involved fusing catalytic particles into the surface of enamel coating. Initially oxides of transition metals and noble metals were widely chosen as catalysts [3]. Subsequently, the use of carbides, silicides, borides and nitrides of transition metals has been proven effective [4]. In 1970s catalytic coatings with new types of catalysts, viz. solid acid cracking catalysts, have been proposed [5]. Easy to clean (ETC) enamels were the next step in facilitating the cleaning of domestic stove surfaces. They were first presented in early 1990s [6]. Residues on their surface of respective coatings are easily cleaned off with detergents under room temperature. Also, enamels cleaned by the action of steam are known [7]. From the viewpoint of energy saving ETC and catalytic coatings are more preferable, with easy to clean coating being more durable (fig.1).

Main conditions of obtaining ETC and catalytic coatings, regardless their type and composition, are following: for easy to clean coatings – obtaining defect-free surface of coatings with reduced surface free energy and increased hardness [1], while for catalytic coatings – obtaining porous sintered structure of vitreous-enamel layer that contains catalytically active particles of filler material [8]. Developed enamels for each of these coating types substantially differ in composition, physico-chemical properties and melting characteristics. That is why development of single composition that would act as a base for obtaining both easy-to-clean and catalytic self-cleaning glass coating is of substantial interest and comprised the **aim** of the work.

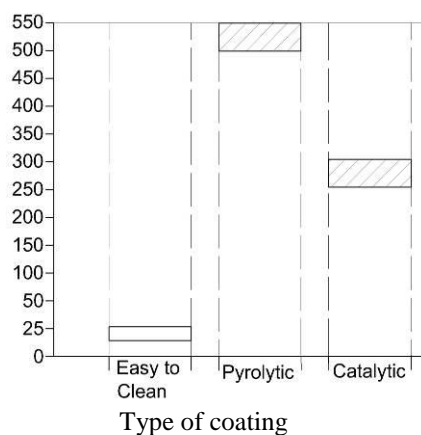


Figure 1: Temperature of self-cleaning (□) and cleaning (▨) of coatings for ovens

Principles of obtaining single composition

For the development of single composition – base of ETC and catalytic coatings the

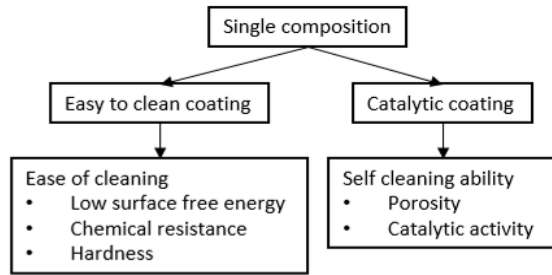


Figure 2: Performance characteristics of Easy to clean and Catalytic coatings

requirements to their performance characteristics are to be considered (fig 2). Complex of these properties is difficult to provide with the use of single frit. That is why the creation of double frit composition containing glass-matrix frit and crystallizing filler frit has been stipulated. The purpose of the first one was to mainly provide high chemical resistance of ETC coatings (A+ ... AA according to EN 14483-1:2007) and the function as a catalyst carrier to the self

cleaning coatings. The second frit must provide hardness to ETC coatings and catalytic activity of self-cleaning coatings. The combination of these frits will provide minimal surface free energy and ease of cleaning of ETC coatings and effective self-cleaning of catalytic coatings. These principles could be implemented under condition of proper selection of compositions of both frits; while the composition of filler frit must provide crystallization of required catalyst during firing, catalyst may also be incorporated into the composition as additive.

Methods

Following method have been used in the work: determination of chemical resistance according to EN 14483-1:2007, gradient thermal analysis, differential thermal analysis, dilatometric method, X-ray diffraction analysis, Owens-Wendt-Rable method for the surface free energy determination, self-cleaning test according to ISO 8291, self-cleaning test based on the loss of plant oil, Plum Jam test, determination of flowability with high temperature microscope, fusibility under loading by K.P. Azarov [9], roughness determination with Surtronic 3+ profilometer, optical microscopy.

Results and Discussion

Development of the composition of frit G – glass matrix of single composition

Composition of developed frit must provide necessary melting properties and high chemical resistance of A+...AA class, required for ETC coatings. On the base of this and with the use of additive dependences $\text{Property} = f(\text{Composition})$ chemical composition of G frit has been calculated. It is corresponding to the following requirements:

- temperature of $\lg(\eta) = 2$ should not be higher than 840 °C – temperature of firing of enamel coatings for ovens;
- TCLE of the frit in the temperature range of 20 – 400 °C should not exceed $110 \cdot 10^{-7} \text{ } ^\circ\text{C}^{-1}$, which will provide absence of tensile stress during the formation of the coatings;
- surface tension of enamel melt should not be higher than 250 mN/m;
- ratio (mole) of the glass forming oxides $\text{SiO}_2:\text{B}_2\text{O}_3$ should be 4:1 respectively;
- ratio (mole) of $\text{Na}_2\text{O}:\text{K}_2\text{O}$ should be 1.5:1 respectively for provision of polyalkaline effect.

Calculated composition of the frit G contains SiO_2 , B_2O_3 , P_2O_5 , CaO , MgO , Na_2O , K_2O , Al_2O_3 , TiO_2 and F. It has been experimentally proved that the beginning temperature of the fusibility

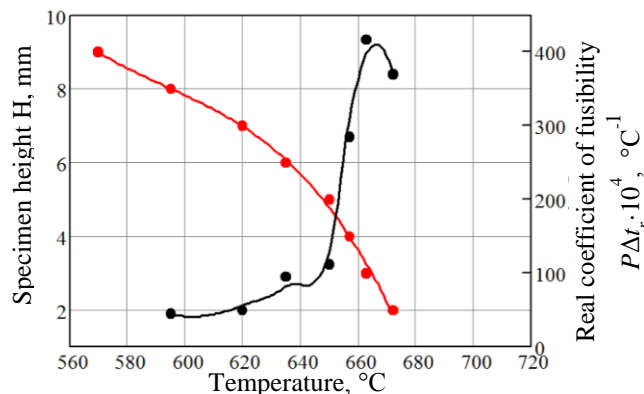


Figure 3: Fusibility of the frit G

under load was $t_{\text{init}} = 595 \text{ } ^\circ\text{C}$, the end $t_{\text{end}} = 670 \text{ } ^\circ\text{C}$, temperature interval of fusibility by K.P. Azarov $\Delta t = 75 \text{ } ^\circ\text{C}$ (fig. 3). Flowability characteristics are shown on the figure 4.

Respective coating had a chemical resistance of AA. Therefore, the frit G may be used as a component of single composition.

Development of the composition of frit W – filler of single composition

The filler frit must crystallize with formation of phases that provide

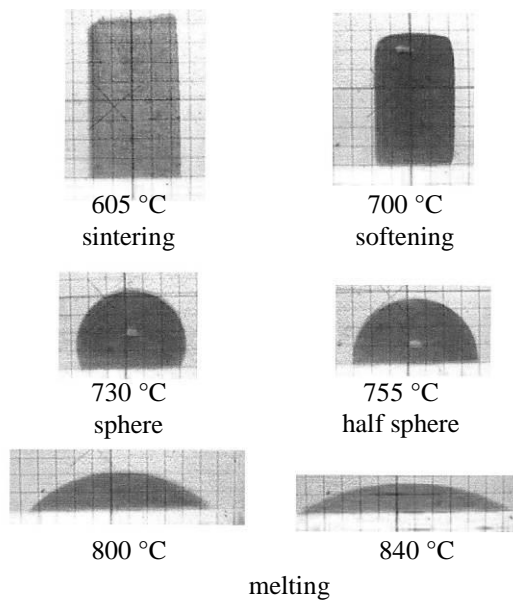


Figure 4: Flowability of the frit G

Assesment of the wollastonite function as a decomposition catalyst – component of the complex catalytic filler has been made in comparison with zeolites, used for the same purposes [4]. In the work zeolite NaA has been used. Low-melting alkali borosilicate enamel has been utilized as a catalyst carrier.

14 compositions has been created on the base of glass-matrix frit and both oxidation and decomposition catalysts. They contained 5 – 40 mass % (over 100 %) catalysts. It has been established that the coatings with highest self cleaning ability by method of weight loss

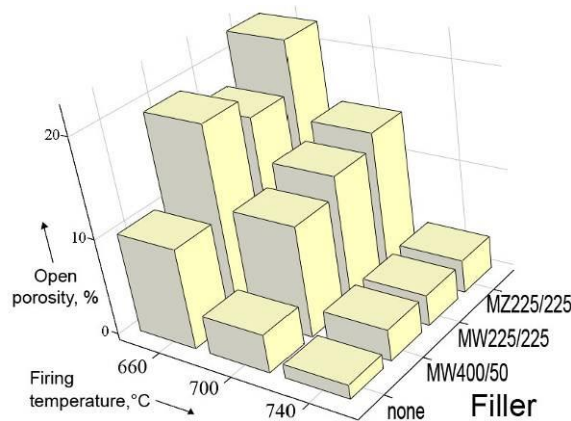


Figure 5: Porosity of self-cleaning coatings

Table 1: Self cleaning ability of the coatings

Coating	Cycles according to ISO 8291
MW400/50	14
MW225/225	18
MZ225/225	16

provides better catalytic activity compared to zeolite NaA under their similar content and can be used in complex catalyst that provides destruction of fats (table 1).

Chemical composition of the glass-ceramic component has been developed in the $\text{Na}_2\text{O} - \text{K}_2\text{O} - \text{CaO} - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ system based on obtained results and considering requirements to both physico-chemical properties of frit-filler and performance characteristics of developed coatings. The crystallization of wollastonite in it has been devised to take place in the conditions of firing. Possibility of wollastonite crystallization in the temperature interval of 600–1000 °C

significant hardness of ETC and catalytic activity of self-cleaning coatings.

With this purpose and considering catalytic activity data for different oxides and salts of metals of 1 and 2 groups of periodic table, assessed by chromatography of soy oil decomposition products [10], the calcium silicate CaSiO_3 – wollastonite. This compound is not only an effective decomposition catalyst, but also a phase that significantly increase hardness of glass-ceramic materials [11].

Development and use of complex catalytic component that contains an oxidation catalyst – MnO_2 apart from the mentioned decomposition catalyst has been assumed important. To obtain self cleaning coatings it has been added as a part of composition in order to exclude the negative effect of this oxide on performance properties of ETC coatings.

determination of vegetable oil after thermal treatment at 250 °C are MW400/50 (40 mass % MnO_2 and 5 mass % wollastonite), MW225/225 (22,5 mass % MnO_2 and 22,5 mass % wollastonite) и MZ225/225 (22,5 mass % MnO_2 and 22,5 mass % zeolite). Regardless of the complex catalyst composition with the increase of firing temperature in the range of 660–700 °C open porosity of the coatings substantially decreases (fig. 5). This is caused by the increase of the liquid phase and decrease of its viscosity accompanied by consolidation of the coating due to melting. For that reason the firing of the coatings on the base of experimental compositions is preferably done at the temperature of 660 °C, that corresponds to the intermediate value of fusibility $t_{\text{init}} - t_{\text{end}}$.

It has been established that wollastonite

has been established by thermodynamic calculations and by plotting projection of chemical composition on ternary subsystems ($\text{Na}_2\text{O-CaO-SiO}_2$, $\text{K}_2\text{O-CaO-SiO}_2$ and $\text{B}_2\text{O}_3\text{-CaO-SiO}_2$) of the chosen system. In the first two subsystems the composition lies in the field of primary crystallization of wollastonite, and in the last one – in the field of primary crystallization of SiO_2 .

Values of viscosity range and surface tension of melts, TCLE and fusibility range of the frit W (fig. 6 and 7) indicate the possibility of use composition for obtaining the glass coatings.

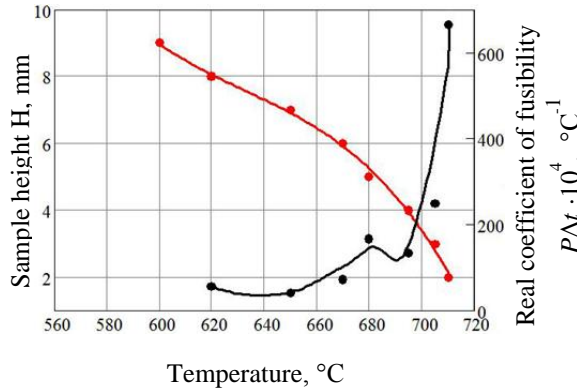


Figure 6: Fusibility of the frit W

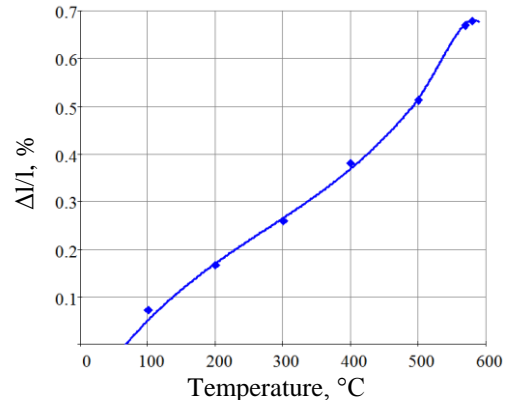


Figure 7: Dilatometric curve of the frit W

In order to determine phases that crystallize under the real firing conditions in the temperature range of 500–900 °C the new formations in the frit W has been investigated. With gradient thermal method and DTA (fig. 8) it has been found that its crystallization begins at 700 °C. Crystalline phase consists of wollastonite and pseudowollastonite, and their content increases with the increase of temperature (fig. 9); and predominant content of wollastonite is observed at temperatures less than 800 °C. Firing temperatures of the catalytic coatings on the base of the compositions contained this frit was assumed 700 °C, when apart from the crystallization of calcium silicates – decomposition catalysts, porous layer structure is formed.

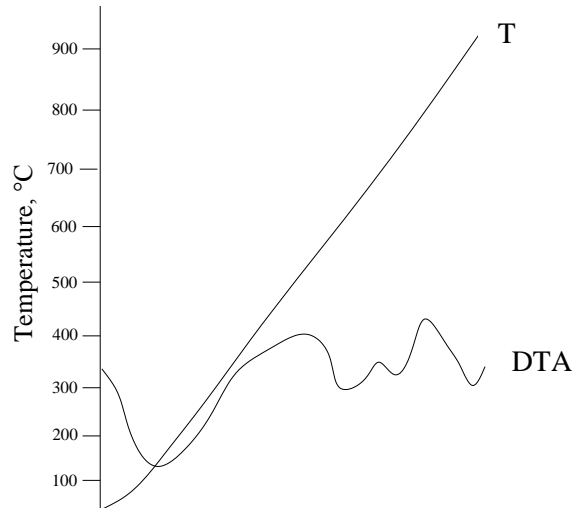


Figure 8. DTA of the frit W

5 coatings marked as GW_n have been obtained on the base of the frits G and W. Their compositions and properties are given in the table 2.

Values of the surface free energy of ETC coatings developed on the base of single composition were 54.38–56.82 mJ/m^2 , which is lower than for traditional glass enamel coatings (60 mJ/m^2). This provided their high level of cleaning ease.

Table 2: Characteristics of ETC coatings on the base of single composition

Coating	Compo- sition, mass %		Cleaning ease, points (Plum Jam test)			Chemical resistance (EN 14483- 1:2007, class)	Thermal resistance GOST R 50696 – 2006	Total Surface Free Energy, γ_s , mJ/m^2	Micro- hardness, GPa
	Frit G	Frit W	Plum Jam	Olive oil	Sum (of 10 points)				
GW1	100	0	5	4	9	AA	+	56,82	4,56
GW2	75	25	5	5	10	AA	+	54,38	5,13
GW3	50	50	5	4	9	A+	+	55,65	6,87
GW4	25	75	4	3	7	< A	+	56,08	7,21
GW5	0	100	4	3	7	< A	+	56,05	7,56

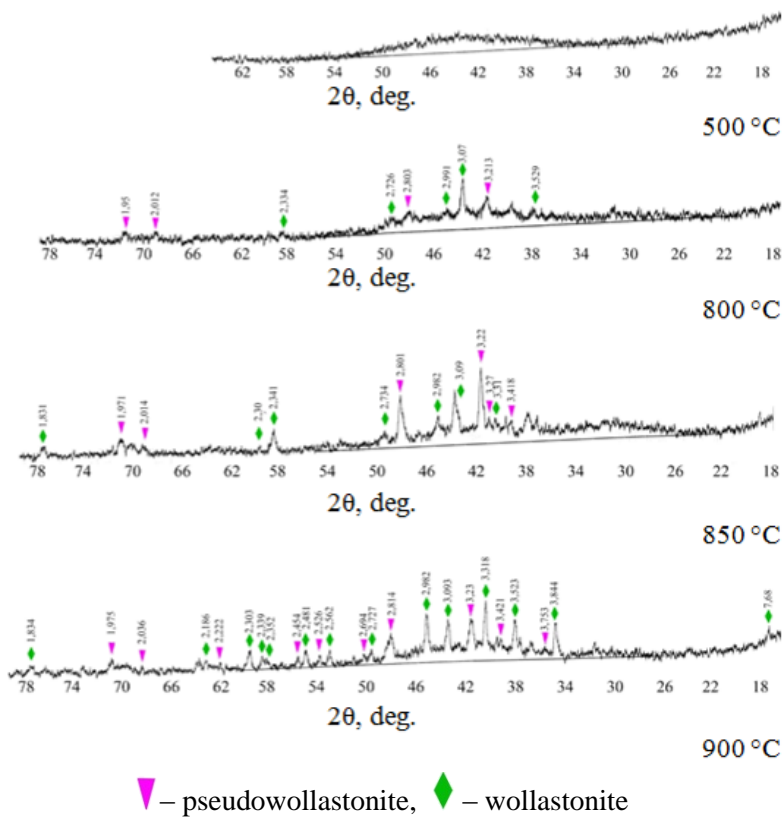


Figure 9. Diffractogram of the frit W under different firing temperatures

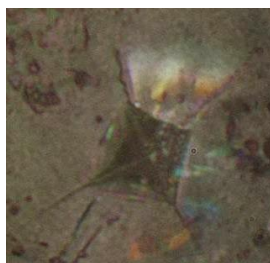


Figure 10: Impress of diamond indenter on the WG2 coating

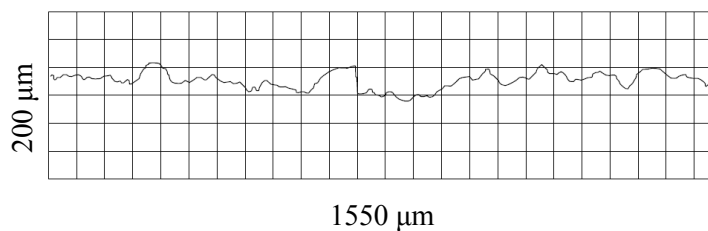


Figure 11: Surface profilogram of catalytic coating

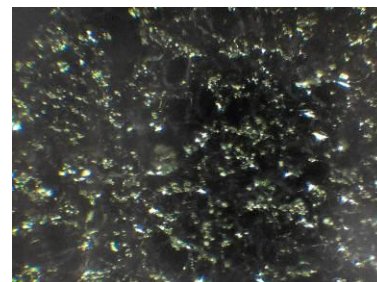


Figure 12: Microphotograph of the catalytic coating ($\times 120$)

Coatings containing glass component in amount of not less than 50 mass % are characterized by significant chemical resistance: class A+...AA according to EN 14483. Increase of the content of the frit W contributes to the increase in microhardness of coatings on the base of composition, which is a prerequisite for their resistance to mechanical damage (table 5; fig. 10). This reduces the likelihood of formation of anchor points that induce mechanical adherence of food residues to coatings during their service, and provides long-term ability of the coatings to easy cleaning. On the base of the combination of physico-chemical and performance properties the composition WG2 has been selected as the most

prospective for obtaining ETC and catalytic coatings. Catalytic coatings have been fired at 700 °C since this temperature corresponded to the intermediate fusibility value of the composition, optimal open porosity of $20\pm 2\%$ and microroughness of coatings (fig. 11 and fig. 12). Self-cleaning ability of developed coating that additionally contains MnO_2 is 10 cycles by ISO 8291. Dependences of the self-cleaning ability of the coating, tested by measuring weight loss of vegetable oil, from the time and exposure temperature (fig. 13 and 14) have linear and exponential character respectively. This is evidence of significant self-cleaning ability of the coatings under the work temperatures of domestic cooking equipment (200–250 °C).

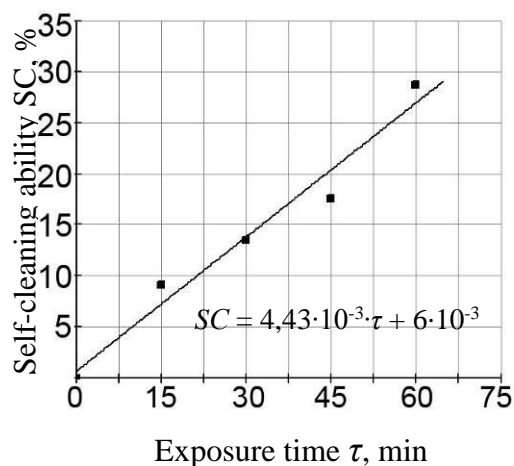


Figure 13: Dependence of self-cleaning ability on exposure time

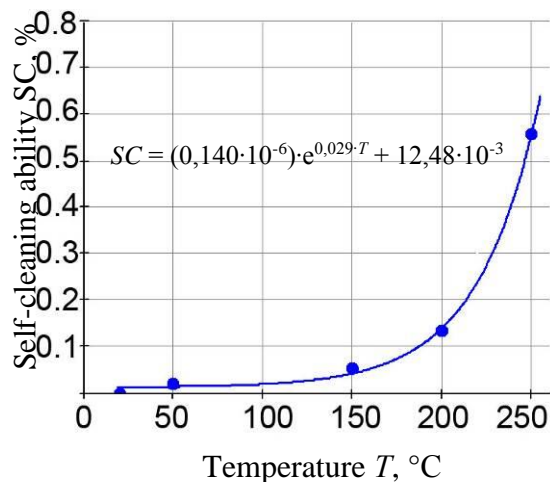


Figure 14: Dependence of self-cleaning ability on temperature

Conclusions

Single composition for obtaining easy to clean and catalytic coatings have been developed. Industrial application of the results of this investigation will allow simplification and increased flexibility of enamelling technology on the enterprises with simultaneous production of the kitchen stoves with easy-to-clean and catalytic self-cleaning coatings.

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