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Modelling glass-ceramic enamel properties

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The results of an investigation of the chemical and thermal characteristics of glass-ceramic enamels, derived from the Li_2O-Na_2O-Al_2O_3-TiO_2-SiO_2 system, obtained by employing the methods of mathematical experiment planning, are presented in this paper. Adequate mathematical models, showing the dependence of the chemical and thermal stability on the chemical composition of enamel systems, after different thermal treatment procedures, were obtained. Based on the testing carried out, it was concluded that in the obtained glass-ceramic enamels the chemical resistance is decreased, but at the same time, the thermal stability is increased, relative to reference coatings.

Keywords: glass-ceramic enamels, mathematical planning, chemical stability, thermal stability.

INTRODUCTION

Glass-ceramic enamels possess better thermal resistance and higher mechanical strength compared to conventional enamels.[1–3] The high thermal stability of glass-ceramic enamels is achieved by increasing the thermal expansion coefficient, which can be achieved by forming crystal phases with high thermal expansion coefficients in the glass silicate base.[4,5]

The structural transformation processes provide a microheterogeneous structure, which enables the destruction of the structure at the phase boundaries, to be delayed and influences the improvement in the thermo-mechanical properties.[6–9]

The corrosion resistance of glass-ceramic enamels also depends on segregated crystal phases, as well as on the residual glass phase. The microstructural inhomogeneities in glass-ceramic enamels influence the decrease of the corrosion resistance.[6–9] The enamels for chemical apparatus are characterized by higher corrosion resistance to the action of acids, alkalies, and even water.[10,11] A better resistance to acid solutions was attained by enhancing the SiO_2 content in the glass-ceramic enamel composition.[12,13]

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The investigation of the dependence of the properties – chemical and thermal stability– of the examined enamel systems on their chemical composition and heat treatment procedure, as well as the establishment of adequate mathematical models, was accomplished by employing mathematical planning methods and presenting the diagrams of the composition *vs*. properties.[14–17]

A planned experiment was based on the method of the modified simplex-latticed scheme with the previous transformation of the simplex subfield into a field of pseudocomponents.[14,15]

EXPERIMENTAL

Experiment planning

The synthesis of the enamel systems, the compositions of which had been defined in the matrix of experiment planning, was carried out according to the procedure described in the previous paper.[18]

Considering that the synthesized and studied enamel system is a multicomponent system Li_2O-Na_2O-Al_2O_3-TiO_2-SiO_2, in order to perform the planned experiment, it was transformed into a ternary system having the form R_2O-(TiO_2+Al_2O_3)-SiO_2, with a constant Al_2O_3 content of 3 mol.%, where R_2O is Li_2O+Na_2O.

A simplex is placed on the ternary system R_2O-(TiO_2+Al_2O_3)-SiO_2 (with constant Al_2O_3 content), defined by the coordinates of the top and inter-points of the triangle.

The field of experiment planning and the position of the experimental compositions are presented in Fig. 1.

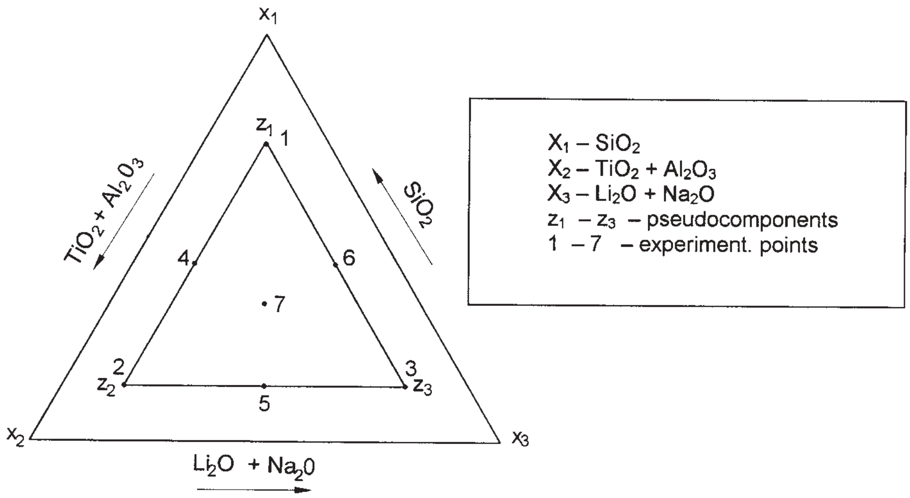

Fig. 1. The area of experiment planning and the positions of the experimental compositions.

The matrix of experiment planning in pseudocomponents and in the basic components is presented in Table I.

The method of the simplex-latticed scheme for a second power polynomial, for a three-component mixture, was employed for performing the planned experiment.[14] The number of experimental points of the scheme was seven, including also the experimental control point, for checking the adequacy of the regression equations.

TABLE I. Matrix of experiment planning

No. of exper.	Planning in pseudocomponents (relative fraction)			Planning in basic components/mol. %		
	z_1	z_2	z_3	x_1	x_2	x_3
1	1	0	0	70	7	23
2	0	1	0	58	19	23
3	0	0	1	58	7	35
4	0.5	0.5	0	64	13	23
5	0	0.5	0.5	58	13	29
6	0.5	0	0.5	64	7	29
7*	0.33	0.33	0.33	62	11	27

7* – The experiment performed for adequacy checking

Thermal treatment of enamel systems

The formation of the reference coating was achieved by heating pulverized glass within the temperature interval of 700–850 ºC, keeping at 850 ºC for about 10 min, and cooling continuously down to the temperature of 600 ºC, and then by further cooling in air (designated as mode I).

The thermal treatment of the synthesized enamels with the view of obtaining glass-ceramic enamels was performed by cyclic heating and cooling of pulverized samples in the temperature interval from 650–850 ºC (designated as mode II), while the other thermal treatment was performed by heating the samples up to the temperature of 900 ºC and maintaining that temperature for 3 h (designated as mode III). The modes of performing the thermal treatment were also described in detail in a previous paper.[18]

Crystallization did not occur during thermal treatment of the samples according to mode I, while crystallization did occur with modes II and III, as was confirmed subsequently by X-ray diffraction analysis.[18]

Determination of the chemical stability

The chemical stability of the synthesized and thermal treated enamels was determined by a modified[5] and simplified method of testing the resistance to aggressive attack by hydrochloric acid, in such a way that the enamel samples were treated with 100 cm^3 of 20 mass % HCl, for four hours at the boiling temperature.

Determination of the thermal stability

A simplified method was used for these tests,[19] whereby the enamel samples were exposed to cyclic heating up to a certain temperature, maintanence of that temperature for 30 min, and then quenching by pouring them into distilled water. Alternate heating and cooling was repeated several times, starting from 200 ºC, whereby the samples were heated each time to a temperature 50 ºC higher than the previous one.

The sample surfaces were observed and evaluated visually until the occurrence of visible surface damage. The temperature difference ΔT (ºC) was determined between the maximal heating temperature, at which, after cooling with distilled water, the destruction of the coating occurred, and water temperature (20 ºC).

RESULT AND DISCUSSION

The resistance of the enamels to the action of boiling HCl is inversely proportional to the mass loss per unit area. The chemical stability was calculated as the loss of mass per sample unit area, according to the equation:[10,11]

$$H = \frac{\Delta m}{P} \quad (1)$$

where: H – chemical stability (mg cm^{-2}); $\Delta m = m_0 - m_1$ (mg) (m_0 – initial sample mass, m_1 – final sample mass); P – area (cm^2).

The results the determination of the chemical and thermal stability are presented in Table II, and they represent the mean values of the results obtained in two parallel, independent experiments.

TABLE II. The results of the determination of the chemical and thermal stability

No. of exper.	Chemical stability/(mg/cm^2)			Thermal stability/ºC		
	H_{I}	H_{II}	H_{III}	ΔT_{I}	ΔT_{II}	ΔT_{III}
1	0.51	0.30	0.79	830	830	830
2	0.69	1.09	1.45	830	830	830
3	2.83	3.45	2.62	650	720	720
4	0.72	0.81	0.70	830	830	830
5	1.10	2.30	3.50	650	830	830
6	0.85	1.37	1.24	650	830	830
7*	0.75	1.47	1.84	700	830	830

7* – The experiment performed for adequacy checking; $H_{(\mathrm{I,II,III})}$ – The chemical stability values after the three different thermal treatment modes; $\Delta T_{(\mathrm{I,II,III})}$ – The thermal stability values after the three different thermal treatment modes

The regression equation coefficients were defined on the basis of the common form of the equation of a second power polynomial, for a three-component mixture:[14]

$$y = \beta_1 z_1 + \beta_2 z_2 + \beta_3 z_3 + \beta_{12} z_1 z_2 + \beta_{13} z_1 z_3 + \beta_{23} z_2 z_3 \quad (2)$$

$$\beta_i = y_i \ (i=1,2,3); \ \ \beta_{ij} = 4y_{ij} - 2yi - 2y_{ij} \ \ (i = 1,2; j = 2,3)$$

where: y – optimization parameter, β_i, β_{ij} – regression equation coefficients, $z_{(1,2,3)}$ – pseudocomponents, y_i, y_{ij} – system response values in the points of the experiment plan.

Three regression equations were obtained for the determination of the chemical and thermal stability, depending on the thermal treatment procedure (for modes I, II and III, respectively):

$$h_{\mathrm{I}} = 0.51z_1 + 0.69z_2 + 2.83z_3 + 0.48z_1z_2 - 3.28z_1z_3 - 2.64z_2z_3 \quad (3)$$

$$h_{\mathrm{II}} = 0.30z_1 + 1.09z_2 + 3.45z_3 + 0.46z_1z_2 - 2.02z_1z_3 + 0.12z_2z_3 \quad (4)$$

$$h_{\mathrm{III}} = 0.79z_1 + 1.45z_2 + 2.62z_3 - 1.68z_1z_2 - 1.86z_1z_3 + 5.86z_2z_3 \quad (5)$$

$$t_{\mathrm{I}} = 830z_1 + 830z_2 + 650z_3 - 360z_1z_3 - 360z_2z_3 \quad (6)$$

$$t_{\mathrm{II}} = 830z_1 + 830z_2 + 720z_3 + 220z_1z_3 + 220z_2z_3 \quad (7)$$

$$t_{\mathrm{III}} = 830z_1 + 830z_2 + 720z_3 + 220z_1z_3 + 220z_2z_3 \quad (8)$$

The adequacy of the formulated mathematical models, *i.e.*, regression equations, was controlled on the basis of the response value of the system in the control point of the experiment planning matrix (composition 7 of simplex), according to the Student criterion.[14,15] The regression equations were considered adequate if the calculated value of the Student criterion was smaller than the table value, for a given number of freedom levels and a chosen level of significance.[14]

The significance of the calculated regression equation coefficients was also been checked in accordance with the Student criterion. The regression equation coefficients was considered significant if they were according to the absolute value, greater than the confidence interval.[14,15]

The values of the Student criterion and the confidence interval are presented in Table III.

TABLE III. The values of the Student criterion and the confidence interval

Equations	Student criterion		Confidence interval
	Table value	Calculated value	
(3)	2.37	0.73	0.09
(4)	2.37	0.67	0.08
(5)	2.37	0.89	0.09
(6)	2.37	0.59	22.34
(7)	2.37	0.78	44.81
(8)	2.37	0.78	44.81

According to these criteria, all the regression equations are adequate, and all the coefficients were evaluated as significant.

The maximal differences between the experimental and calculated values for the chemical and thermal stability are 2.0 % and 1.6 %, respectively.

The obtained regression equations served as the basis for establishing the corresponding isolines,[14–15] whereby those of the chemical stability are presented in Fig. 2, and those of the thermal stability in Fig. 3.

The results of the performed experiments show that the chemical resistance to the action of hydrochloric acid of the obtained glass-ceramic enamels decreased in the examined composition range in all the system (thermal treatment mode II and III), what was to be expected.[6–9]

An increase in the resistance was noticed in the experimental compositions No. 3 and No. 4, *i.e.*, in thermal treatment mode III relative to mode II, namely, the values for the chemical stability are at the level of the values for the reference coatings. The experimental composition No. 1 is an exception, as a better resistance was obtained with mode II relative to the reference coating.

The maximal values of chemical stability were achieved in the area of compositions approaching the top of the ternary diagrams, namely, compositions with the highest SiO_2 content and minimal TiO_2 and R_2O contents (Fig. 2b and c).

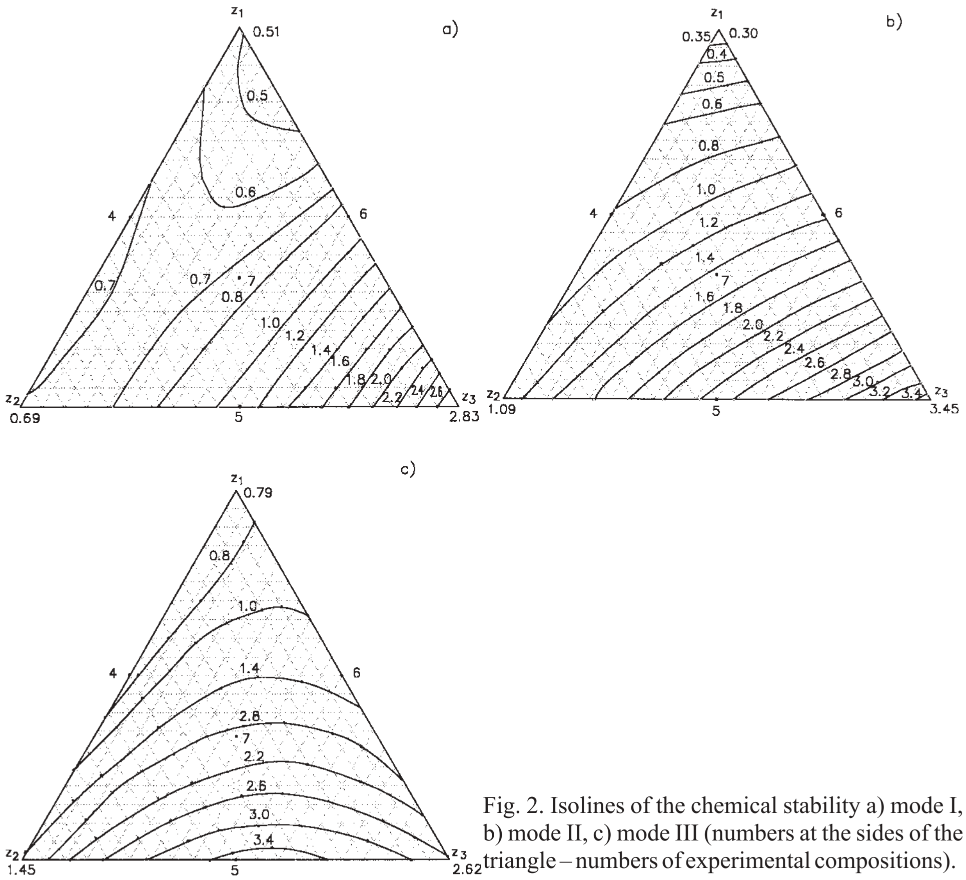

Fig. 2. Isolines of the chemical stability a) mode I, b) mode II, c) mode III (numbers at the sides of the triangle – numbers of experimental compositions).

The obtained data show that an increase in thermal stability is realized in all the examined glass-ceramic enamels, and there is no difference between the thermal treatment mode II and III. Thereby, the forms of the isolines in the composition *vs.* properties diagrams are the same.

The maximal values of thermal stability are in the area of compositions corresponding to enhanced SiO_2 content. The systems which have compositions in the middle region of ternary diagrams have maximal thermal stability for thermal treatment procedure I, while for mode II and mode III those composition areas directly approaching triangle side SiO_2-(TiO_2+Al_2O_3) have maxmimal stability.

The enhancement of SiO_2 content, with decrease of TiO_2 content and alkali metal oxides content in the tested systems, leads to a simultaneous increase in both the chemical and thermal stability.

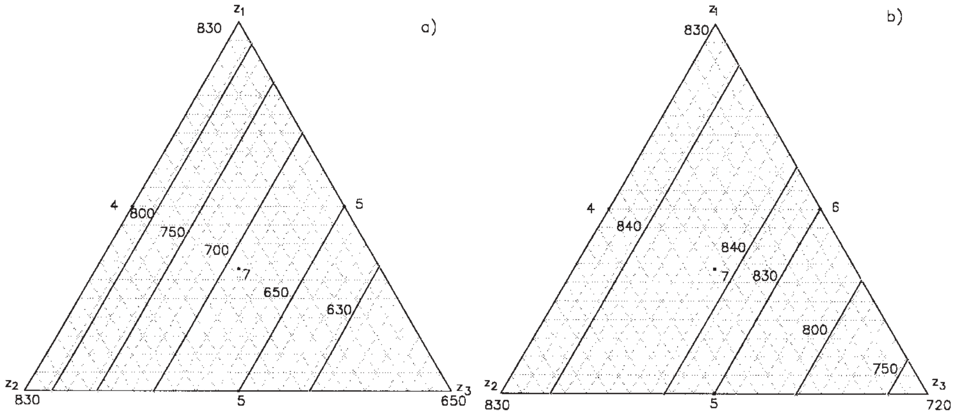

Fig. 3. Isolines of the thermal stability a) mode I, b) mode II and mode III (numbers at the sides of the triangle – numbers of experimental compositions).

CONCLUSION

The dependencies of the chemical and thermal characteristics of glass-ceramic enamels on the initial composition of the tested systems and on the heat treatment procedure, were established by the obtained mathematical models.

The dependence of the chemical stability, as well as of thermal stability, on the chemical composition for the examined composition ranges, can be defined by second power polynomial equations. The results of the experiments performed show that a decrease in the chemical resistance to hydrochloric acid action occurs in all the systems, with obtained glass-ceramic enamels, but simultaneously the thermal stability increases.

This is explained by the microheterogeneous structure, obtained by structural transformation processes, which enables the relaxation in the destruction of the structure at the phase boundaries, whereby the thermal stability of the glass-ceramic enamels increases but, simultaneously, the chemical stability decreases.[6–9]

An increase of the SiO_2 content, with a decrease of the TiO_2 content and alkali metal oxides content, in the tested systems leads to a simultaneous increase in both the chemical and thermal stability.

The obtained mathematical models enable the corrosion resistance, as well as the thermal stability of an enamel to be predicted and evaluated, *i.e.*, enable the corresponding compositions to be defined and selected for a particular application under given operating conditions.

И З В О Д

МОДЕЛИРАЊЕ ОСОБИНА СТАКЛО-КЕРАМИЧКИХ ЕМАЈЛА

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У раду је приказано испитивање хемијских и топлотних карактеристика стакло-керамичких емајла, изведених из система Li_2O-Na_2O-Al_2O_3-TiO_2-SiO_2, коришћењем метода математичког планирања експеримента. Добијени су адекватни математички модели који приказују зависност хемијске и топлотне постојаности од хемијског састава емајлних система, при различитим режимима топлотне обраде. На основу изведених испитивања закључено је да се код добијених стакло-керамичких емајла смањује хемијска отпорност, али истовремено повећава топлотна постојаност, у односу на референтне превлаке.

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