ISSN 1027-5495. Functional Materials, 22, No.4 (2015), p. 547-551.
doi:http://dx.doi.org/10.15407/fm22.04.547

Directed phase formation of functional glass-crystalline coatings for ceramics in TiO_2–Al_2O_3–SiO_2 system

***G.V.Lisachuk, L.O.Bilostotska, Yu.D.Trusova,
K.P.Vernygora, K.V.Podchasova, R.V.Krivobok***

National Technical University "Kharkiv Polytechnic Institute",
21 Frunze St., 61002 Kharkiv, Ukraine

Received June 28, 2015

Possibility of obtaining of thin crystallization (less than 4 μm) of non-fritt coatings by adding significant number (up to 15 wt.%) of tin dioxide (SnO_2) to their compounds was studied. It was found that titaniferous coatings, containing SnO_2 as mineralizer, promotes the directed mullite and stable anosovite phase formation. Glass-crystalline coatings with the easy-to-clean and biostability properties were obtained upon moulding temperature up to 1200°C.

Keywords: functional coatings, uniform thin crystallization, anosovite phase, bioresistant and easy-to-clean coatings.

Предложена возможность получения тонкой (менее 4 μm) кристаллизации нефриттованных покрытий путем введения в их составы значительного количества (до 15 масс.%) диоксида станнума (SnO_2). Установлено, что в титансодержащих покрытиях присутствие SnO_2 в качестве минерализатора способствует направленному образованию муллита и устойчивой аносовитовой фазы. Получены стеклокристаллические покрытия с температурой формирования до 1200°C, которым присущи свойства биостойкости и легкого очищения.

Скероване фазоутворення функціональних склокристалічних покриттів для кераміки в системі TiO_2–Al_2O_3–SiO_2. *Г.В.Лісачук, Л.О.Білостоцька, Ю.Д.Трусова, К.П.Вернигора, К.В.Подчасова, Р.В.Кривобок.*

Запропоновано можливість одержання тонкої (менше 4 μm) кристалізації нефритованих покриттів шляхом введення у їх склади значної кількості (до 15 мас. %) діоксиду станнуму (SnO_2). Встановлено, що у титанвмісних покриттях присутність SnO_2 у якості мінералізатора сприяє скерованому утворенню муліту та стійкої аносовітової фази. Одержано склокристалічні покриття з температурою формування до 1200°C, яким притаманні функції біостійкості та легкого очищення.

1. Introduction

A promising direction meeting trends of innovation economy development is a creation of fundamentally new functionally organized gradient structures, such as surface layers or ceramics coatings.

Properties of such materials allow the use of products made of non-metallic glass-crystalline coatings in difficult operating conditions under simultaneous exposure of several destructive factors (extreme temperature changes, corrosive environments, wear abrasion, etc.). Functional purpose of the coatings includes the following properties: decorativeness, abrasive resistance, self-cleaning ability, corrosion protection, thermal stability. The coatings may serve

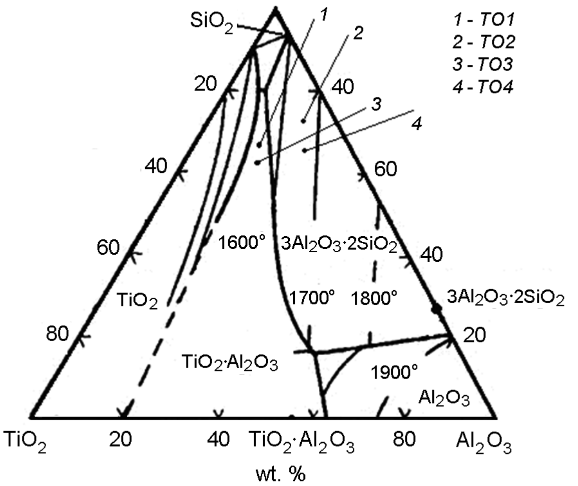

Fig. 1. Diagram of TiO_2–Al_2O_3–SiO_2 system.

the special purposes, such as medical and antibacterial, lining and resistant to atmospheric attacks and damaging effects of biofactors. Alongside with the antibacterial action a very important problem is cleaning of the surfaces from dirt, which spoils the esthetics of products and promotes the generation of viruses and bacteria.

A necessary condition for obtaining the new coatings is the development of compositions of non-fritt glazes, containing oxides, forming on the surface of coatings given spatial structures for creation conditions for hydrophobic or hydrophilic purposes of the surface, which also are characterized by high physical and chemical, physical and mechanical and surface properties, and are durable and have reduced moulding temperatures.

Based on the mentioned above, the aim of the research is directed titaniferous phase formation by using a complex of modifying mineralized oxides for the development of the non-fritt functional coatings compositions at moulding temperature not above 1200°C.

2. Results and discussion

The problem of obtaining the glass-crystalline coatings with a given set of properties is quite difficult, as it requires true knowledge of the material structure, its change depending on the chemical composition. This problem is partially solved for crystalline phases by using physical and chemical methods of forecasting in diagrams of state of the oxide systems. Multicomponent systems containing titanium dioxide are the basis of a number of industrial glasses. In aluminosilicate systems of $R_2O(RO)$–Al_2O_3–TiO_2–SiO_2 type glass-forming ranges are very extensive. These ranges include significant portion of high-silica compositions (at least 40 % of SiO_2). Adding of TiO_2 to their composition in amount up to 15 % extends the glass-forming ranges by lowering the temperature of liquids and reducing the viscosity of melts. The process of phase distribution under the heat treatment goes as follows: segregational aluminum-titanate heterogeneities appear first and then simultaneously or sequentially titaniferous phases crystallize in them – solid solution of anosovite and anatase type. The latter, as the heat temperature rises, recrystallize in the stable phase – rutile [1].

2.1. Diagram of state of TiO_2–Al_2O_3–SiO_2 system

To obtain the functional coatings we have chosen highly silicious area in the given system (Fig. 1), divided into three elementary triangles TiA–A–A_3S_2, TiA–S–A_3S_2, TiA–S–Ti, wherein such crystalline phases as rutile (TiO_2), silica (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$) and tialit (Al_2TiO_5) are predicted to be present [2]. Fig. 1 shows the points of model compositions in the diagram TiO_2–Al_2O_3–SiO_2, located both in the mullite and in tialit crystallization fields. The choice of specified range of compositions was conditioned by the possibility of directed formation of the crystalline phases providing simultaneous formation of the complex of properties: mechanical strength, low TCLE (temperature coefficient of linear expansion), increased chemical resistance and heat resistance. The ranges of compositions content has been chosen on the basis of the earlier undertaken researches [3].

To consider the phase changes, occurring upon dropping of the melt temperature of the given composition, it is necessary to trace its course of crystallization. Table 1 shows results of calculations made for the model compositions of the above selected contents.

The qualitative phase composition and the expected number of phases have been determined by the calculation of crystallization courses of the studied compositions. Table 1 shows that the increase of TiO_2 content reduces the initial and final crystallization temperature and simultaneously increases the melt amount. It should be also noted that at the lower TiO_2 content the

Table 1. Calculation of courses of crystallization for described compositions

Code of composition	Oxide content of model compositions			Crystallization products, wt.%	Amount of melt, %	Crystallization temperature, °C	
	TiO_2	SiO_2	Al_2O_3			Initial	Final
TO1	18.52	62.96	18.52	SiO_2 – 64.9; TiO_2 – 7.0; $TiAl_2O_5$ – 28.1	83.2	1520	1470
TO2	7.04	71.83	21.13	$TiAl_2O_5$ – 18.8; SiO_2 – 63.4; $3Al_2O_3{\cdot}2SiO_2$ – 18.8	63.6	1630	1550
TO3	21.13	61.27	17.61	SiO_2 – 61.97; TiO_2 – 8.45; $TiAl_2O_5$ – 29.58	75.3	1550	1480
TO4	6.17	72.23	21.6	$TiAl_2O_5$ – 21.9; SiO_2 – 63.0; $3Al_2O_3{\cdot}2SiO_2$ – 15.1	64.8	1650	1520

Table 2. Estimated rating melts properties of the coatings

Calculated parameters	Properties indicator values			
	TO1	TO2	TO3	TO4
Logarithmic viscosity number, lg η at a temperature of 1150°C	2.28	2.99	1.54	3.64
Interface tension, $\sigma{\cdot}10^3 N/m^2$ at a temperature of 1150°C	305.38	310.9	309.57	306.7
Flow temperature, °C	954	1021	1024	951
f_{Si}	0.3	0.32	0.28	0.34
K_{cr}	7.08	6.74	7.28	6.94

temperature range of crystallization phases defined by the calculation expands.

2.2. Research of melt properties

A large amount of the melt is formed in the mentioned titaniferous compositions (Table 1). Its properties could be estimated by the complex of calculation criteria [4], in particular: logarithmic viscosity number – lgη, interface tension indicator – $\sigma \cdot 10^3$ N/m, connectivity coefficient of silicaoxygen glass frame – f_{Si}, empirical crystallinity coefficient – K_{cr}. These criteria allow predicting crystallization ability of the melt forming during firing of the coatings shown in Table 2.

Analysis of Table 2 shows that the smallest index of the logarithmic viscosity number has the composition of TO_3, indicating the more active melt components. According to [4], values of f_{Si} are less than 0.5 and K_{cr} are above 4.5 in the case of interface tension of at least $300{\cdot}10^3$ N/m, forecasting increased tendency of the melt to formation of the defined crystalline phases at the moulding temperatures no higher than 1200°C.

3. Experimental

Quartz-fieldspar and technical materials were used to produce actual compositions of the coatings. The chemical composition of the experimental coatings was represented by such oxides as: SiO_2, Al_2O_3, CaO, MgO, BaO, Na_2O, K_2O, TiO_2 and SnO_2, of which SiO_2, Al_2O_3 are glass-forming; Na_2O and K_2O – fluxing agents, CaO, MgO, BaO – modifiers. Tin dioxide (SnO_2) at the concentration of 5 and 15 wt.% was applied as a mineralizer, which with its molecular-energy properties [5] stimulates uniform microcrystallization of the given phases.

Components of the non-fritt glazes were received by wet milling to the remainder on the sieving area 0063 – 0.15 %. The resulting slurry had the following parameters: humidity – 28 – 30 %, density 1.72 – 1.74 g/cm^3 and was applied by pouring on porcelain base. Firing of samples was carried out at temperature of 1200°C. Table 3 shows the properties indicators of the experimental coatings.

Analysis of the table data has shown the high level performance of the functional coatings, corresponding a number of ceramic production technologies (different types of porcelain, chemically resistant, construction and

Table 3. Physics-chemical properties of the developed coatings

Experimental properties parameters	Properties indicator values			
	TO1	TO2	TO3	TO4
TCLE, 10^{-6} K^{-1}	5.77	5.41	5.80	5.32
Acid resistance, %	99.6	99.1	99.8	99.2
Heat resistance, cycles	> 10	> 10	> 10	> 10
Elasticity modulus, GPa	0.9585	0.9405	0.9805	0.9050
Microhardness, MPa	6500	6000	7800	7200

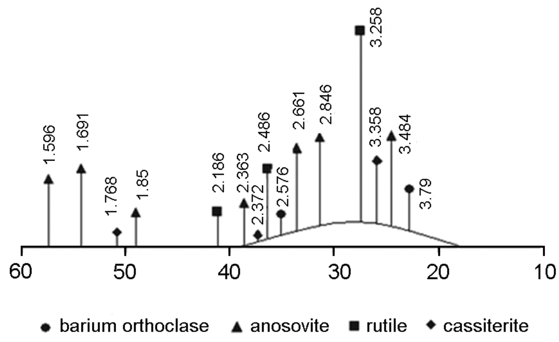

Fig. 2. X-ray diagram of TO_3 coating.

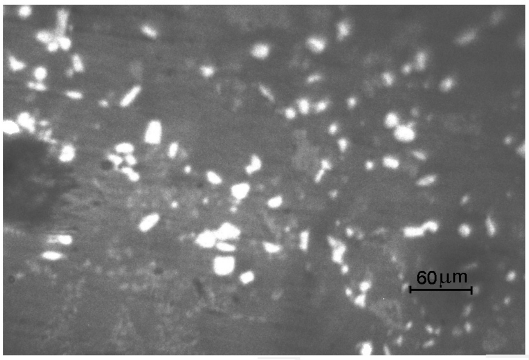

Fig. 3. Microstructure of TO_3 sample.

building ceramics, etc.). Such high rates of physical and chemical properties are defined by peculiarities of the phase composition of the developed coatings.

Research of the samples phase composition was conducted by method of X-ray diffraction analysis (XDA) using DRON-4-07 diffractometer under its standard operation conditions. ASTM card-catalogue was used for identification of the phases. X-ray phases researches of optimal composition of the coating TO_3, shown in Fig. 2, indicated phases of rutile, cassiterite (SnO_2), barium orthoclase ($BaAlSi_4O_8$) and anosovite (Ti_3O_5).

The microstructure of TO_3 sample were investigated by petrographic method in polished sections in reflected light under increase of $80–320^x$ with the help of microscope NU-2E and both in transmitted polarized light in immersion solutions under the increase of $100–480^x$ with the help of microscope MIN-8.

The investigations have shown that the coating consists of colourless transparent isotropic material with the refraction index of glassy phase $N_{sum} = 1.540 \pm 0.003$, in which there are evenly distributed scattered inclusions of irregular, rectangular and rhombic shape (thin section cut); they are isometric and elongated, angular and halfrounded (Fig. 3).

Inclusions birefringence is strong, reflecting capacity is high, the number of inclusions is about 30 %. There are mullite needles having a width of less than 2 μm and a length of up to 20 m. Their number is no more than 2–3 %. Mullite is distributed locally, i.e. unevenly. The average pore size of the sample is 15–30 m. Compared to the maximum size of the pore (Fig. 3) it is possible to assess very fine crystallization of the given phases.

Study of the phase composition of the experimental samples, using XDA and petrography, has shown the presence of rutile microcrystals, cassiterite, some silica, amorphous and intermediate products.

The obtaining of solid solutions of titanium pentoxide Ti_3O_5 of high temperature modification with different orthorhombic structure of pseudobrookite and deformed monoclinic structure has been specified. Anosovite practically doesn't interact with silica and is the most stable and titaniferous phase. The resultant coating phase composition has been defined, %:

* glass phase – 60–65
* relict grains of silica and corundum – 2–3
* cassiterite – 15
* rutile – 10
* mullite – 3–5
* anosovite – 3–5.

The experimentally obtained phase composition of the coatings, burnt at 1200°C, corresponds to the predicted calculations. The complex of chemically inert phases provides the functional sustainability of the structure and properties of the surface, and as a result – the resistance to biodestruction [6].

The obtained coatings are also capable of easy cleaning that was demonstrated by determining the topography of the sample surface with scanning 3-*d* microscope Keyence VK-9700K with a range of digital and optical zoom ×200 ÷ 3000 and × 10 ÷ 150, respectively [7, 8]. Fig. 4 illustrates profilogram of the optimal sample of TO_3.

While studying the topography of the sample surface, in accordance with the requirements of ISO 4287:1997 [9], certain parameters of the surface roughness were established:

R_P – 0.221 μm, R_v – 0.163 μm, R_{max} – 0.174 μm, R_s – 0.344 μm.

Average arithmetic value of deviations of the higher profile point is 0.187 μm and the lower profile point – 0.156 μm. Limits of variation of the coatings roughness parameters indicating the high constancy of the material surface and as a result – the high biostability were defined on the basis of the obtained data analysis [10].

Functionality of the developed coatings was investigated by conducting bench tests. Testing time of the samples was 30 days, slope angle of the samples to the plane was 75°. Basic compositions of the glazes were selected for comparison. The tests shown that water consumption for decontaminating for the basic compositions was five times higher than the water consumption for the developed compositions what allowed to refer their functionality to as easy-to-clean.

4. Conclusions

Compositions of non-fritt glass-crystalline coatings with moulding temperature 1200°C were developed. Tin dioxide of concentration of 5 and 15 wt.% was applied as mineralizer to obtain the given phase composition in the titaniferous system providing conditions of thin (less than 4 μm) uniform crystallization of the phases. The high-temperature modification of titanium Ti_3O_5 – stable phase of anosovite was determined as the main carrier of titanium. Compatible presence of tin dioxide and anosovite phase in the phase composition of the coatings provides additional functionality – hydrophilic surface with the easy-to-clean and antibacterial properties.

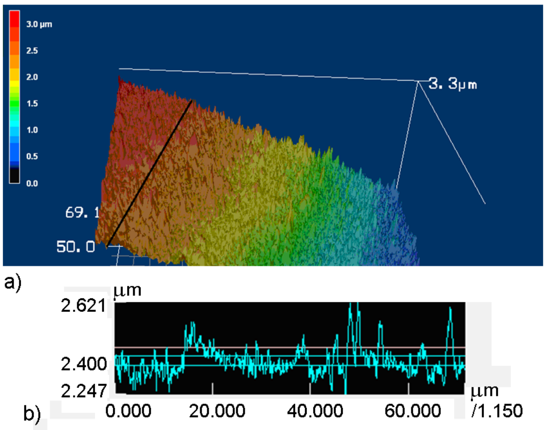

Fig. 4. Topological parameters of TO_3 sample surface a) Profilogram of TO_3 sample in 3D image; b) Image of the sample section.

References

1. I.A.Levitskiy, Low Melting Glazes for Ceramic Tiles and Household, BSTU, Minsk (1999).
2. Ya.M.Pitak et al., *Vestnik BSTU Shukhov, Part II*, **5**, 215 (2003).
3. G.V.Lisachuk, Yu.D.Trusova, N.V.Trusov, *Vestnik NTU KPI*, **19**, 14 (2001).
4. G.V.Lisachuk, M.I. Ryshchenko, L.O.Bilostotska, Glass-ceramic Coatings: Monograph, NTU "KPI", Kharkov, Ukraine (2008).
5. E.M.Nikiforova, Mineralizer in the Ceramic Industry, St. Univ. Nonf. Met. and Gold, Krasnoyarsk (2004).
6. L.Koss, Biostability without Biocidal Facade Ceramics: Monograph", NTU "KPI", Kharkov, Ukraine (2014).
7. L.Koss, N.Lesnych, H,Vensmer, Moglichkeiten und Grenzen der Benetzungswinkelmessung zur Beurteilung der Algenanfalligkeit von Fassaden, Altbauinstandsetzung, 5/6 (2003).
8. L.Koss, N.Lesnych, H,Vensmer, Benetzungswinkel-Stabilitat und Algebesiedlung Ausgewahlter Fassadenoberflachen, Reihe Altbausanierung, Berlin, Beuth Verlag GmbH, 2 (2008).
9. Geometrical Product Specification – Surfase texture: Profile Method – Terms, Definition and Surface Texture Parameters (ISO 4287:1997-04 (E/F)) [Published 1997-01-04] International Organizaition for Standardization, 23 (1997).
10. L.Koss,N.Lesnych, H,Vensmer, Algenbesiedlung und Algenbesiedlungsresistenz – Bauphysikalische Untersuchungen Energetisch Sanierter Fassaden, Fassadensanierung, Praxisbeispiele, Produkteigenschaften, Schutzfunktionen, Berlin (2011).