CORRELATION AMONG COMPOSITION PROPERTIES OF SnO_2 OPACIFIED GLAZES

Irina ATKINSON[1], Ion TEOREANU[2], Maria ZAHARESCU[3]

Este discutată posibilitatea producerii de glazuri nefritate cu adaos de SnO_2 ca opacizant pentru ceramică sanitară. S-au sintetizat o serie de glazuri cu 3, 5 si respective 10 % grav SnO_2 plecând de la o compoziție etalon de glazură nefritată (materii prime: feldspat, caolin, cuart, dolomit si ZnO). Glazurile au fost perparate prin metoda ceramică uzuala, aplicate prin pulverizare pe substratul ceramic crud si tratate termic in cuptor electric la temperatura maximă 1250^0C, palier 1 h. Glazurile obținute au fost caracterizate prin difracție de raze X, microscopie electronică de baleiaj, dilatometrie, microscopie de temperatură inaltă şi spectrocolorimetrie.

The possibility of producing raw glaze with SnO_2 addition, as opacifier for sanitary ceramics is discussed.. A series of glazes with 3%, 5% and 10% of SnO_2 were synthesized using a standard raw glaze composition (raw materials: feldspar, kaolin, quartz, dolomite and ZnO). The glazes were prepared using the traditional ceramic route applied on the green ceramic substrate by spraying and then thermally treated in electrical furnace at maximum temperature of 1250 ^0C, 1 h plateau. The obtained glazes were characterized by X-Ray diffraction, scanning electron microscopy, dilatometry, hot stage microscopy and spectrocolorimetry.

Keywords: glaze, SnO_2, melt viscosity

1. Introduction

Opaque glazes provide good properties for glazed products, which are used to decorate most household ceramic products. Sanitary wares are usually produced using raw opaque glazes, whose process requires a higher temperature and a longer heat treatment than in other traditional ceramic processes [1].

Opacity is introduced into the glaze by adding a substance to the coating formulation a substance that disperses in the glaze as discrete particles which

[1] Chemical engineer, Dept. of Oxide Materials Science, Institute of Physical Chemistry of the Romanian Academy Bucharest, Romania
[2] Prof., Dept. Of Science and Eng. of Oxide Materials and Nanomaterials, University "Politehnica" Bucharest, Romania
[3] PhD Dept. of Oxide Materials Science, Institute of Physical Chemistry of the Romanian Academy Bucharest, Romania

scatter and reflect some of the incident light. The dispersed substance must have a low solubility in the molten glaze and a refractive index that differs from that of the main glaze. The refractive index of the glaze depends on its chemical composition. A transparent vitreous glaze has a refractive index of about 1.50 [2].

The degree of opacity of the glazes depends on the dispersion and uniformity of the fine crystalline opaque phases. The particles size for an optimum opacity should be as small as possible.

Tin oxide is used in glazes to create varying degrees of opacity; a typical amount of 5-10 wt% can be used to obtain a good opaque glossy glaze. The addition of larger amounts of tin oxide to low temperature glazes increases the glaze viscosity and also the possibility of pinholing and crowling.

Nowadays, the use of tin oxide is diminishing being replaced by other materials as: TiO_2, ZrO_2, $ZrSiO_4$, which are cheaper alternatives. However, currently tin oxide is still used because it confers a more pleasing aspect to the final product than other materials [3].

The purpose of this paper is to investigate the effect of SnO_2 addition on the raw glazes properties for sanitary ceramics.

2. Experimental

2.1 Glazes preparation

A standard raw ceramic glaze was formulated containing 60 wt% feldspar, 15 wt% quartz, 8 wt% kaolin, 12 wt% dolomite and 5 wt% zinc oxide[4]. A series of glazes with 3%, 5% and 10 wt%, respectively of SnO_2 was synthesized starting from this composition. The oxide composition of glazes is presented in Table 1.

The raw glazes were synthesized by traditional ceramic method. The raw materials in adequate proportions were wet milled up to 0.1% residue on the 63μm sieve. The material: balls: water ratio was 1: 1.5: 0.6.

Each resulted glaze suspension was then applied on the green ceramic substrate by spraying. The glazed ceramic substrates were thermally treated in a laboratory electrical furnace for 1 hour at a temperature of 1250^0C.

Table 1

The oxide composition of the studied glazes (mol % / weight %)

Sample		Na_2O	K_2O	Al_2O_3	ZnO	CaO	MgO	SiO_2	SnO_2
G0	mol %	3.66	3.46	9.43	3.97	8.02	8,02	63.44	-
	weight %	3.55	5.07	15.03	5.00	7.00	5.00	59.35	-
G1	mol %	3.60	3.40	9.36	3.86	7.92	7.85	62.71	1.30
	weight %	3.44	4.92	14.58	4.85	6.80	4.85	57.56	3
G2	mol %	3.57	3.37	9.26	3.81	7.81	7.75	62.25	2.18
	weight %	3.37	4.82	14.27	4.75	6.65	4.75	56.40	5
G3	mol %	3.74	3.26	9.00	3.75	7.63	7.57	60.55	4.50
	weight %	3.20	4.56	13.52	4.5	6.30	4.5	53.42	10

2.2 Characterization methods

Crystalline phases, formed in glazes during firing, were determined with a DRON UM1 diffractometer with Co Kα radiation.

Thermal expansion coefficients of body and glaze were measured by a quartz dilatometer, up to 1000^0C, heating rate 2^0 C/ min.

The behavior of the glazes under heat treatment was studied with a Zeiss Jena hot stage microscope in the range of $20–1350^0$ C with a heating rate of 10^0/ min. The following characteristics were determined: $T_{1/2}$ (half-sphere) and $T_{1/3}$ (melting) and contact angle.

Colour characteristics have been estimated with MiniScan XE Plus, HunterLab spectrocolorimeter.

3. Results and discussion

3.1 Glazes properties additive calculated. Theoretical aspects.

The thermal expansion coefficient, which influences the adherence of the glaze to the ceramic substrate, was calculated for each glaze using the additive law Eq. 1 (Appen method). This law states that each oxide has a different contribution to the final α value [5]:

$$\alpha = \frac{1}{100}\sum \alpha_i p_i \cdot 10^{-7} \quad , \qquad (1)$$

where: α_i is the characteristic parameter of the oxide *i* and p_i - the molar fraction of the *i* oxide.

Similarly, it is possible to calculate *the surface tension* using (Eq. 2):

$$\sigma = \frac{1}{100}\sum \sigma_i \gamma_i \qquad , \qquad (2)$$

where: γ_i is the content of the initial oxides *i* expressed in molar fraction; σ_i -the characteristic parameter for each oxide (Appen method) for 1300^0C [6-7]. Dietzel indicates the same formula for 900^0C, but γ_i is expressed in weight fractions.

For *density calculation* Appen [8] recommended Eq. 3:

$$d = \frac{100}{\sum(\gamma_{im}\upsilon_i)} \qquad , \qquad (3)$$

where: γ_{im} is the content of the oxide expressed in mol fractions; υ_i - the partial molar volume for each oxide introduced in glaze composition. The values of υ_{SiO_2} depend on SiO_2 content. If the content of SiO_2 is less than 67 mole %, the value of υ_{SiO_2} is equal to 26.1. If thes content is greater than 67 mole %, then υ_{SiO_2} is calculated with Eq. 4[8].

$$\upsilon_{SiO_2} = 26.1 + 0.035(\gamma_{SiO_2} - 67) \qquad (4)$$

The refractive index calculation was done using Demkina [9] method (Eq. 5):

$$n = \frac{\frac{p_1 n_1}{S_1} + .. + \frac{p_n n_n}{S_n}}{\frac{p_1}{S_1} + .. + \frac{p_n}{S_n}} \qquad (5)$$

where $p_1 \ldots p_n$ represents the content of oxide in weight fractions; $S_1 \ldots S_n$- the molecular mass of oxide; $n_1 \ldots n_n$ – their refractive index coefficients

The light dispersion, $D=n_F-n_C$ at 20^0C, was also calculated with the formula Eq. 6 recommended by Demkina[9]:

$$D = \frac{\frac{p_1 D_1}{S_1} + .. \frac{p_n D_n}{S_n}}{\frac{p_1}{S_1} + .. \frac{p_n}{S_n}} \qquad (6)$$

where: $p_1 \ldots p_n$ represents the content of oxide in weight fractions; $S_1 \ldots S_n$- the molecular mass of oxides; $D_1 \ldots D_n$ – their dispersion coefficients[9-10].

The melt viscosity can be estimated from dilatometric and hot stage microscopy based on three known reference points Tg –the glass transition temperature, Ts- the softening point and $T_{1/2}$ the half sphere point. This reference can be inputed into the Vogel-Fulcher-Tamman (VFT) equation to determine the unknown A, B and T_0 constants. The VFT equation provides a good fit to viscosity data over a wide range temperature and is commonly used to calculate the viscosity of industrial glasses and glazes [11-12].

$$\log \eta = A + B / (T - T_0) \quad , \qquad (7)$$

where : A, B and T_0 are constants.

$$T_0 = \frac{12Tg - 3.55T_{1/2} + (9.25Ts - 12Tg)\dfrac{T_{1/2} - Tg}{Ts - Tg}}{8.45 - 2.75\dfrac{T_{1/2} - Tg}{Ts - Tg}} \qquad (8)$$

$$A = (9.25\ T_s - 12T_g + 2.75\ T_0) / (T_s - T_g) \qquad (9)$$

$$B = (T_g - T_0)(12 - A) \qquad (10)$$

In the field of materials and silicates the properties calculation is valid especially for those materials, which after the heat treatment have passed through melt phase and can be found in vitreous state [5].

For instance viscosity variation is calculated based on the content of SnO_2.

Fig. 1 shows the variation of log η calculated with Eq 7 versus temperature in the range 1200^0C-1250^0C. Viscosity increases as SnO_2 concentration increases from glazes G0 to G4.

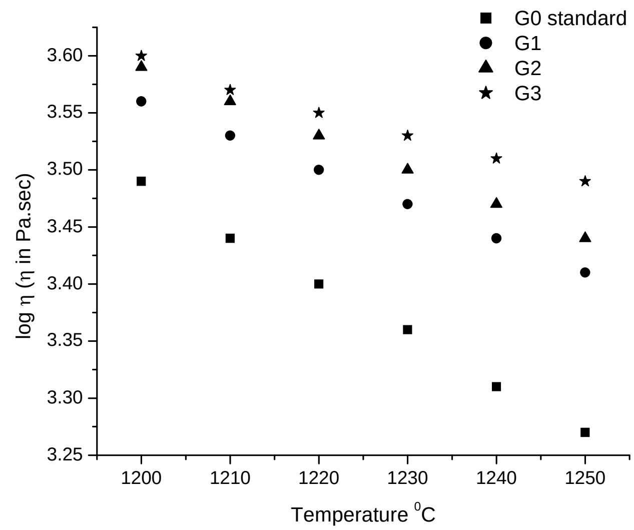

Fig. 1 log η vs. temperature based on the VFT equation.

The values of coefficients from equations 7-10, presented in Table 3 were determined based on hot stage microscopy and dilatometry results (as it can be seen further).

Table 3

Calculated Vogel-Fulcher-Tamman constants

Sample	VFT constants		
	To	A	B
G0	524.25	0.14	2264.86
G1	609.25	2.07	881.28
G2	617.02	1.70	1100.82
G3	641.90	2.27	740.45

3.2. Experimental results

The glazes melting behavior was estimated by hot stage microscopy. The melting temperature of glazes was 1250 ^{0}C±10 ^{0}C. In Fig. 3 the thermal behavior of G1 glaze is presented. The values of contact angle between 61 and 70 degrees of the obtained glazes also confirm their adequate adherence to the ceramic substrate. The contact angles were determined by drawing tangents to outer surfaces of the hot stage microscopy images.

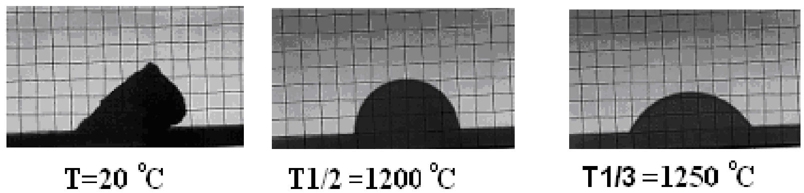

Fig. 2 Thermal behavior of G1 glaze

The measured values of reference temperatures presented in Table 4 were used to calculate VFT constants using equations 8-10. Based on these constants the values of glaze melting viscosity were obtained.

Table 4

The measured values of the reference temperatures

Sample	Reference temperature (^{0}C)			
	Tg	Ts	$T_{1/2}$	$T_{1/3}$
G0	713	770	1180	1240
G1	698	732	1200	1250
G2	724	763	1220	1250
G3	718	748	1230	1260
Tg is glass transition temperature; Ts is dilatometric softening temperature; $T_{1/2}$ is hot stage microscopy half sphere temperature; $T_{1/3}$-melting temperature				

The phase analysis of the glazes by X-Ray diffraction through the selected thermal treatment that was based on their thermal behavior emphasized the presence of quartz and plagioclase for standard glaze G0 and SnO_2 in the case of G1-G3 glazes (Fig. 3-4).

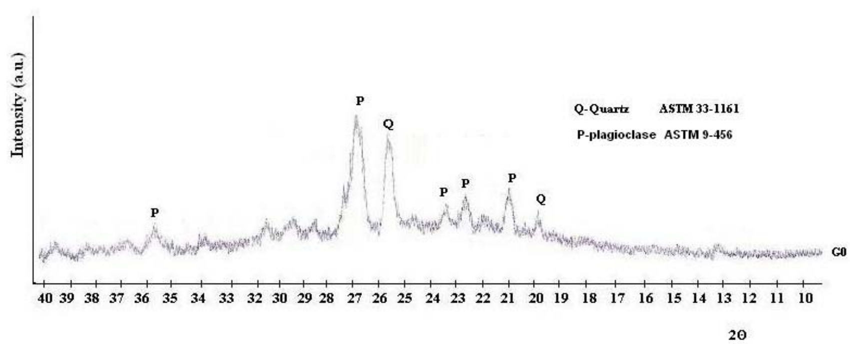

Fig. 3 XRD pattern of standard glaze-G0

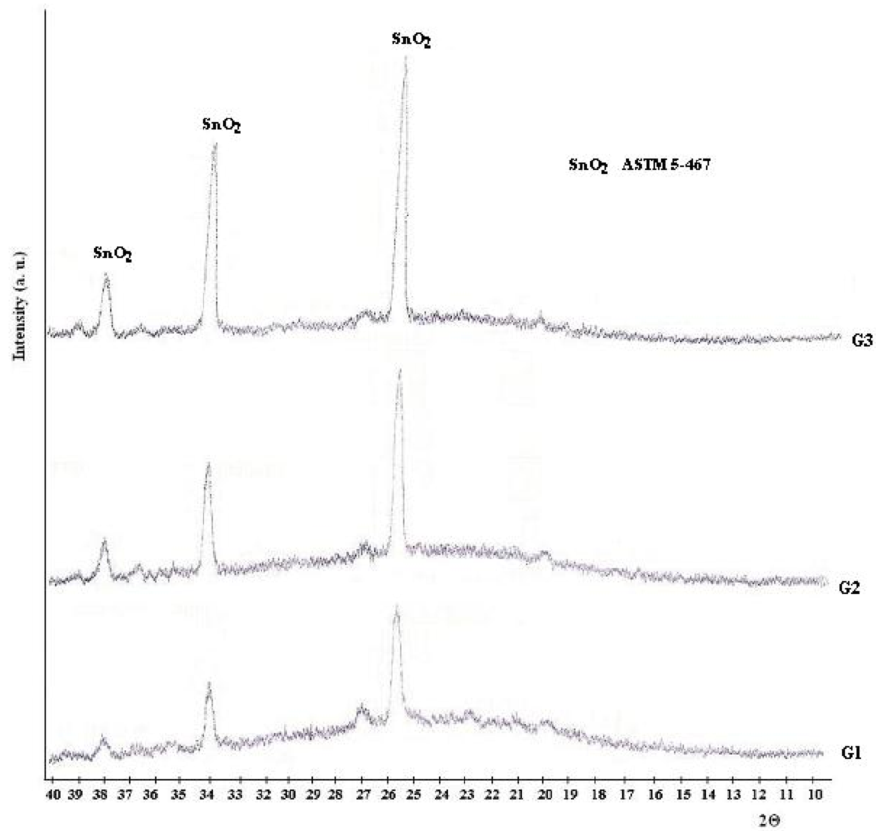

Fig. 4 XRD patterns of G1-G3 glazes

The result of the phase analysis indicates that the reaction between compounds is incomplete for the used thermal treatment, a part from quartz remaining unreacted. The presence of SnO_2 in the glaze-ceramic substrate interface for sample G3 was also evidenced by SEM as can be seen in Fig. 5.

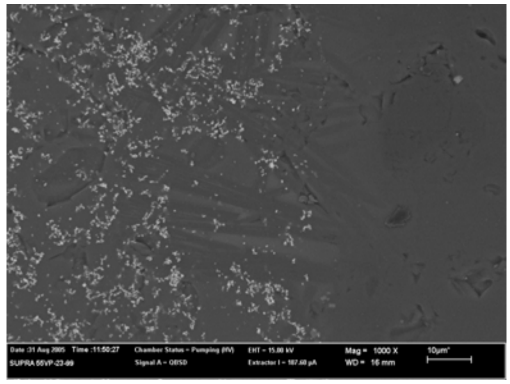

Fig. 5 SEM micrograph of G3 glaze-ceramic substrate interface layer

The thermal expansion coefficients determined experimentally and calculated are presented in Table 5.

For non-homogeneous glasses, as in the case of the glazes where phase separation or crystallization may occur, the values of α calculated by Eq.1 may be considerably different from the experimental values.

The X-Ray diffraction results confirm the non-homogeneous character of the obtained glazes and therefore the difference between the calculated and experimentally values of the thermal expansion coefficients.

The difference between thermal expansion coefficient of the glazes and thermal expansion coefficient of the ceramic substrate both experimentally determined is under 15%, a value accepted for a good adherence.

Table 5

The thermal expansion coefficients experimentally determined and calculated

Sample	α_{300}experimental [1/grd]	α calculated [1/grd]
G0	$5.37 \cdot 10^{-6}$	$6.90 \cdot 10^{-6}$
G1	$5.42 \cdot 10^{-6}$	$6.62 \cdot 10^{-6}$
G2	$5.30 \cdot 10^{-6}$	$6.52 \cdot 10^{-6}$
G3	$5.04 \cdot 10^{-6}$	$6.25 \cdot 10^{-6}$
$\alpha_{substrate}$ experimental	$5.50 \cdot 10^{-6}$	

The colour measurements in polar coordinates $L^* c^* h^*$were carried out on the glazed green ceramic substrate and thermally treated at 1250 ^{0}C, Table 6.

Table 6

Colorimetric characteristics of glazes

Sample	L^* [%]	C^* [%]	h^* [degree]
G0	81.73	3.81	101.53
G1	92.22	2.12	92.20
G2	93.17	2.55	100.60
G3	93.47	1.83	85.44
L^*-luminosity; C^*-colour chromaticity ; h^*- hue			

The diffuse reflection spectra are presented in Fig. 6.

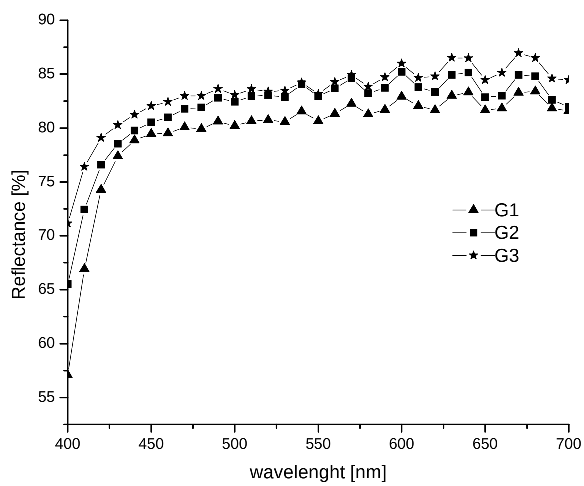

Fig. 6 The diffuse reflection spectra of G1-G3 glazes

According to the hue values h* 85-102 degrees glazes are placed in the quadrant II, close to yellow axis (h* = 90 degrees). The luminosity of the glazes, which is a measure of reflectivity, is close to 100 showing a good reflecting surface.

The whiteness degree of the glazes G1-G3 increased with the increasing of SnO_2 content and varies between 71 and 75 (Fig. 7). The whiteness degree expresses the white of the analyzed material and depends on the following properties: hue, saturation and luminosity.

The best quality glazes are obtained when the colour of the ceramic substrate cannot be seen through the glaze and the appearance of the piece is white.

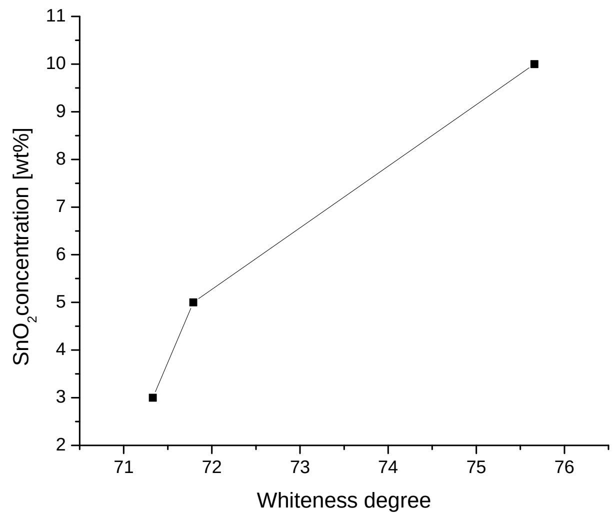

Fig. 7 Whiteness degree of G1-G3 glazes

4. Conclusions

Glazes for sanitary ceramic opacified with SnO_2 were obtained.

The dilatometry results pointed out the adequate glaze-ceramic substrate adherence for all glazes.

The correlation of the results from the hot stage microscopy and dilatometry revealed information related to viscosity. The viscosity increases as SnO_2 concentration increases, but in all cases at 1250 ^{0}C, a smooth glaze surface being obtained.

The optical properties of glazes are enhanced by SnO_2 addition.

Following the experimental investigations and respectively, the analyzed results, this paper concludes that raw glazes with SnO_2 addition can be recommended for glazing sanitary ceramics.

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