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Composition effects on the whiteness and physical-mechanical properties of traditional sanitary-ware glaze

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Abstract

Whiteness and physical-mechanical characteristics of sanitary glazes are usually controlled and improved by changing chemical composition of the raw materials. In this study, ten glazes of industrial interest, with different composition, were prepared by spraying, using the traditional ceramic substrate, and then thermally treated in industrial tunnel kiln at temperature of 1250 °C. The obtained glazes were characterized by X-ray diffraction in order to reveal their mineralogical composition, also confirmed by FTIR spectra, and were observed by backscattered electron images to study their microstructure and to derive the thermal expansion coefficients. Whiteness characteristics were obtained by a Micro color colorimeter data station. The results showed a difference of 10% between calculated and experimentally derived thermal expansion coefficients and the improvement of whiteness (up to 85.7%) and flexural strength (47.61 MPa) at a maximal content of zircon (14.5 wt%) and a low content of ZnO (2.5 wt%).

Keywords: Physical-mechanical properties; Whiteness; Glaze; Ceramic sanitary-ware

1. Introduction

Ceramic glazes are thin glassy layer on ceramic products surface which play both decorative and functional basic roles. Those roles are mutually combined, and, from a commercial point of view, they mainly depend on surface properties of the glazes.[1–4] The whiteness of the ceramic bodies (granted by the deposited glaze) is the main esthetical factor that determines the quality of any product. It must meet the requirements for domestic sanitary ware (Wh. > 80%) and be attractive, at lower prices, for users. ZrO_2, ZnO, TiO_2, and SnO_2 are used as opacifying agents. $ZrSiO_4$ was proved to enhance opacity, especially in the presence of ZnO with a $SiO_2/A1_2O_3$ molar ratio equal to 10.[1,2] The coverage capacity and wetting characteristics of a glaze are controlled by its surface tension, contact angle, viscosity and opacity.[5] The properties of glaze depend on a variety of aspects: the effects of raw materials and oxide compositions on one hand and the firing conditions on the other hand.[6,7] The final formulation of the enamel depends on both physical as well as esthetical properties. Among the first, important properties are the maturation time, the thermal expansion coefficient values and the reactivity with the ceramic support. In particular, the thermal expansion coefficient value of the enamel must be close to the body's one (in most cases around $7 \times 10^{-6}\,°C^{-1}$) to avoid strains on the tile[8] and several investigators have proposed methods for calculating these coefficients.[9,10] Whiteness, depending on the amount of coloring oxides in the raw materials, is used to compare ceramic pieces and evaluates their quality. For a white ceramic, the amount of (Fe_2O_3, TiO_2) should not exceed 0.3–0.4 wt%. Experiments showed that the zircon gives a large increase in whiteness and shine, extends the softening range up to 150 °C, and hence correspondingly increases the firing range of the glaze.[11] The zircon amounts should be not less than 10%.[12] From a phase composition point of view, glaze is generally constituted by a dominant amorphous phase in which other crystalline phases (such as zircon, diopside, wollastonite,

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and quartz) are dispersed providing opacity and giving a thermal shrinkage fitting with the ceramic bulk.[13,14] The assessment of the quality of a glaze mainly relies on its fusibility behavior and rheological properties, on its color, opacity and on its thermal expansion.[15]

In the present study, we investigated the effect of varying the chemical composition (amount of raw materials and accordingly the oxides contents) on the glaze properties (whiteness, flexural strength, etc.) in order to improve the quality of the obtained sanitary ware glaze. We prepared ten different glazes: (i) three samples varying the zircon and ZnO quantities, (ii) four samples varying the dolomite grain size distribution, (iii) two samples using talc in substitution of dolomite and one sample as reference. The glazes were characterized using X-ray powder diffraction image processing of backscattered electron images, electron microprobe analysis and the results used to calculate the thermal expansion coefficients. We measured whiteness, flexural strength, porosity and chemical durability, and calculated fusibility, surface tension and thermal expansion coefficients, these lasts were compared with the values resulted from experimental data.

2. Experimental procedure

2.1. Preparation of glazes

All experiments were prepared in the laboratories of the Société Céramique Sanitaire El-Milia, (Jijel, Algeria). The raw materials used for preparation of the glazes were kaolin, sodium feldspar, quartz, calcite, zircon, dolomite, and zinc oxide, all of industrial grade, and the overall composition in weight % is reported in Table 1, together with a reference sample G_{ref}. The raw materials were milled in humid conditions up to 1% residue using 63 microns sieve.[16,17] and the experimental glazes were prepared by grinding the necessary weight of quartz and dolomite or (talc) in the rotary jar and mixing it with 3/4 of the 40 wt% of water for 2–3 h with few drops of sodium silicate (to avoid flocculation) and adding the remaining water and raw materials afterwards.

The oxide compositions of the studied glazes (in molar fraction: Table 2) are calculated according to the Seger formula[18] where SiO_2 is the major oxide ranging from 1.147 to 4.236, while Al_2O_3 content varies in the range from 0.145 to 0.409. Finally, for each composition, raw mixture was sprayed upon a traditional ceramic slip (6–9 wt% Kaolin Remblend (RMB), 33–34 wt% sodium feldspar, 24–26 wt% quartz), and then thermally treated at temperature of 1250 °C under industrial conditions.

Table 2
Starting molar composition in oxides of the glazes on study.

Sample	Basic oxides	Neutral oxides	Acid oxides
G1	0.128 Na_2O		
	0.007 K_2O	0.199 Al_2O_3	2.203 SiO_2
	0.602 CaO	0.003 Fe_2O_3	0.002 TiO_2
	0.164 MgO		0.164 ZrO_2
	0.099 ZnO		
G2	0.130 Na_2O		
	0.007 K_2O	0.201 Al_2O_3	2.242 SiO_2
	0.610 CaO	0.003 Fe_2O_3	0.002 TiO_2
	0.166 MgO		0.172 ZrO_2
	0.086 ZnO		
G3	0.132 Na_2O		
	0.007 K_2O	0.204 Al_2O_3	2.281 SiO_2
	0.619 CaO	0.003 Fe_2O_3	0.002 TiO_2
	0.168 MgO		0.181 ZrO_2
	0.073 ZnO		
G4	0.157 Na_2O		
	0.009 K_2O	0.269 Al_2O_3	2.862 SiO_2
	0.527 CaO	0.006 Fe_2O_3	0.002 TiO_2
	0.168 MgO		0.193 ZrO_2
	0.139 ZnO		
G5, G6, G7, and G8	0.127 Na_2O		
	0.007 K_2O	0.196 Al_2O_3	2.166 SiO_2
	0.593 CaO	0.003 Fe_2O_3	0.001 TiO_2
	0.161 MgO		0.156 ZrO_2
	0.112 ZnO		
G9	0.239 Na_2O		
	0.013 K_2O	0.409 Al_2O_3	4.236 SiO_2
	0.379 CaO	0.010 Fe_2O_3	0.003 TiO_2
	0.322 MgO		0.263 ZrO_2
	0.047 ZnO		
G_{ref}	0.127 Na_2O		
	0.009 K_2O	0.222 Al_2O_3	2.148 SiO_2
	0.603 CaO	0.003 Fe_2O_3	0.002 TiO_2
	0.179 MgO		0.105 ZrO_2
	0.082 ZnO		

Table 1
Raw materials (wt%) used for glazes preparation.

Sample	Kaolin RMB[a]	Sodium feldspar	Quartz	Calcite	Zircon	Dolomite	Dolomite grain size (μm)	Talc	ZnO
G1	6	34	26	10	13.5	7	63	0	3.5
G2	6	34	26	10	14	7	63	0	3
G3	6	34	26	10	14.5	7	63	0	2.5
G4	6	34	26	10	13	0	63	7	4
G5	6	34	26	10	13	7	63	0	4
G6	6	34	26	10	13	7	65	0	4
G7	6	34	26	10	13	7	45	0	4
G8	6	34	26	10	13	7	<45	0	4
G9	6	38	27	5	13	0	63	10	1
G_{ref}	6–9	33–34	24–26	8–10	7–9	7–8	63	0	2–3

[a] Kaolin Remblend.