ELABORATION OF ADVANCED GLASS-CERAMIC GLAZE FOR ANTI-SLIP PORCELAIN STONEWARE

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ABSTRACT

The present communication describes the synthesis of anti-slip enamel exhibiting glass-ceramic nature using new matte frits and raw materials. The glass-ceramic glazes obtained are characterized by various instrumental techniques (X-ray fluorescence (XRF), scanning electron microscopy (SEM), X-ray diffraction (XRD), mechanical profilometry and microhardness measurements) to elucidate the nature of the crystallized phases, their morphology, surface roughness and the finished tile microhardness. The quality of the glazed piece is evaluated by the regulations of chemical resistance, stain-resistance and slipperiness. The enamel obtained devitrifies in crystals of calcium and barium silicoaluminates. It complies with anti-slip and stain-resistance standards, because its surface roughness is similar to that of non-slip enamel.

Keywords: ceramic, anti-slip, crystallochemistry, porcelain stoneware, glass-ceramic.

INTRODUCTION

The ceramic glazes are expected to have the characteristics of the ceramic tiles classified according to the final application or use. In that sense, the anti-slip resistance is an indispensable property of tiles as it is a basic security requirement [1 - 3].

The standard anti-slip ceramic floor tiles are usually made of matt glazes, which are produced through surface application of granulated frits, corundum and other particles providing the surface roughness required [4]. However, even when this type of ceramic products cover the UNE-EN 12633:2003 requirements having anti-slip resistance values close to class 3, their rough surface exhibits cleaning problems because of the dust retained. Besides, their touch is rather rough, being difficult to market it. In that sense, there are numerous investigations aiming at the development of glass-ceramic glazes of a high wear and tear, tenacity, chemical corrosion with resistance and ability to adapt to polished treatments through improving the properties of their glassy precursors. Thus, the most studied compositions are based on $MgO•Al_2O_3•SiO_2$ and $CaO•MgO•Al_2O_3•SiO_2$ systems, which are able to devitrify in cordierite (Fig. 1) or on calcium and magnesium solid solutions containing silicoaluminates [5 - 20].

In this sense, great efforts are recently devoted on the elaboration of advanced nepheline ($Na_2O•Al_2O_3•2SiO_2$), and/or forsterite ($2MgO•SiO_2$) [21 - 27], anorthite ($CaO•Al_2O_3•2SiO_4$) [28 - 32], as well as glass-ceramic materials, obtained from recycled precursors [33 - 38].

The glass-ceramic materials can be considered as inorganic and polycrystalline materials of multiphase nature. They are synthesized in the course of thermal

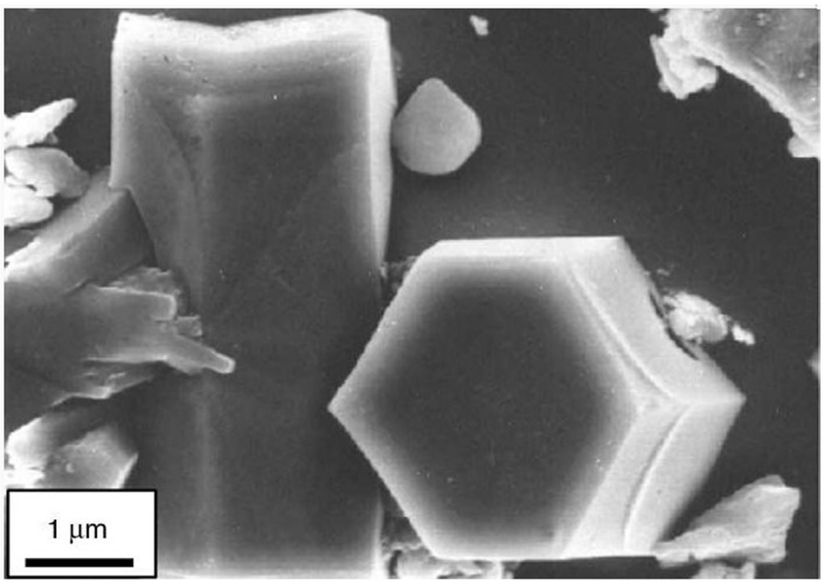

Fig. 1. SEM micrograph of alfa cordierite crystals in the form of hexagonal prisms in a glass.

processes promoting the controlled nucleation and crystallization of some glassy precursors, generally induced by nucleation agents such as TiO_2 [39 - 42] and ZrO_2 [43 - 47]. The adequate controlled inner crystallisation is directly influenced by an efficient nucleation providing the random formation of tiny crystals free of porosity and microfractures. Thus, crystallinity ranging from 0.5 % to 99.5 % [48 - 50] is reached. Sometimes, the crystallization results in new functionalities or effects different from the mechanical properties observed [51].

According to Stookey [52, 53] the glass-ceramic materials possess various advanced properties like appropriate flexibility to be shaped, low porosity, etc., which make them essential technological materials. Besides, the corresponding technological regimes used enable ease modification for obtaining glass-ceramics suitable for specific heavy duty applications.

In this sense, the current study describes the development of an advanced glass-ceramic glaze composition combining not only the surface hardness and the anti-slip properties, but also the easy-cleaning and the soft touch.

EXPERIMENTAL

Preparation of the glass-ceramic glaze

The selected raw materials were mostly ceramic frits and minerals, corresponding to the matt glazes of Ba and Ca. The chemical analysis was performed by X-ray fluorescence using a Pioneer Bruker model S4. The results obtained are shown in Table 1.

The laboratory procedure consisted of selecting and mixing adequate frits and raw materials, followed by wet grinding in a planetary mill loaded by alumina balls as grinding media aiming to obtain slurry particles of size dimensions lower than 45 µm. Afterwards, the liquid glaze obtained was allowed to fall freely through a nozzle with appropriate aperture (i.e. a narrow rectangular vent) onto a ceramic body surface in correspondence with the waterfall method, which is the most widely used in the ceramic industrial branch for glaze application. Finally, the glazed porcelain stoneware was fired in a muffle kiln (Nannetti) for 1 h reaching maximum temperature of 1190ºC.

Table 1. Chemical analysis of used matt frits (mass %) determined by XRF.

mass %	SiO_2	Al_2O_3	B_2O_3	CaO	BaO	K_2O	Na_2O	ZnO
Barium matt frit	40-60	10-20	0-5	0-5	20-40	0-5	-	-
Calcium matt frit	40-60	20-40	-	10-20	-	0-5	0-5	0-5

Table 2. Chemical analysis of synthesized glaze (mass %) determined by XRF.

mass %	SiO_2	Al_2O_3	RO	R_2O
Glaze	40-60	10-30	20-30	5-10

Glass-ceramic glaze characterization

Structural, compositional and morphological analyse

The instrumental techniques used to characterize the glaze obtained referred to: (i) elemental analysis by X-ray Fluorescence (XRF) performed in the wavelength dispersion regime using a Pioneer Bruker model S4; (ii) X-ray diffraction (XRD) executed on "Bruker D4 Endeavor" X-ray diffractometer in 10° - 80° (2θ) range with a step of 0.05°/2s; (iii) Scanning Electron Microscopy (SEM) performed on JEOL 7001F; (iv) Energy Dispersive X-ray analysis (EDX) for element content determination.

Surface properties evaluation

The application of the analytical methods described required the assessment of the thermal and mechanical properties of the obtained glass-ceramics obtained. The measurements were performed by the methods described below: (i) Dilatometry coefficient determination performed on "DIL801 Bahr" dilatometer; (ii) The surface roughness was evaluated by a mechanical profiler, model "Dektak 6M" product of Veeco; (iii) The Vickers microhardness was measured using a Hardness Testing Machine "HM Mitutoyo" model.

Referring to the final product quality testing, the anti-slip resistance (UNE-ENV 12633:2003), the chemical resistance (ISO 10545-13:1995) and the stain resistance (ISO 10545-13:1995) were analysed to compare the glass-ceramic glaze with the conventional anti-slip glazes.

RESULTS AND DISCUSSION

Characterization of glass-ceramic glaze

The chemical analysis of the optimal glazes presenting the highest devitrification capability during porcelain stoneware firing cycle are shown in Table 2, where the alkaline and the alkaline earth oxides are assigned as "R_2O" and "RO", respectively. These oxides are added to the glaze compositions to decrease their melt-

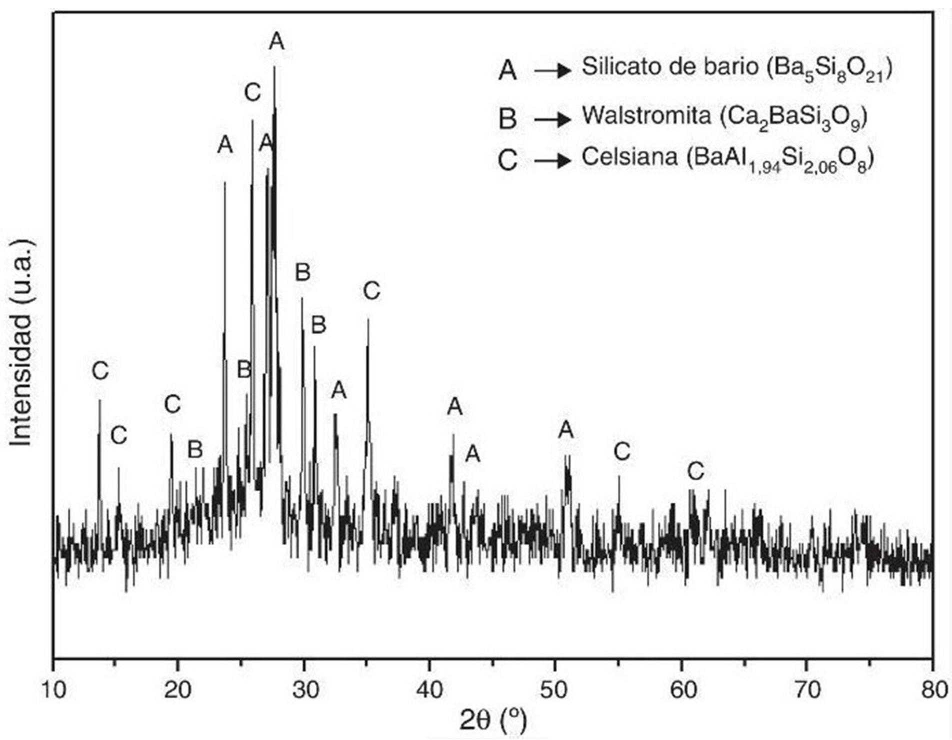

Fig. 2. Diffractogram of the glass-ceramic glaze applied on a porcelain stoneware tile.

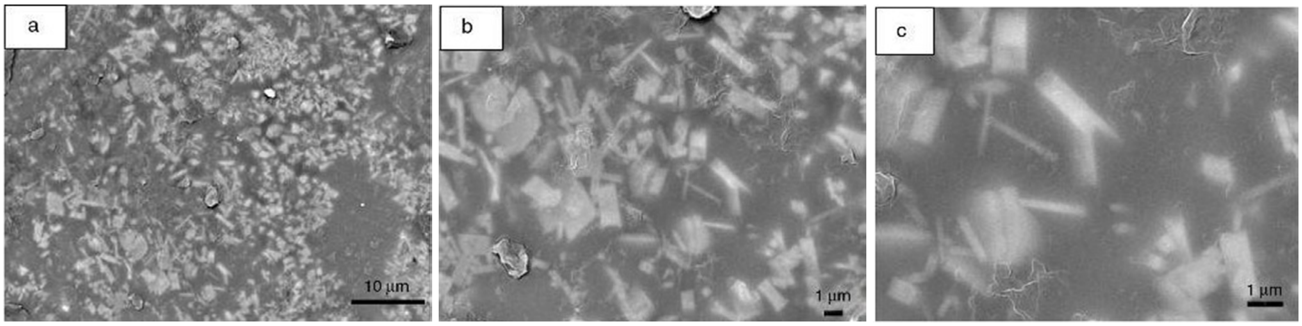

Fig. 3. SEM micrographs of an anti-slip glaze: a) x2000, b) x5000 y c) x10000.

Table 3. Microanalysis of glazed Surface (mass %) determined by EDX.

wt%	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	BaO
Crystal	5.04	19.11	49.69	2.96	5.30	17.90
Matrix	5.22	15.54	57.58	3.49	9.48	8.69

ing points. As seen from Table 2, these glazes possess a high content of alkaline earth oxides as they are based on calcium and barium matt frits. The crystallinity study of the glass-ceramic glaze is illustrated by the diffractogram of the glazed porcelain stoneware tile (Fig. 2). The peaks identified there correspond to solid solutions of silicoaluminates and barium and calcium silicates.

The micrographs of the glaze studied show crystals of a rectangular shape uniformly spread inside the vitreous matrix, i.e. they visualize the high surface density of a glass-ceramic material (Fig. 3).

The microanalysis determined by EDX (Table 3) indicates that Ba migrates from the vitreous matrix to the crystalline zones as BaO content (mass %) is twice higher inside the crystals than in the vitreous matrix. The case with Ca content is reversed. Consequently, the crystalline phase is rich in Ba presenting ca 50 mass % of Si.

Fig. 4 compares the dilatometry analysis data referring to the glaze synthesized and a standard matt glaze. It is evident that both curves are very similar. Their softening points are at 1002ºC and 979ºC, respectively. Consequently, the anti-slip ceramic glaze is completely compatible to the already developed conventional porcelain stoneware bodies.

The Vickers microhardness of the investigated glass ceramic glaze is measured and compared to those

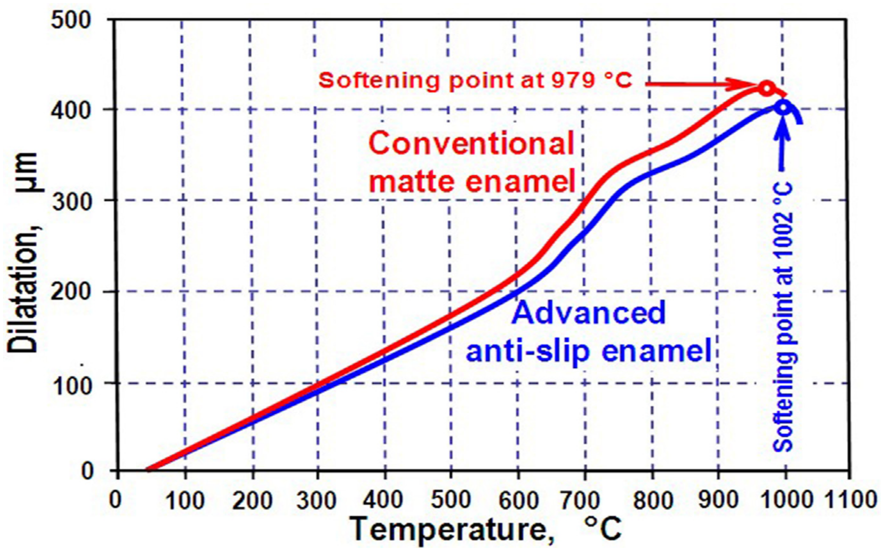

Fig. 4. Comparison of dilatometry analysis data referring to the new anti-slip glaze and a standard anti-slip glaze.

Table 4. Summary of the final product quality testing of the glass-ceramic glaze on porcelain stoneware tile.

Final product quality testing	Result	UNE-ISO
Physical properties		
Anti-slip resistance	3 class	UNE-ENV 12633:2003
Chemical properties		
Stain resistance	Clase 5	UNE-EN ISO 10545-14
Cleaning products and swimming-pool salts resistance	GA	UNE-EN ISO 10545-13
Acids and bases in low concentration resistance	GLA	UNE-EN ISO 10545-13
Acids and bases in high concentration resistance	GHA	UNE-EN ISO 10545-13

of a non-anti-slip glaze, a standard anti-slip glaze containing corundum, and a standard anti-slip glaze with incorporated granulated frits. The results obtained are represented in Fig. 5.

The glass-ceramic glaze of microhardness (measured applying 1 N for 30 seconds) higher than 3700 HV-1N 30s is found remarkably excelling the standard anti-slip glaze with incorporated fritted granules of microhardness of about 1700 HV-1N 30s, and both the non-anti-slip glaze and the corundum doped standard anti-slip glaze which show microhardness even less than 600 HV-1N 30s. Besides, the roughness of the newly developed hard glaze is similar to that of the non-anti-slip glaze (from 3.2 μm to 0.8 μm in the non-anti-slip one) providing the soft touch of the final product. Meanwhile, both standard anti-slip glazes possess roughness around 12 μm (corundum) and 32 μm (fritted granules).

Finally, Table 4 collects the results corresponding to the final product quality.

The anti-slip resistance of the new glaze presents an R_d value of 45 (dimensionless factor) which is related to class 3, i.e. the highest class for high anti-slipperiness ceramic tiles according to UNE-ENV 12633:2003 standard. Referred to the chemical resistance, the new glaze in not stained when treated with cleaning products (GA class) or with acidic and alkaline swimming-pool salts at high (GHA) and low concentration (GLA) according to ISO 10545-13:1995 standard. The stain-resistance reaches the maximum level (5) referred to all stains studied: the stain agent of green spots in light oil, the

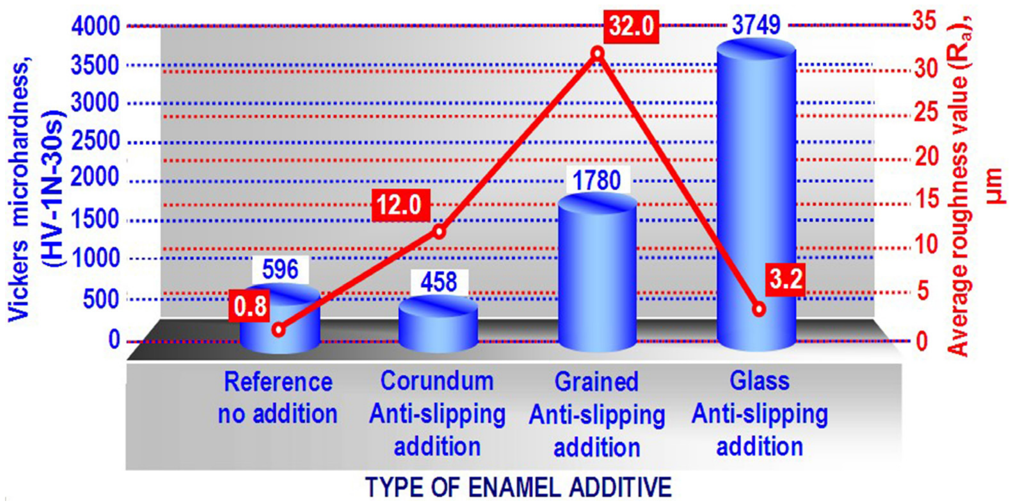

Fig. 5. Vickers microhardness and roughness variation vs. glaze typology.

stain agent forming a film (olive oil) and the stain agent of an oxidizing chemical action (iodine).

CONCLUSIONS

A new kind of an advanced glass-ceramic glaze composition is synthesized using matt frits and other mineral raw materials able to devitrify in calcium and barium silicoaluminates and silicates. Thus, an anti-slip and stain resistance glass-ceramic glaze of suitable surface roughness resulting from these phases crystallisations is successfully elaborated. The soft touch of the product developed is similar to that of a non-anti-slip glaze, but shows higher microhardness compared to that of the standard anti-slip glazes. Consequently, this new glaze composition is completely appropriate for application to porcelain stoneware bodies for high pedestrian traffic areas. Besides, it excels the nowadays existing compositions because of the specific combination of beneficial properties as mechanical strength, surface roughness, and chemical durability. These remarkable advantages enable elaboration of anti-slipping ceramic tiles of significantly extended service life time.

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