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Development of a glass-ceramic glaze formulated from industrial residues to improve the mechanical properties of the porcelain stoneware tiles.

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ABSTRACT

In this research a mixture of 90%wt of industrial residues (recycled soda-lime glass and ashes from a coal power thermal plant) have been vitrified for their use as "secondary raw material". Then, a glaze suspension was prepared to be applied as a glaze suspension on the porcelain stoneware tile. The tested pieces have been fired by a conventional porcelain cycle at 1180ºC of maximum temperature. The XRD, XRF, SEM/EDS and the dilatometric analysis have been the instrumental techniques used to characterize the final material. Finally, an ecological glass-ceramic glaze perfectly fitting on porcelain ceramic tile has been produced, exhibiting a unique phase, anorthite, which ensures a high flexural strength (around 96 MPa) and a significant Vickers microhardness of 250 GPa, improving the mechanical properties of a conventional the porcelain ceramic tile.

Keywords

Circular economy, revalorization of industrial waste, glass-ceramic glaze, porcelain stoneware, mechanical properties

1. Introduction

Citizen environmental awareness has increased in the past decade, due to the publication of many studies on the impacts of environmental degradation. In that sense, scientific research is contributing to arouse public awareness about the new technological challenges in society. One of the concepts which at the moment seems to be proliferating in a significant way is the circular economy. It has appeared as a new industrial model focused on the optimization of resources and the reduction of waste, having particular regard in the product design. In fact, the transition to a circular economy may be the biggest revolution of production and consumption in the global economy for next centuries [1].

Consequently, the revalorization of industrial wastes is the key to remaining competitive in the global marked, according to this concept. In that sense, the ceramic sector also includes the recycling of all by-products and part of the residues derived from depuration treatments, even residues from other sectors [2,3]. Consequently, a large variety of research about the incorporation of industrial waste in this sector has been published, obtaining products with high added value: ceramic frit waste to formulate glass-ceramic materials glass waste to produce glass-ceramic glazes or ecologic ceramic bodies; waste from building infrastructures; sanitary waste products; metallurgy dusts and fly ashes; spent FCC catalyst, waste serpentine and kiln rollers waste; marble and granite waste; water sludge from fresh water processing plant, municipal solid waste, etc. [4–6].

This work is based on the revalorization of a mixture of recycled glass and ashes from a coal power thermal plant to obtain a glass-ceramic glaze [7], containing 90 wt% of these industrial residues, which was applied on a porcelain body. The final tile exhibits a perfect coupling of the glaze with the body tile and high mechanical strength, due to the presence of anorthite as unique phase in the glaze. Consequently, it is possible to obtain glass-ceramic glazes with high performances, only using industrial residues as raw materials.

2. Experimental

The waste mixture (50%wt fly ash (FA)+ 50%wt glass cullet (GC)) was micronized in a planetary alumina ball mill, model Nannetti. Then it was melted at 1500ºC during 1 hour of residence time to be quenched in cool water. The glass obtained was micronized again in ball milling less than 45μm. Then, a glaze suspension was prepared using the waste powder, 0.1%wt CMC, 5 wt% kaolin and 0.5 wt% deflocculant. The slip was applied on a porcelain green body using the “doctor blade” method, to be fired according to a conventional porcelain firing cycle at 1200ºC.

The waste powder used was chemically characterized by an X-ray fluorescence dispersion wavelength equipment, model S4 Pioneer – Bruker (XRF). The mineralogical analysis of the glass-ceramic glaze was determined through the X-ray diffraction technique (XRD), by means of a diffractometer X-ray Bruker-AXS D4 Endeavor in the range of 10°- 80 ° (2θ) with a step 0.05 ° / 4s. The microstructure of the glass-ceramic glaze on the porcelain stoneware was studied by a scanning electron microscopy (SEM) model JEOL 7001F attached with an energy dispersive X-ray spectrometer (EDS). The determination of the flexural strength and the breaking load of the final tile were determined by the three point flexural test using a Plasticimeter HOYTOM (UNE-EN-ISO 10545-4). The Vickers microhardness of the glaze was measured using a Hardness Testing Machine HM Mitutoyo model, under the conditions of 1N applied on material for 30 seconds.

3. Results and discussion

The XRF results expressed in oxide form, of the industrial waste used in this study are included in Table 1. While FA are rich in silica, alumina and iron oxide, CG presents a higher silica content, together with sodium oxide and calcium oxide, but it is almost free of alumina and iron oxide. Consequently, both wastes exhibit different chemical composition, indicating that a melting stage of the mixture is needed to get a perfect homogenized precursor material to obtain a glass-ceramic glaze.

Table 1. Chemical analysis determined by XRF of industrial waste: fly ash (FA) and glass cullet (GC) (wt%).

wt%	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	L.O.I.*
FA	0,20	1,23	26,63	44,44	1,23	5,53	0,92	18,43	0,15

GC	12,59	3,75	0,85	73,16	0,30	8,94	0,05	0,10	0,10

* **L.O.I.**: loss on ignition

The chemical analysis of the glassy powder is shown in Table 2, where it can be observed that it is a silica-based composition with the presence of aluminium, calcium and iron. So, it is expected the devitrification of phases belonging to the Si-Al-Ca-Fe system.

Table 2. Chemical analysis determined by XRF of the glass-ceramic glaze (wt%).

wt%	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**L.O.I.***
glaze	4.13	1.81	16.32	55.96	0.83	11.66	9.29	0.05

* **L.O.I.**: loss on ignition

The mineralogical analysis (Fig.1) shows a diffractogram characterized by numerous well-defined and intensive peaks, corresponding to a unique phase, the anorthite (JCPDS card No. 86-1650), whose main peaks were indexed. The glass-ceramic glaze has devitrified in quite crystallized anorthite and without the presence of secondary phases such as pyroxenes, which would have appeared due to the presence of iron in the composition [8]. Consequently, it is expected a microstructure with abundant and large crystals of anorthite.

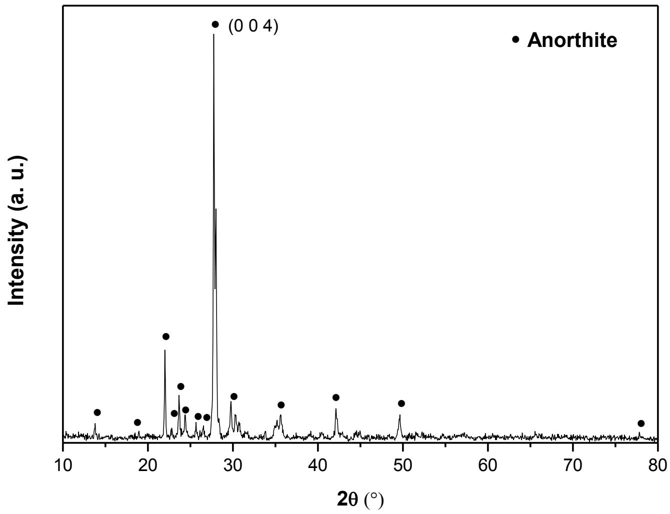

Figure 1. Difractogram of the glass-ceramic glaze applied on a porcelain stoneware tile

The Fig. 2 shows two micrographs at different magnification, corresponding to the glass-ceramic glaze. At x500 magnification (Fig. 2a), a well crystallized and homogeneous surface is observed. This SEM microstructure shows a network of interconnected platelet with needles edged crystals. At x5000 magnification (Fig. 2b) the interconnected plates show clearly edges of acicular growth with sizes larger than 10 μm approximately with residuals areas of glassy phase.

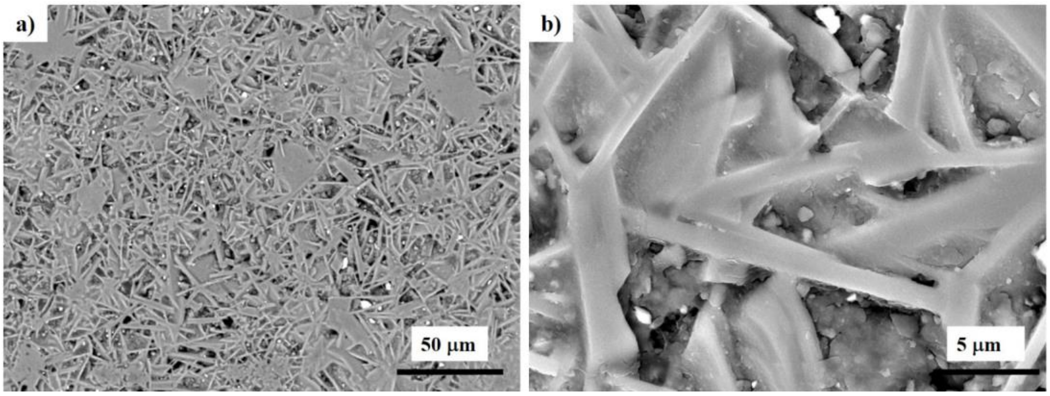

Figure 2. Scanning electron micrographs of the glass-ceramic glaze on a porcelain ceramic tile: a) x500, b) x5000**.**

Table 3 shows the corresponding microanalysis to a crystallized zone (crystals) on a platelet and to another zone between crystals (residual glassy phase). Both analysis are very similar, remaining a difference in alumina and iron content.

Table 3. Chemical analysis determined by EDX of the glaze-ceramic glaze (wt%).

wt%	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3
Crystals	4.71	1.88	15.93	57.17	0.92	10.90	8.49
Residual glassy phase	4.94	-	21.47	56.42	0.48	10.38	6.31

The flexural strength of the glass-ceramic tile with the new glaze based on residues has a value around 96 MPa, while a conventional glaze on a porcelain ceramic body is under 60 MPa. The Vickers microhardness corresponding to this glass-ceramic glaze is 250 GPa, whereas a typical glaze used in porcelain ceramic tiles has about 100 GPa. These results make this glass-ceramic glaze formulated from industrial residues, adequate for being used in high pedestrian and machinery traffic applications, such as airports or industries. Besides, this material is synthetized according to the concept of circular economy, which enhances the revalorization of industrial residues and the environmentally friendly design of product, while is able to give new functionalities to the ceramic tiles[9].

4. Conclusions

A glass-ceramic glaze applied on porcelain ceramic tile has been produced from 90%wt industrial residues using the conventional firing cycle of the porcelain stoneware (1200ºC). The ecological glass-ceramic glaze exhibits high flexural strength (around 96 MPa) and a significant Vickers microhardness of 250 GPa, almost doubling the mechanical properties of a conventional porcelain ceramic tile, with a 90 %wt of industrial residues revalorised.

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