THIN GLASS-CERAMIC GLAZES FOR PORCELAINIZED STONEWARE TILES

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ABSTRACT

A thin glass-ceramic layer belonging to the LiO_2-ZrO_2-SiO_2-Al_2O_3 system (LZSA) was used over porcelainized stoneware floor tile surfaces to protect them and improve product properties. A glaze of the studied glass-ceramic was obtained, appropriately prepared and applied over the surface of a glazed porcelainized stoneware. This material was sintered for 70 min at 900°C. The results obtained showed that abrasion resistance (PEI) rose from 3 to 5 and hardness (Mohs scale) rose from 4 to 9.

INTRODUCTION

The Porcelainized Stoneware share in the world ceramic tile market has grown, due to certain properties such as very low porosity and high mechanical strength. However, when polished, its closed porosity (about 6 to 8 %) becomes exposed, allowing penetration of dirt and surface staining. To overcome this problem, the application of a traditional glaze layer over the ceramic body in a single fire cycle has been shown to be a possible alternative, and has found some following. Nevertheless, for polishing this product exhibits the same problem with time, since these glazes also have closed porosity, low hardness and low abrasion resistance, so that the final product also loses its aesthetic characteristics. A technical alternative could be the application of a thin layer (about 5 to 10 mm) of a glass-ceramic material over the porcelainized stoneware surface. Such materials have been used widely in different areas of society and industry[1], including the ceramic tile area[2]. One of the glass-ceramic systems of practical interest is the LZS system (Li_2O-ZrO_2-SiO_2), which has interesting properties for applications as glazes in covering ceramic plates. Previous research works carried out by Novaes de Oliveira et al[2-4] show that certain compositions of the LZS system exhibit, in particular, high bending strength as well as high abrasion and chemical resistance, when compared with traditional materials. With respect to the manufacturing process, these materials can be obtained at lower temperatures (800-900°C) and in extremely short times (35-60 minutes) using the same conditions and machines of a traditional ceramic industry. However, it is necessary for this layer to be compatible with the ceramic base. For example, this system has a high coefficient of thermal expansion (9-11 x 10^{-6} °C^{-1}) compared to the ceramic base (5.5-7.0 x 10^{-6} °C^{-1}). In recent researches of the authors[5], the chemical composition of the LZS system has been modified with the addition of Al_2O_3 to correct the coefficient of thermal expansion. This new system, LZSA, has shown a wide range of coefficient of thermal expansion values, being easily adjustable for the purposes of this work. Moreover, it is desirable to maintain the design of the product, including the brightness, and if possible to add aesthetic value. This work shows the results obtained in the development of a glazed porcelainized stoneware product covered by a thin glass-ceramic glaze, using a glass-ceramic belonging to the LZSA system, thermally treated at 900°C for 70 min, with the objective of improving the mechanical properties, maintaining its brightness.

EXPERIMENTAL PROCEDURES

A composition of the LZSA system was prepared from appropriate amounts of Li_2CO_3, $ZrSiO_4$, SiO_2, Al_2O_3 and spodumene as raw materials. The batch composition of about 1 kg was placed in a mullite crucible and melted at about 1470°C for 2 h in a gas furnace. The melt was quenched in water and dried. Subsequently, an addition of 10 wt% of Al_2O_3, SiO_2 or $ZrSiO_4$ was made to the glass (frit) as a second phase, and referenced P10A, P10B and P10C, respectively. Each composition was dry milled in porcelain ball mills for 3 h and then sieved to yield a powder. Each composition was appropriately prepared and applied over a glazed porcelainized stoneware product. The samples were isothermally sintered in a laboratory roller kiln (± 5°C) for 70 min at 900°C. Subsequently, the samples were subjected to surface abrasion and stain resistance tests, according to ISO 10545, and the Mohs hardness test.

RESULTS AND DISCUSSION

There is a demand in the ceramic tile market for a product with high resistance to abrasion (PEI 5), high stain resistance (class 5), and high Mohs hardness (above 8). On the other hand, it is important for this product to have a pleasant aesthetic appearance. It was thus thought that a high performance glass-ceramic could be used as a protective coating of a glazed porcelainized stoneware tile. This protective coating, compatible with the glazed base, must have high mechanical properties and also allow the brightness of the glazed product to be observed. According to recent work by the authors[5], a glass ceramic containing 11.7 % Li_2O, 68.6 % SiO_2, 12.6 % ZrO_2 and 7.1 % Al_2O_3 wt% would present some of the desired mechanical properties. This composition achieves a relative density of 92 % when it is sintered for 70 min at 900°C. In these conditions, this composition shows an interesting coefficient of thermal expansion (5.5×10^{-6} °C^{-1}) when compared with the porcelainized stoneware glaze. Nevertheless, it is an opaque material. Therefore, a full layer could not be used. An appropriate design was then sought, illustrated in figure 1, containing points of the protective layer applied in a geometrically regular arrangement. Several situations were tested varying the number of points per square centimetre, from 44 to 576 points, over an appropriately chosen glazed porcelainized stoneware product, containing a low porosity glaze and high brightness; however the Mohs hardness was low (4).

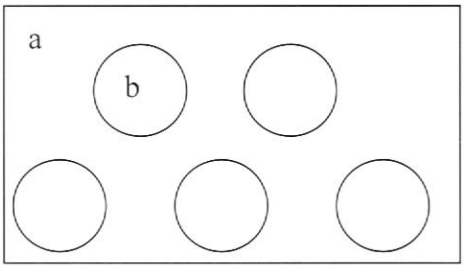

Figure 1- Schematic picture showing the design tested:
(a) original surface (porcelainized stoneware glaze) and (b) glass-ceramic glaze.

The studied glass-ceramic has low hardness (6 on the Mohs scale) for the purposes of this work. To attempt to overcome this limitation, 10 wt% of a second phase was added to the composition: Al_2O_3, SiO_2 and ZrO_2, referenced P10A, P10B and P10C, respectively. This addition increased the hardness to 9 on the Mohs scale. The sintered samples showed a good brightness and appearance. The tests with regard to the design (number of points per square centimetre) showed that the samples with 144, 324 and 441 points per square centimetre showed better brightness and abrasion resistance. However, the P10A sample, containing 10 % Al_2O_3, showed low surface abrasion resistance. The final results of Mohs hardness, abrasion resistance and stain resistance are given in Table 1.

SAMPLES	STAIN RESISTANCE (CLASS)	ABRASION RESISTANCE (PEI)	HARDNESS (Mohs)
P10A	5	4	> 9
P10B	5	5	> 9
P10C	5	5	> 9

Table 1 – Results obtained of the tested samples.

CONCLUSION

This work showed that the glass-ceramic belonging to the LZSA system applied as geometrically regular points over a glazed porcelainized stoneware tile is an interesting technological solution to obtain a high performance product, with regard to mechanical resistance and brightness.

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