

Poster 132

Development of matte glazes highly resistant to chemical attack

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ABSTRACT

Ceramic tiles with silky matte glazes possess good technical characteristics and have gained increasing ground in the consumer market. This type of product has traditionally been well accepted in the American market, but its acceptance in Brazil's domestic market, historically dominated by glossy finishes, has also grown in recent years.

The greatest deficiency of this type of product is its susceptibility to chemical attack^{1,2}, especially products fired in rapid firing cycles. This article analyzes commercial products with silky matte finish and glaze formulations highly resistant to chemical attack.

The study began with the characterization of the resistance to chemical attack of various products commercial available on the Brazilian market. Our objective in this step was to correlate the chemical resistance and the microstructural characteristics of the tested products, aiming to identify the factors that favor the manufacture of products with matte finish and high chemical resistance. Considering that matte glazes are composed of three distinct phases (glassy³, crystalline, and interfacial¹), one must analyze, case by case, which of these phases is attacked primarily, in the case of products susceptible to chemical aggression, keeping in mind that all of them can be attacked by different reagents. The image in Figure 1, obtained by scanning electron microscopy (SEM), shows the surface of a matte glaze.

The commercial products, which subjected to chemical resistance tests following the NBR 13.818 (ISO 13.006) standard, showed very different results. They were then microstructurally characterized by X-ray diffraction and analyzed by SEM, which revealed the following:

- The samples which displayed low chemical resistance showed primary crystalline phases of silicates and calcium aluminosilicates (anortite, wollastonite, guelenite).
- The samples with high chemical resistance were the only ones whose microstructure showed signs of quartz crystals. Mullite (aluminum silicate) and diopside (calcium-magnesium silicate) were also crystalline phases identified in the samples with high chemical resistance.
- The samples with low chemical resistance showed the highest concentrations of alkaline elements (above all potassium) in their glassy matrix. The samples with good chemical resistance, on the other hand, displayed glassy phases with high concentrations of zinc in detriment to the alkaline elements.

- The presence of silica in the glassy phase is also associated with samples showing good chemical durability.

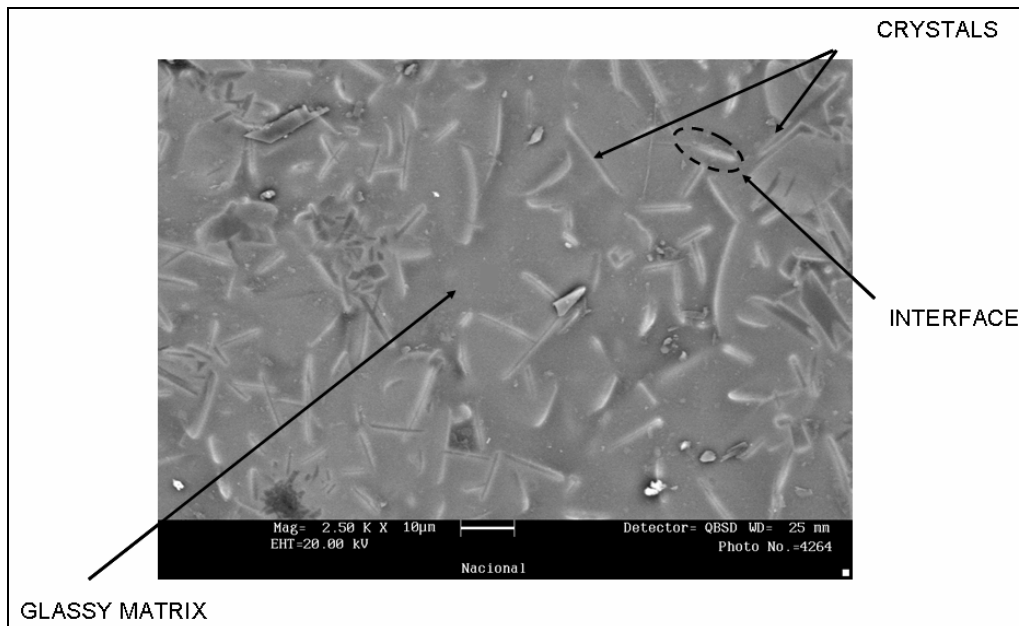


Figure 1 – SEM micrograph of a matte glaze surface, indicating the presence of crystals.

In the second step of this study, alterations were made to the chemical composition and processing conditions (firing temperature and milling residue) of a silky matte glaze which had shown low chemical resistance, aiming to apply the concepts highlighted in the previous step of the study to obtain matte glazes with good esthetic characteristics and high chemical resistance. The processing variables (firing temperature and milling residue) were not effective in producing improvements in the chemical resistance of this glaze.

The glaze which showed low chemical resistance had only wollastonite as the crystalline phase due to the frit used in its composition. Our objective was to alter the crystalline phases and the composition of the glassy phase by modifying the proportions of the raw materials that make up the composition. The best results were achieved with the compositions that contained crystalline quartz in the microstructure of the glaze after firing. The addition of diopside and especially of dolomite failed to produce the desired effects on the crystals, so the expected gain in chemical resistance was not achieved.

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