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Industrial-Scale Application of Characterization Techniques to Improve Surface Quality of Opaque Floor Tile Glazes

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Improvement of surface quality of opaque floor tile glazes was the main purpose of this study. Opaque floor tile glaze was produced by mixing different frit compositions. Effects of softening point on glaze surface properties were investigated by thermal analysis. It was found that by increasing softening point of glaze composition surface defects can be solved and nanosized crystals similar to the wavelength of incident light can be achieved to obtain high opacity.

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1. Introduction

The opacity and covering characteristics of glasses and glazes depend on the amount of diffuse light reflected by top surface, before reaching the bottom surface [1]. The opacity power depends on light scattering by particles or nuclei present in the binary system, directly related to size, form, concentration and refractive index of the secondary phase [2–4]. To maximize the diffuse reflection, secondary phase particles must have a sufficiently different refractive index related to the matrix, and must have a particle size similar to the wavelength of the incident light [1].

Opaque glazes are used to cover unwanted body color and in the situations where aesthetics is important [2]. In a single firing process through which green ceramic body is fired, there occur a number of solid-gas reactions by which the clay and calcium present in the body get separated and organic substances get burned. These reactions should be completed before melting frit particles can cover the surface of the body. Otherwise, the resulting gas disrupts the quality of the surface of glaze by causing a pinhole defect while passing through the fused layer [5, 6]. Similarly some surface defects (puncturing, pockets, etc.) are caused by bubbles in the glaze which rise to the surface during the firing process, remaining there subsequently following the product cooling phase [5].

In the present study, the S glaze with defect over its surface has been investigated. Then, to solve this problem a new glaze composition S50C was developed by increasing the frit amount which has high softening point.

2. Experimental procedure

To prepare glazes, three different frits that have different softening points (softening point for frit A: 1097 °C, for frit B: 1127 °C, for frit C: 1200 °C) and kaolin were used. Carboxyl methyl cellulose and sodium tripolyphosphate (STPP) were employed to improve glaze slip properties. The glazes were prepared under laboratory working conditions and applied on engobed green commercially available floor tile bodies made by Vitra Tile Cooperation. The dried samples were heat-treated according to fast-firing procedure used at Vitra Tile Company, maximum sintering temperature is 1180 °C and firing time is 32 min.

The sintering behaviour was investigated by hot stage microscope (Misura 3.32 ODHT-HSM 1600/80) measuring linear shrinkage in an industrial-like cycle. The colour values L^*, a^*, and b^* of all fired tiles were measured using a Minolta CR-300 series chroma meter. In order to study the effect of softening point of glazes on the size of the opacifying crystal phases, the samples were subjected to scanning electron microscopy (SEM) (SUPRA-Zeiss-50) attached with an energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

To increase softening point of glaze S, the amount of frit that has high softening point (frit C) was increased. This prescription of glaze was codified as S50C. Final composition of the glazes was given in Table I (LOI – loss of ignition).

TABLE I

Composition of the glazes (wt%).

Glaze	Na_2O	K_2O	CaO	MgO	ZnO	Al_2O_3	SiO_2	B_2O_3	ZrO_2	LOI
S	0.27	2.99	9.24	3.62	10.78	7.09	55.94	2.98	7.78	1.10
S50C	0.29	2.87	9.52	4.15	10.36	6.49	55.94	3	5.79	1.59

TABLE II

Values of temperature [°C] obtained from sintering curves.

Glaze	$T_{sintering}$	$T_{softening}$	T_{sphere}	$T_{half\ sphere}$
S	1000	1139	–	1176
S50C	1015	1146	1175	1176

Figure 1 shows sintering curves of glazes, while Table II summarizes the results obtained from the sintering curve. The softening value of the S50C glaze was determined to have increased.

Table III presents the results of the production experiments with S and S50C glazes. While there was a pinhole defect in 8% of the tiles coated with the S glaze, this rate was reduced to only 1% in the tiles coated with the S50C glaze. The S50C glaze was also observed to have achieved the targeted properties in terms of opacity.

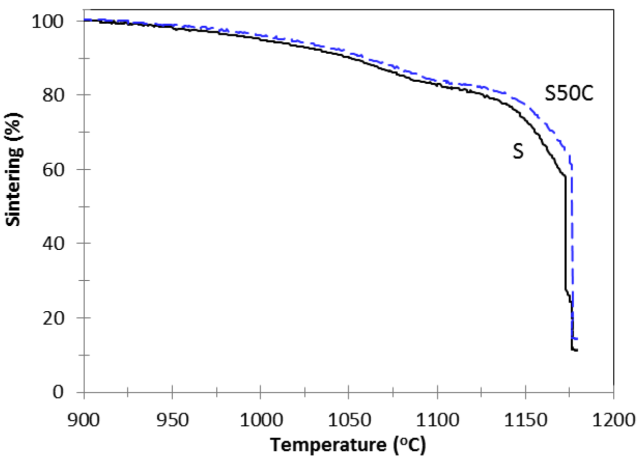

Fig. 1. Sintering curves of glazes S and S50C measured by hot stage microscope.

TABLE III

L^*, a^*, b^* and pinhole defect value of fired glazes.

Glaze	L^*	a^*	b^*	Defect [%]
S	89.99	0.63	0.39	8
S50C	91.82	0.59	0.17	1

The general micro structural view of the glaze S50C is depicted in Fig. 2. Acicular and round-shaped white crystals are homogenously-distributed, as seen in the glaze, in the glassy matrix. EDX analyses related to these crystals are presented in Fig. 3. The white crystals belong to zircon.

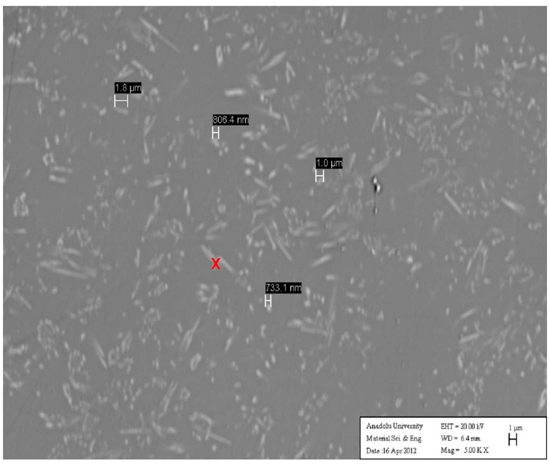

Fig. 2. SEM images of the glaze S50C taken from the cross-section.

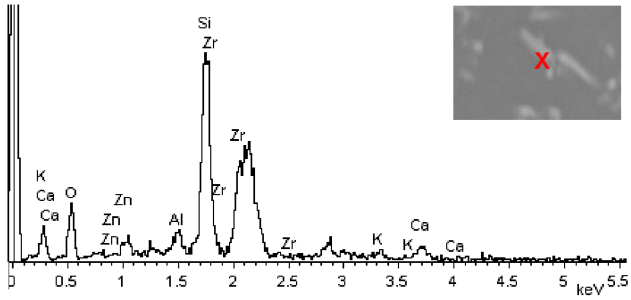

Fig. 3. EDX analyses of the white coloured fibrous shape particles by the points labeled (x).

The size of the majority of the homogeneously--distributed round shaped crystals varies between 0.3 and 0.5 μm. Others have a needle shape in a size varying between 0.3 and 1 μm. The crystals occurring in the glaze whose softening point increased seem to have lacked enough time to grow.

4. Conclusions

The present study suggests that the surface problem observed under industrial conditions could be solved rapidly with the help of simple thermal analysis techniques. The ratios of the frit can be adjusted in such a way as to increase the softening point by analysing sintering behaviour of the frits added into the glaze by means of the hot stage microscope. The crystals tend to fail to find enough time for remelting at high temperatures once softening temperatures have been raised. The sizes of the forming crystals appear close to the wavelength of incident light. These crystals are really effective in light scattering and therefore cause a rise in opacity.

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