



Short communication

Clustering of zircon in raw glaze and its influence on optical properties of opaque glaze

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Abstract

The cluster of zircon ($ZrSiO_4$) is always observed on the surface of a zircon-containing raw glaze. This work studied the cluster's formation mechanism and its influence on optical properties of opaque glaze by comparing a zircon-containing raw glaze with a zirconium-based frit one. It was observed that the cluster of zircon occurs during the densification of the raw glaze. We found evidences that this phenomenon is caused by the releasing of gas when the glaze is vitrifying. The optical analysis revealed that the cluster of zircon has a significant effect on the scattering of light and also on the color of the studied glazes.

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1. Introduction

Opaque glaze is widely used to cover over the ceramic body and provide a satisfactory appearance. Traditionally, the opaque glaze applied on a sanitary ware is made from several raw materials, such as clay, feldspar, quartz, and zircon.^{1,2} Among them, zircon ($ZrSiO_4$) not only introduces a high opacity owing to its high refractive index, but also imparts excellent mechanical and chemical resistance properties to the glaze.^{3–5} However, previous studies have shown that zircon crystals distribute unevenly on the surfaces of raw glazes.^{6–8} Castilone et al.⁶ suggested the cluster of zircon was attributed to the removal of gas during firing. But up to now, the detailed formation process of zircon cluster is still unclear. Moreover, to our knowledge, little work has been done regarding the influence of this phenomenon on glaze properties.

In general, a highly opaque glaze is favorable for sanitary-ware products. The glaze opacity is produced by the interaction between the crystalline phases that was dispersed in a glass matrix and the incident light, which results in the reflection and scattering of the light.⁹ Thus, the opacity achieved is strongly dependent on the refractive index, the grain size, the amount, and the distribution of crystals.^{9,10} Schabbach et al.¹¹ studied the

influence of grain size and shape of zircon crystals on the color of ceramic glaze and found that the maximum light scattering and whiteness occur with a particle size range of 0.6–0.75 μm and an aspect ratio of about 1. They also reported that fine particles are always needed for high opacity when zircon is directly added into glazes,¹² but bearing in mind that the cost is increased by finer grinding.¹³ It is unlike the size and shape of crystals that the influence of crystals' distribution on the optical behavior of opaque glaze has received little attention, despite the fact that it can also affect light scattering significantly.

The aim of this work was to investigate the formation mechanism of zircon cluster in raw glaze and its influence on optical properties of white opaque glaze. First, samples coated with zircon-containing raw glaze or zirconium-based frit one were quenched at different temperatures to study their phase and microstructural evolution during firing. Second, optical properties of the samples after a slow firing cycle were compared to investigate the influence of zircon cluster on glaze properties.

2. Experimental procedure

2.1. Sample preparation

The starting materials were feldspar, quartz, zircon, kaolin, calcium carbonate, talc, zinc oxide, and frit in industrial grade. Their constituents are shown in [Table 1](#).

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Table 1
Chemical compositions of raw materials (wt%).

	Kaolin	Feldspar	Quartz	Calcium carbonate	Talc	Zinc oxide	Zircon	Industrial frit
SiO ₂	47.86	68.62	98.20	–	25.87	–	30.14	63.84
Al ₂ O ₃	35.42	17.15	0.73	–	1.24	–	1.24	9.28
CaO	–	0.48	0.44	53.02	18.08	–	0.04	8.29
MgO	–	–	0.63	3.53	29.35	–	–	4.20
ZnO	–	–	–	–	–	≥99.9	–	3.23
BaO	–	–	–	0.88	0.30	–	–	1.12
PbO	–	–	–	–	–	–	–	2.28
Na ₂ O	–	7.32	–	–	–	–	0.11	5.43
K ₂ O	1.09	5.95	–	–	–	–	0.07	2.33
ZrO ₂	–	–	–	–	–	–	68.40	–
I.L. ^a	15.63	0.48	–	42.57	25.16	–	–	–

^a I.L. = ignition loss.

Table 2
Chemical compositions of the studied glazes.

Sample	Composition (wt%)									
	SiO ₂	Al ₂ O ₃	CaO	MgO	ZnO	BaO	PbO	Na ₂ O	K ₂ O	ZrO ₂
RG	62.40	11.17	10.27	0.90	2.37	0.07	0.14	3.14	2.02	7.52
FG	61.96	10.09	10.37	0.90	3.55	0.13	0.23	3.25	2.03	7.49

Table 2 gives the chemical compositions of the zircon-containing raw glaze (denoted as RG) and the zirconium-based frit glaze (denoted as FG). The RG slurry was prepared by directly milling the weighed starting materials with water, sodium carboxyl methyl cellulose (CMC), and sodium tripolyphosphate (STP) for 1 h. Then the slurry was sprayed onto 10 cm × 10 cm biscuits. The FG was prepared as follows. The weighed and thoroughly mixed raw materials were first melted in an alumina crucible in an electric furnace at 1500 °C for 1 h and the melt was poured into water to obtain a glassy frit. Then the frit (95 wt%) and kaolin (5 wt%) were wet milled for 1 h to form the slurry of FG. Afterwards, the slurry was sprayed onto 10 cm × 10 cm biscuits in the same way as the slurry of RG.

After drying, the green RG and FG were fired at two different ways: (1) fast-firing at various top temperatures ranging from 1000 °C to 1200 °C at a heating rate of 10 °C/min and then quenched in water after soaking for 5 min and (2) a slow firing cycle consisting of an 8 h 20 min heating ramp to 1200 °C, a soaking time of 40 min at this temperature, and a natural cooling in the furnace, which was used to imitate industry production of sanitary ware. The thicknesses of all coatings were about 0.3–0.4 mm after the slow firing cycle.

2.2. Characterization

The crystalline phases were determined by X-ray diffraction analysis (XRD; PANalytical X'pert PRO, Almelo, Netherlands) using Cu K α radiation (40 kV and 40 mA). XRD patterns were recorded in the 2θ range from 10° to 60° with a step of 0.017° and a duration time of 8 s for each step. The (3 1 2) reflection peak ($2\theta = 53.50^\circ$) of zircon was chosen for quantitative analysis due to its location above the amorphous hump and less susceptible to orientation.¹⁴ Back-scattered electron (BSE) images

were observed by a scanning electron microscopy (SEM; ZEISS EVO 18, Oberkochen, Germany) and the chemical compositions of different phases were obtained by an attached energy dispersive spectrometer (EDS; INCA Energy 300, Oxford instruments, High Wycombe, UK). Glaze surfaces were etched by 5 vol% HF solution for 30 s before observation. The reflectance curves and the CIE $L^*a^*b^*$ parameters of the samples were measured by a spectrophotometer (X-RiteColor Premier 8200, Grand Rapids, USA) with illuminant D65 and a 10° observer.

3. Results and discussion

3.1. Formation of zircon cluster in raw glaze

Fig. 1 gives the XRD patterns of RG quenched at various temperatures. At 1000 °C, most of the starting materials are present in RG, while wollastonite (CaSiO₃) and hardystonite (Ca₂ZnSi₂O₇) are assumed to be reaction products of the raw materials. All of these components, except for zircon, experience evident dissolution above 1050 °C. As temperature increases, feldspar gradually melts, generating liquid phase¹⁵ to facilitate the dissolution of other constituents, and disappears at 1150 °C. After firing at 1200 °C, the crystal phase of RG is zircon together with trace residual quartz. It is worth noting that the (2 0 0) ($2\theta = 26.98^\circ$) and (4 0 0) ($2\theta = 55.62^\circ$) peaks of zircon increase dramatically with temperature, indicating the alignment of zircon on glaze surface. It has been established that the tetragonal structure of zircon tends to orient along the c -axis on coating's surface and leads to the enhanced ($h 0 0$) reflections.^{14,16} This orientation in RG is mainly due to the transport of zircon from bulk to surface during firing. This can be confirmed by the BSE images in Fig. 2, where more zircon crystals can be seen on the surfaces fired at higher temperatures.

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