

THE EFFECT OF DIFFERENT CHEMICAL FORMULAS ON THE FIRING TEMPERATURE OF R_2O - RO - ZNO - R_2O_3 - SiO_2 -BASED CRYSTALLINE GLAZE

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Abstract

Ceramic products with a crystalline glaze are attractive ceramic crafts. Willemite (Zn_2SiO_4) crystalline glaze is the most widely known due to it having crystals large enough to see with the naked eye. However, this crystalline glaze system requires a high firing temperature and the firing curve design is complicated. The present study studied the development of a glaze formula to reduce the firing temperature. Samples were fired at different firing temperatures, ranging between 1,200-1,290°C. X-ray diffraction and energy dispersive X-ray spectrometer analysis of the crystal phases after being fired at all temperatures confirmed the willemite crystals. Crystalline glaze formula 2 is a successful crystal phase at 1,250°C and the crystals can be observed with the naked eye. Therefore, crystalline glaze formula 2 is a candidate for reducing the firing temperature in crystalline glaze production.

Keywords: Willemite, ceramic, firing temperature, glaze

Introduction

Crystalline glaze is a favored special artistic glaze and makes final products attractive and unique (Jamaludin *et al.*, 2010; Bocker *et al.*, 2017). Crystalline glaze is a devitrified glaze consisting of the crystalline phase produced by 2 mechanisms of the nucleation and crystal

growth processes, as shown in Figure 1. Controlling the nucleation and crystallization by heat treatment helps to appropriate the mixture of raw materials which are formed in the crystalline phase. The amount of the crystal phase is dependent on the maximum firing

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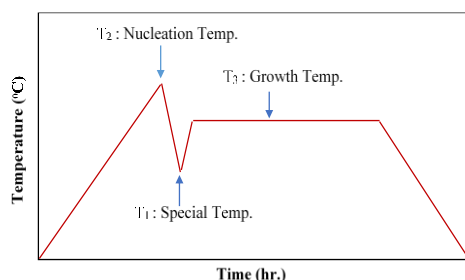
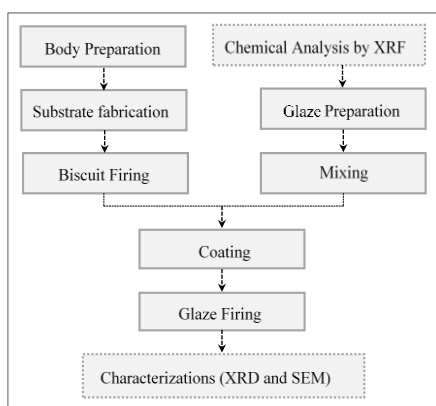


Figure 1. Firing curve design for crystalline glaze system



temperature and the soaking times. However, crystal growth is related to the cooling-soaking part of the firing curve. Long soaking periods may result in large crystal sizes which overlap or stand out on the glaze surface (Pekkan, 2015; Wannagon *et al.*, 2013; Wang *et al.*, 2015).

The firing temperature of a crystalline glaze is higher than an ordinary ceramic glaze so that it can achieve the molten state of the glaze. The firing temperature of a crystalline glaze can range between 1,250-1,480°C, dependent on the category of the substrate or ceramic bodies. Crystalline glaze is therefore typically coated onto porcelain bodies due to their stability at high temperatures. Furthermore, the final crystalline appearance is improved by the white color and suitable chemical constituent of the porcelain bodies (Karasu *et al.*, 2000; Caselli *et al.*, 2007;

Cannio and Bondioli, 2012). Additionally, other factors including the viscosity and glaze thickness also affect the growth of crystallization. During the firing stage, the melted glaze diffuses into the pores via capillary forces and creates an interface layer between the glaze and the body. The chemical reaction at the glaze-body interface and the interactive diffusion of the materials change the glaze's viscosity and surface tension (Taylor and Bull, 1986; Price and Price, 2003; Lee, 2013).

Zinc oxide (ZnO) is used to form a micro-crystalline glaze with a chemical composition of Zn_2SiO_4 (willemite crystalline glaze). This glaze is striking because the crystal sizes are large enough to be observed with the naked eye. Many reports have studied the nucleation and crystallization of the ZnO-containing crystalline glaze by using fritted compositions and high firing temperatures. The objective of the present study was to focus on low firing temperatures. The crystal glaze of the $\text{R}_2\text{O}-\text{RO}-\text{ZnO}-\text{R}_2\text{O}_3-\text{SiO}_2$ system was created, indicating that the cost of the crystalline glaze can decrease. The chemical compositions, structural phase, and microstructure of all the compositions were investigated using X-ray fluorescence (XRF), an X-ray diffractometer (XRD), and a scanning electron microscope (SEM), respectively.

Materials and Methods

Figure 2 shows the experimental procedure and its mixed design methodology for the crystalline glaze. The step-by-step procedure is summarized below.

Compound clay (commercial grade) was used for the body preparation. The chemical composition of the compound clay is shown in Table 1. The biscuit body was pressed with the following dimensions: 50×50×7 mm³. After drying, the firing curve of the clay bodies was conducted at 850°C for 1 h in air.

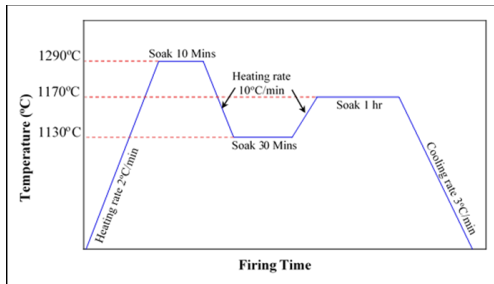
For the glaze preparation, the chemical compositions of the raw materials were checked and are presented in Table 1. The chemical composition of the $\text{R}_2\text{O}-\text{RO}-(\text{ZnO})-$

Table 1. Chemical compositions of raw materials

Raw materials	Compositions (wt. %)							
	Na ₂ O	K ₂ O	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	LOI
Ceramic body	-	2.484	-	23.410	1.164	72.372	0.441	0.129
Na-feldspar	9.995	0.159	0.787	15.352	0.424	72.771	0.381	0.131
K-feldspar	-	8.074	-	16.623	0.133	74.841	0.224	0.105
Sand	-	0.055	0.014	-	0.067	99.630	0.152	0.082

Table 2. The Seger formula of crystalline glaze

Formula	Seger Formula		
Formula 1	0.280 Li ₂ O 0.158 Na ₂ O 0.053 BaO 0.509 ZnO	0.198 Al ₂ O ₃	1.720 SiO ₂
Formula 2	0.281 Li ₂ O 0.079 Na ₂ O 0.075 K ₂ O 0.053 BaO 0.512 ZnO	0.194 Al ₂ O ₃	1.702 SiO ₂
Formula 3	0.283 Li ₂ O 0.150 K ₂ O 0.053 BaO 0.514 ZnO	0.191 Al ₂ O ₃	1.681 SiO ₂

**Figure 3. Firing curve design for crystalline glaze system**

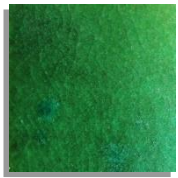
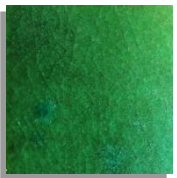
Al₂O₃-SiO₂ glaze system was created. The Seger formula of glaze is calculated and listed in Table 2. After accurate weighing, all the raw materials and water were mixed in a mortar for 20 min. The slip was applied on the biscuit body using the dipping technique.

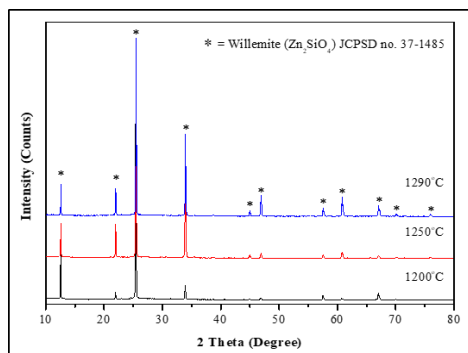
The crystalline glaze was succeeded by 3 stages of a special firing cycle, as depicted in Figure 3. During the first stage the temperature was increased at a heating rate of 2°C/min from

room temperature to the firing temperature. Next, the firing temperature was completed at 1,200-1,290°C with a soaking period of 10 min. In the second stage, the temperature was decreased to 1,130°C with a high cooling rate of 10°C/min, with the specimens held at that temperature for 30 min. In the third stage, the temperature was increased again to 1,170°C for the crystalline growth period, using a rapid heating rate of 10°C/min. In the crystal growth stage, crystallization was completed after soaking for 1 h. Finally, the temperature was decreased from 1,170°C to room temperature at a slow cooling rate of 3°C/min.

The glaze surfaces were recorded by digital photography, as shown in Table 3. To support the results, the structural phase of the crystal glaze was identified by X-ray diffraction using a Bruker D2 Advance (Bruker Corp., Billerica, MA, SA) with CuKα₁ in the 2-theta range of 10°-80°. The microstructure of all the compositions were investigated using a JEOL series no. JSM-6010LV (JEOL Ltd., Tokyo, Japan) SEM. The chemical composition of the

Table 3. The digital photograph results of all the crystal glaze formulas

Formula	Maximum temperature		
	1,200°C	1,250°C	1,290°C
Formula 1			
Formula 2			
Formula 3			

**Figure 4. XRD analysis of crystalline glaze system**

samples was analyzed by energy dispersive X-ray spectroscopy (EDX).

Results and Discussion

Table 3 shows the digital images of all the crystal glaze compositions at different firing temperatures. At the normal firing temperature

of 1,290°C, the crystal growth for all the glaze compositions can be clearly observed with the naked eye. After the firing temperature was decreased to 1,250°C, the crystal growth of the crystalline glaze with formula 2 was still dense on the substrate body. This is due to the mixture of Na-feldspar and K-feldspar in the recipe of the crystalline glaze in formula 2, indicating that the firing temperature of this composition decreased. Additionally, this result was supported by using the theoretical eutectic point of the mixture of the 2 solids. But the crystal growth of the crystalline glaze for formulas 1 and 3 were not clearly observable with the naked eye. These compositions consisted of pure Na-feldspar in formula 1 and pure K-feldspar in formula 3, indicating that the firing temperature of these glaze compositions remained high. Furthermore, at the lowest firing temperature of 1,200°C, crystal growth for all the glaze formulas was not seen on the substrate body. XRD analysis therefore supports the crystalline phase of the different firing temperatures.

Figure 4 presents the XRD diffraction pattern of the crystalline glaze system. Although

the crystal growths recorded in the digital images are not observable with the naked eye, each glaze formula at different firing temperatures achieved a pure phase of willemite crystal (Zn_2SiO_4) with JCPDS no. 37-1485. This observation confirms that the firing temperature of all the glaze formulas can be reduced to below $1,290^\circ\text{C}$.

SEM analysis was used to confirm the crystalline glaze morphology, as shown in Figure 5. The glaze background is used to refer to the surface without a crystal phase. The crystal structure zone is identified as the area with a spherical crystal shape. EDX analysis of crystalline glaze formula 2 after being fired at $1,250^\circ\text{C}$ was checked. The crystal structure zone appeared to have a high amount of Zn (20.73 wt.%), Si (33.82 wt.%), O (30.22 wt.%), Al (10.22 wt.%), and K (5.01 wt.%) elements. The proportionate elements of Zn, Si, and O in these results reflect that the crystal type is the willemite phase.

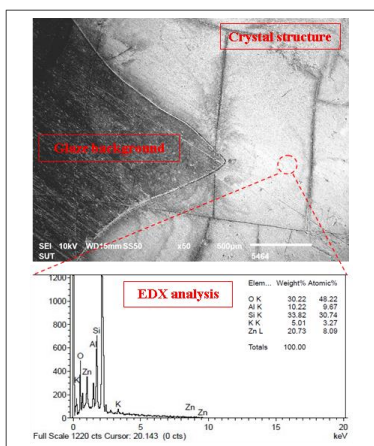


Figure 5. SEM micrograph with EDX analysis data of crystalline glaze system

Conclusions

The firing temperatures of all the crystalline glaze formulas can be reduced from $1,290^\circ\text{C}$ to $1,200^\circ\text{C}$. This result was confirmed using XRD analysis which indicated that the crystalline phase formed on the glaze surface is willemite (Zn_2SiO_4). The SEM micrograph of the crystal

structure showed a spherical crystal shape. The high weight percentage of the Zn, Si, and O elements was detected by EDX, meaning that these are willemite crystals. This study shows that developing the crystalline glaze formula is a candidate for reducing the firing temperatures used in crystalline glaze production

Acknowledgment

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