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The Development and Characterization of Willemite Crystal Glazes Used for Porcelain

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Abstract

This study aimed to investigate the development of willemite crystal glazes to be suitable for porcelain clay and analyze the crystallization behavior of willemite under the firing condition at 1250 °C. Later 40 minutes, the temperature was decreased to 1100 °C and was soaked at this level for 4 hours. The results showed that porcelain clay had a thermal expansion coefficient at 700 °C of 4.20 x 10^{-6} °C^{-1} and for the glazes formulas 1, 11 and 21, their thermal expansion coefficients were 9.86 x 10^{-6} °C^{-1}, 6.13 x 10^{-6} °C^{-1} and 4.16 x 10^{-6} °C^{-1}, respectively. The suitability of porcelain clay for willemite crystallization was ordered as follows: glazes formulas 1, 11 and 21, respectively. This was consistent the analysis of chemical compositions of glazes formulas 1, 11 and 21, consisting of ZnO and SiO_2 as major compositions with ZnO content at 42.78, 40.67 and 34.58 wt.% , respectively meanwhile SiO_2 content at 39.35, 39.89 and 41.55 wt.% , respectively. The results of analyzing mineral compositions consisted of willemite as the major composition. The glazes formula 1 had the highest relative intensity, followed by glazes formula 11 and 21, respectively. With XRD technique, the results of analyzing microstructure analysis of the glazes formula 1, 11 and 21 were characterized by the needle shape and spherical growth, consisting of ZnO and SiO_2 through SEM and EDS techniques.

Keywords: Glazes, Crystal, Willemite, Porcelain, Thermal Expansion Coefficient

Introduction

Currently, the crystal willemite glazes ($2ZnO.SiO_2$) became popular because the crystal can grow larger inside the glazes. The size of crystal is approximately 150 millimeters or above and is visible with the naked eyes [1]. The crystal structure of willemite is trigonal-rhombohedral which can grow bigger horizontally, yet its size is limited by the thickness of glazes [2]. However, when the glazes contains the large crystal, the strength is decreased. The issue is interesting and required study to generate more strength to the zinc glazes containing big crystal [3]. Since the zinc glazes containing crystal willemite has the hardness level = 5.5 [4], the more amount of crystal willemite, the stronger the zinc glazes become. The crystallization behavior of willemite according to the phase diagram system (SiO_2-Al_2O_3-ZnO) in the firing process to completely solubility the zinc glazes process and form the crystallization at 1310 - 1345 ° C [5]; the temperature is considered higher than that used for firing the porcelain. It has been examined for temperature reduction to meet the requirement of the porcelain and motivate the crystallization. By calculating the integration of oxides in a ceramic glazes system: Na_2O-K_2O-Li_2O-CaO-(ZnO)-Al_2O_3-SiO_2, it can be divided into 3 groups based on Seger's unity formula [6]: 1) Alkali or Modifier oxides which is usually named as Flux. The substance is known as a network modifier to reduce the melting point and the viscosity of the glazes and results in reduction of the temperature used for firing the glazes, melting the glazes much faster and facilitating the flow of the glazes so the crystallization process can occur much easier and better. The substances consist of Na_2O, K_2O, Li_2O, CaO and ZnO. 2) Neutral or the Cofermer oxides or Intermediate is responsible for the stability; it helps creating viscosity of the glazes. When the glazes is form from the substances, it would not flow too much to prevent from crystallization, to decrease chance of glazes crazing, and to remain the stability. The substances consist of AI_2O_3 which can be found in kaolinite or clay mineral. 3) Acidic or Forming oxides are applied as raw materials with the glass former properties or Network former. The compositions can turn into glass once it is melted reduce. The heat-resistant compositions are applied in the glazes due to its high melting point; this quality has strengthen the glazes and abrasion resistant. It is also resistant to acids and alkalis. The substance consists of SiO_2. Once the amount of the SiO_2 compositions is added more, the viscosity of the glazes is increasing. Therefore, SiO_2 compositions should be added in appropriate quantity for the crystallization with ZnO compositions to form crystal willemite as well as to increase the quantity of crystal willemite in the glazes [5-7].

The crystallization behavior of willemite consists of 2 main processes: Nucleation and Crystal growth formed by firing process. During the first step, crystallization can be achieved by heat treatment method until the clay and the glazes are melted appropriately. Under this temperature, many atoms are grouped together and form a small crystal called nucleus to form the nucleation. Then, the temperature is decreased, so the crystallization process occurs. In case of willemite crystallization, it the crystal is formed due to lower temperature which causes the lower solubility of ZnO, which is considered a super saturated solution with an excessive solubility. Thus, secondary nucleation is formed. And when ZnO crystallize together with SiO_2, the chance of willemite crystallization is increasing. This type of crystal can be processed through crystallization at the temperature between 700-1345 ° C. In the second process is the crystal growth process to increase its size and make the crystallization complete. However, it depends on the soaking time or the stability of temperature during the crystallization process for longer time. Accordingly, the study aims to investigate the development of willemite crystal glazes to be suitable for porcelain clay and analyze the crystallization behavior of willemite under the firing condition at 1250 °C. Later 40 minutes, the temperature was decreased to 1100 °C and was soaked at this level for 4 hours [5, 8-11].

Materials and Methods

Table 1. shows the Seger formula of the glaze studied. Raw materials used for the preparation of willemite crystal are sodium feldspar, potassium feldspar, lithium oxide, calcium oxide, zinc oxide, kaolinite clay from Lampang, silica and cobalt oxide 0.2% coloring agent in the glazes because cobalt oxide is stable and do not destroy the crystal structure [12]. Also, it could support the crystallization process of crystal willemite. The preparation of glazes formula is calculated: The ratio of $Al_2O:SiO_2$ = 1:10 and contribute to 25 glazes formula. The compositions are crushed and mixed in alumina ball mill for 1 hour to form glazes slip the measurement of specific gravity = 1.5 g/cm^3.

Using the test pieces with clays for porcelain; the clays produced by Sin Fa Industrial (Thailand) Co., Ltd. which have been through biscuit firing at 850 °C, glazes slip by the prepared glazes for 25 seconds with the thickness of 1.5-2.0 mm. Wait until the glazes dry. Then, fire the test pieces at 1250 °C, the heating rate = 2 °C/min. After that 40 minutes, wait until the temperature dropped down to 1100 °C and soaking time at this temperature for 4 hours. The study conducted on characterization of crystals formed in the glazes is derived from chemical analysis by using X-ray fluorescence spectrometry (XRF) (Megix Pro MUA/USEP T84005, Philips), mineral compositions analysis by using X-ray diffraction (XRD) (X'Pert MPD, Philips), microstructure analysis and specific mineral compositions analysis using Scanning electron microscope (SEM/EDS) (JSM-6301F, Jeol) and the coefficient of thermal expansion analysis by using dilatometer (KD-1500, Toyoden)

Table 1. The Seger formula of the glaze studied

Modifier oxides	Cofermer oxides	Forming oxides
Na_2O : 0.06	Al_2O_3 : 0.15-0.35	SiO_2 : 1.50-3.50
K_2O : 0.07		
Li_2O : 0.09		
CaO : 0.19		
ZnO : 0.59		

Results and discussion

Figure 1. shows the results of analyzing the coefficient of thermal expansion from 20-750 °C. Based on the equation 1 [13], it was found that at 700 ° C, the coefficient of thermal expansion of porcelain clay was 4.20 x 10^{-6} °C^{-1} and for the glazes formulas 1, 11, and 21, their thermal expansion coefficients were 9.86 x 10^{-6} °C^{-1}, 6.13 x 10^{-6} °C^{-1} and 4.16 x 10^{-6} °C^{-1}, respectively. After firing, the physical properties of porcelain clay under three glazes formula showed good fusibility and adhesion without defects. The glazes formula 1 yielded the highest coefficient of thermal expansion because it had the highest content of ZnO which is alkali group causing the glazes flow and crystallization. The results were consistent with the analytic results of chemical compositions with high content of 42.78 % and mineral analysis in formula 1 with the highest content of willemite. The coefficient of thermal expansion affected willemite crystallization in the glazes. The high coefficient of thermal expansion in the glazes and high difference between porcelain clay led to higher willemite crystallization due to ZnO content, melting point of 419.6 °C [14], being classified as alkali, which reduces the melting point and viscosity of the glazes. This led to decreased temperature of firing glazes, increased flowing, stimulating the formation of crystal nucleus.

$$\frac{\Delta L}{L_0} = \alpha \Delta T \quad (1)$$

Where α is the coefficient of thermal expansion in the dilatometer, t is the room temperature, t´ is the maximum temperature measured, L_o is the length at room temperature, L is the length of test piece at maximum temperature.

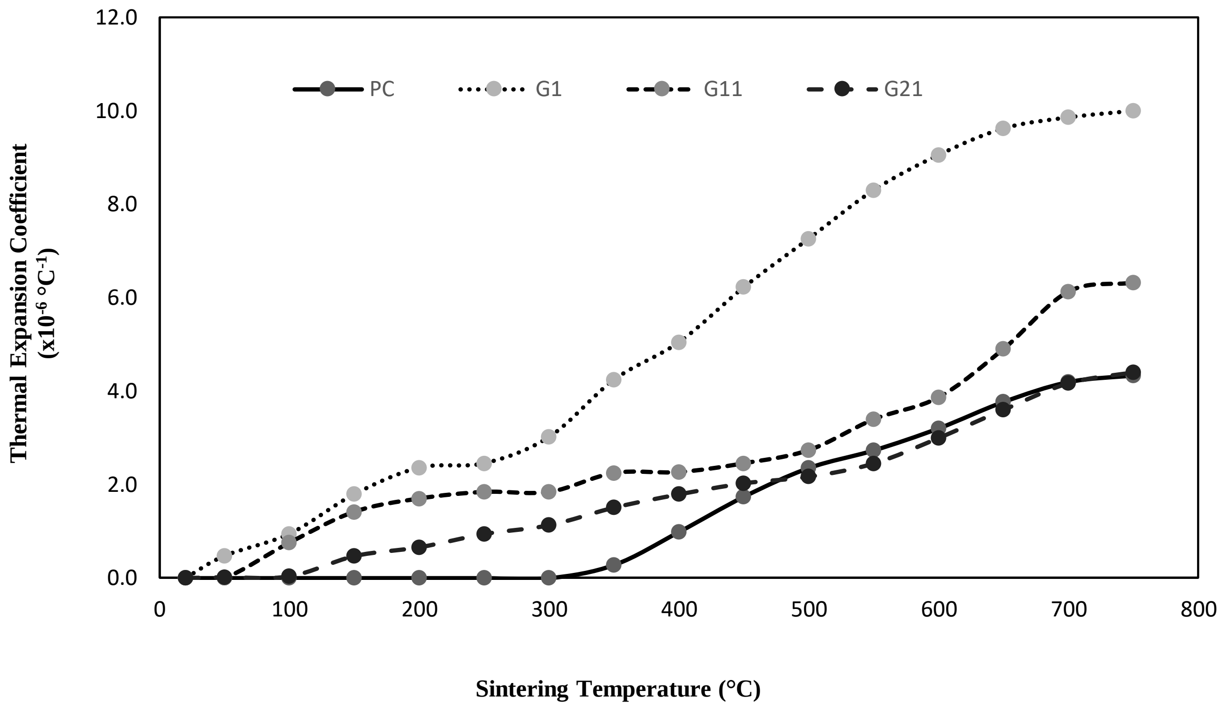

Figure 1. Plot of coefficient of thermal expansion; PC = porcelain clay, G1 = glazes formula 1, G11 = glazes formula 11 and G21 = glazes formula 21

Table 2. shows chemical composition of the glazes G1, G11 and G21. The characterization of crystal willemite found in ceramic glazes was derived from chemical compositions analysis by using XRF. The finding indicated that the glazes G1, G11 and G21 were consisted of Al_2O_3, SiO_2, K_2O, CaO, Fe_2O_3, CoO and ZnO where ZnO and SiO_2 were the main compositions. The quantities of ZnO were 42.78, 40.67 and 34.58 wt.% respectively. The quantities of SiO_2 were 39.35, 39.89 and 41.55 wt.%, respectively. The reason of such occurrence is that when the glazes is melted at the period of the temperature as mentioned while the heat is maintained, the nucleation takes place. When the temperature is reduced at one point, the process of crystallization is achieved where the amount of ZnO and SiO_2 that exceeds the solubility go through the crystallization altogether and generate the chance to obtain crystal willemite. The results is in accordance with the mineral compositions analysis using XRD with glazes G1, G11 and G21 as illustrated in Figure 2. The findings revealed that willemite is the mineral that could be found the most. Also, glazes G1 contains the highest relative intensity, followed by G11 and G21 respectively.

Table 2. Chemical composition of the glazes (%)

Glazes formulas	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	CoO	ZnO
G1	5.39	39.35	3.21	8.77	0.18	0.32	42.78
G11	6.28	39.89	3.39	9.06	0.40	0.31	40.67
G21	8.23	41.55	4.00	10.61	0.50	0.34	34.58

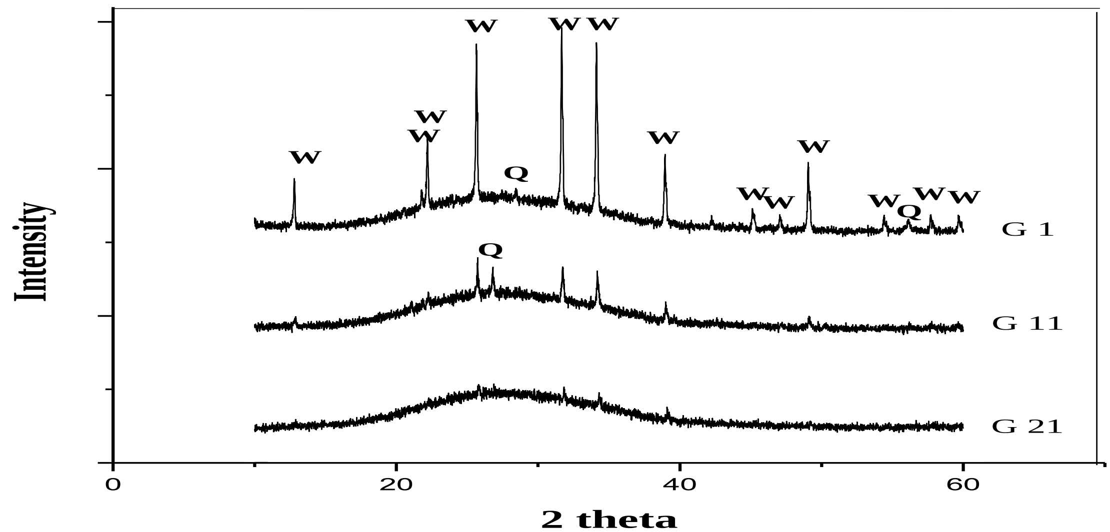

Figure 2. XRD patterns of glazes G1, G11 and G21 heat-treated at 1250 °C and soaking time at 1100 °C for 4 hour; Q = Quartz and W = Willemite

Figure 3. shown the microstructural analysis of glazes G1, G11 and G21 by using SEM, the findings found that the crystal willemite formed during the crystallization process in the glazes are big and perfect; the crystal size are 5-7 mm. The soaking time is that the temperature is maintained at 1100 °C for 4 hours. The duration is appropriate for the growth of crystal and the shape is similar to needles and the crystal grows in circular shape. The results implied the similarity to the property of crystal willemite. The results could be confirmed from the results of mineralogical analysis to study the specific area, consisting of ZnO and SiO_2 with the application of EDS technique as shown in Figure 4. and Table 3.

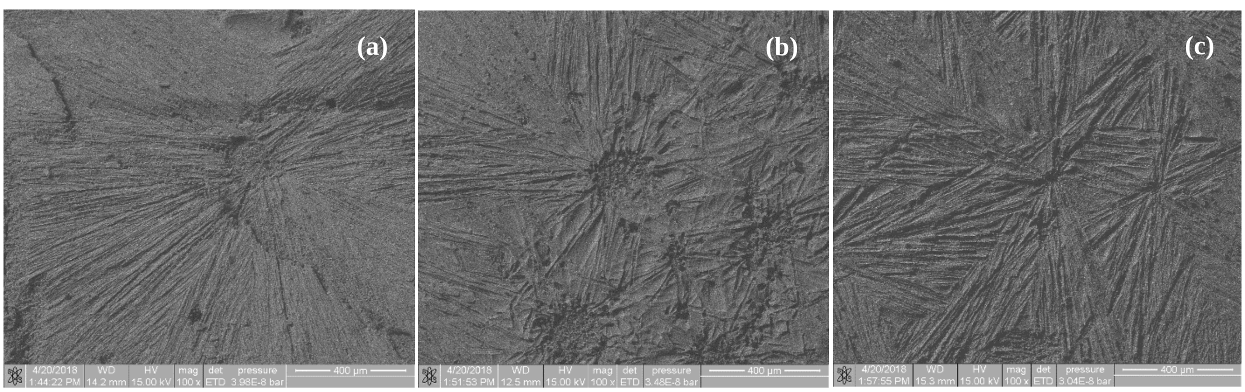

Figure 3. Microstructural analysis of glazes heat-treated at 1250 °C and soaking time at 1100 °C for 4 h ; (a) G1, (b) G11 and (c) G21

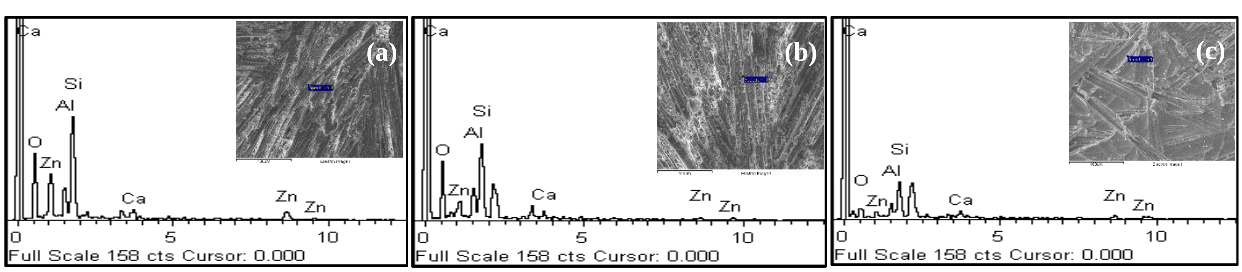

Figure 4. EDS analysis of glazes heat-treated at 1250 °C and soaking time at 1100 °C for 4 h ; (a) G1, (b) G11 and (c) G21

Table 3. EDS mineralogical analysis to study the specific area of glazes G1, G11 and G21

Glazes formulas	Crystallized phases	O	Al	Si	Ca	Zn
G1	β-Quartz, Willemite	39.48	7.04	27.33	3.59	22.56
G11	β-Quartz, Willemite	44.78	9.40	30.55	4.02	11.25
G21	β-Quartz, Willemite	28.65	9.95	38.49	11.95	10.95

The crystallization in glazes systems Na_2O-K_2O-Li_2O-CaO-(ZnO)-Al_2O_3-SiO_2 can motivate the crystallization of willemite in porcelain clays; the occurrence is motivated by alkali oxide which reduce the melting point and viscosity of the glazes [6]. The temperature used for glazes, as a result, is decreased and helps the glazes to be melted faster. Accordingly, Increase the flow to the glazes is increased and the crystal nucleus can be formed easier and better. Also, the precedures could stimulate the crystal willemite to be formed by both ZnO and SiO_2, altogether at the temperature between 700-1345 °C [8]; the temperature could form perfect crystal willemite with the crystal size of 6-10 mm, thus the crystal can be seen with the naked eye by firing condition at 1250 °C. After that 40 minutes, the temperature was decrease to 1100 °C and was soaking time at this level for 4 hours, the microstructure is growing in needle and circular shape.

Conclusions

The development of willemite crystal glazes to be suitable for porcelain clay could be concluded that:

1. The suitability of porcelain clay for willemite crystallization was ordered as follows: glazes formulas 1(G1), 11(G11) and 21(G21), respectively and the coefficient of thermal expansion affected willemite crystallization in the glazes.
2. The crystallization in glazes systems Na_2O-K_2O-Li_2O-CaO-(ZnO)-Al_2O_3-SiO_2 can motivate the crystallization of willemite in porcelain clays at temperature from 1250 °C. After that 40 minutes, cooling down to 1100 °C and soaking time at this temperature for 4 hours.

Summary

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