The Effect Of CaCO₃ Addition on the Crystallization Behavior of ZnO Crystal Glaze Fired at Different Gloss Firing and Crystallization Temperatures

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Abstract:
A glazed ceramic product with crystalline structure gives an artistic effect. In this study, the effects of calcium carbonate (CaCO₃) addition into glaze batches on the crystallization behavior of crystal glaze were studied. Samples were fired at different gloss firing temperatures ranging from 1000-1200°C with 1060°C crystallization temperature. X-ray diffraction (XRD) and energy dispersive X-ray spectrometer (EDX) analysis of the phases identified these crystals as willemite (Zn₃SiO₄) in the form of spherulites. Scanning electron microscope (SEM) analysis indicated that willemite crystals are in the acicular needle like shape. XRD result showed that the intensities of crystal peaks decreased with the addition of CaCO₃ up to 3.0 wt%. However, there was no willemite crystals formation as the amount of CaCO₃ raised to 5.0 wt%. Besides that, the results also indicated that willemite growth occurs during isothermal holding at crystallization temperature instead of during cooling from gloss firing temperature.

Keywords: Crystal glaze; CaCO₃ addition; gloss firing temperature; crystallization temperature; willemite; spherulites

1. Introduction

Crystalline glaze is one of the ceramic craft that has been produced since 19th century in Europe [1-2]. Knowless and Freeman [3] stated that crystalline glazes are devitrified glazes within which spherulites consist of crystalline phase (willemite) produced during controlled nucleation and growth process. Devitrified glaze literally means the loss of glassy characteristic as what happen with crystalline glaze products. Besides that, crystalline glazes have a higher gloss firing temperatures when compared to ordinary glaze in order to achieve the molten state of glaze.

Depending on the type of substrates used, the glaze gloss temperatures can be ranging from 1250 to 1480°C [4]. Therefore, the temperature can be reduced by adding the correct amounts of fluxing agents into the glazes. Furthermore, metal oxides addition as fluxing agents can caused marked changes in the crystal growth rate, although the activation energy of crystal growth was changed a little, similarly, the minor additions of various metal oxides influence the crystal growth rate but do not affect the crystal structure to any great extent [5].

In this study, calcium carbonate (CaCO₃) was used as a fluxing agents besides zinc
oxide (ZnO) in the crystalline glaze formula. In some glaze batch, within certain composition limits, CaCO3 vigorously attack clay and silica but its fluxing action is best shown at medium to higher temperature of Cone 4 (approximately 1165°C) and above [1,6]. CaCO3 tends to act more refractoriness compared to other types of fluxes at temperatures below 1100°C. But, at high temperatures, it can produce very fluid liquids. Besides that, the additions of CaCO3 into glaze batch also help to improve the properties of the glaze by increasing hardness, resistance to weathering, solvent action of water, the tensile strength and lowering the coefficient of thermal expansion (CTE). Since CaCO3 is an inexpensive raw material and can be found abundantly in Earth crust it was chosen for this study.

ZnO is introduced into glazes being fired up to about 1050°C as an auxiliary fluxing agent [7]. A glaze with excess amount of ZnO in its composition is known for years that it would produce crystals if the correct firing and cooling procedure is adopted. When a high level of ZnO like more than 10 wt.% in a crystal glaze composition, willemite (Zn2SiO4) crystals tend to occur during cooling and give a naturally brilliant decorative effects on the surface of the glaze [4,8-9]. Moreover, ZnO also helps to improve the glossiness of glaze surface, modifying the action of chromospheres, and sometimes contributing to opacity. Furthermore, if coloring agents like transition metals are incorporated into the glaze, this would give beautiful appearance with different colours and lead to the formation of willemite crystals. The fine crystals collect any pigment or colouring ion present in the glaze to give highly decorative effects [7]. For the formation of the decorative crystals, it is a very well known fact that lower crystal growth temperatures should be employed then, the final shape of crystallites becomes spherical, unlike those achieved at higher growth temperatures in the shapes of single bars or double axe-head shaped crystals.

In this study, the effects of CaCO3 addition on the gloss firing and crystallization temperature were investigated. Moreover, the crystallization behaviors of the glaze regarding to the addition of CaCO3 were also studied. All the bisque substrates and specimens were fired under oxidizing atmosphere in an electrically heated furnace. The phase and microstructure development of crystals have been examined for each amount of CaCO3 addition and varying firing temperature.

Experimental procedure

The chemical compositions of the raw materials used in the present study are shown in Tab. I. The Seger Formula for four crystal glaze batches is listed in Tab. II. The amount of CaCO3 added is 1 (CG1), 3 (CG3), and 5 (CG5) wt%, respectively. Another glaze batch without CaCO3 is coded as CG0 being the reference glaze. To form colored crystal glaze, 0.05 wt% CoO was incorporated into CG0. Each glaze batch was wet milled in a porcelain jar for 5 hours. The milled slurry was sieved to pass through 75 μm and aged for 24 hours. For the CG0 with cobalt oxide (CoO), the addition was carried out at the last 45 minutes of the wet mixing process. The glazes were applied onto bisque fired (850°C for half an hour) porcelain bodies using dipping technique. After that, the glaze was fired in UNITEK Muffle Furnace following six different firing cycles (denoted as FC1 to FC6) ranging from 1000°C to 1200°C with heating rate of 5°C/min. Cooling rate from gloss firing temperature to crystallization temperature (CT) was 3°C/min and CT to room temperature 2°C/min as shown in Tab. III. To investigate the effects of CaCO3 addition, the entire crystal glaze batches (CG0-CG5) were fired according to FC1. The digital photographs were taken using Sony DSC-T700 and morphology of colored crystal glaze (CG0 added with 0.05 wt% CoO) was identified using optical microscope (Dino-Lite Digital Microscope). The phases present in the fired glazes were identified via X-ray diffraction (XRD) analysis (Bruker D8 Advance) with CuKα radiation (1.5406 Å). The glazes microstructure was examined using scanning electron microscopy (SEM) (VP FESEM ZIESS SUPRA 35VP) analysis and the chemical
compositions were captured using an energy dispersive X-ray spectrometer (EDAX) attached to the SEM.

**Tab. I.** Chemical compositions of the ceramic body and raw materials

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Composition (wt.%)</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>ZnO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
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<td>69.00</td>
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<td>-</td>
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<tr>
<td>Feldspar</td>
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<td>2.00</td>
<td>12.00</td>
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<td>-</td>
<td>-</td>
<td>19.00</td>
<td>-</td>
<td>67.00</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>Titanium dioxide</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>93.00</td>
<td>-</td>
<td>5.10</td>
<td>-</td>
<td>-</td>
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<td>Barium carbonate</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>89.00</td>
<td>0.85</td>
<td>-</td>
<td>-</td>
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<td>Silica</td>
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<td>-</td>
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<td>98.00</td>
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<td>Frit 1050</td>
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<td>10.00</td>
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<td>Kaolin</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>1.00</td>
<td>57.00</td>
<td>-</td>
<td>0.507</td>
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<tr>
<td>Calcium carbonate</td>
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<td>-</td>
<td>98.00</td>
<td>1.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>0.615</td>
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**Tab. II.** The Seger formula of the glazes studied

<table>
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<tr>
<th>Glaze</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>LOI</th>
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<tbody>
<tr>
<td>CG0 (no CaCO₃)</td>
<td>0.044</td>
<td>0.100</td>
<td>-</td>
<td>0.203</td>
<td>0.200</td>
<td></td>
<td>2.043</td>
<td></td>
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<tr>
<td>CG1 with (1.0 wt% CaCO₃)</td>
<td>0.040</td>
<td>0.090</td>
<td>0.183</td>
<td>0.180</td>
<td></td>
<td>1.844</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CG3 with (3.0 wt% CaCO₃)</td>
<td>0.033</td>
<td>0.075</td>
<td>0.153</td>
<td>0.151</td>
<td></td>
<td>1.542</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CG5 with (5.0 wt% CaCO₃)</td>
<td>0.028</td>
<td>0.065</td>
<td>0.131</td>
<td>0.130</td>
<td></td>
<td>1.326</td>
<td></td>
<td></td>
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</table>
The effect of CaCO₃ on the glaze fluidity was obtained from through the comparison between CG0 and CG5 using glaze flow trial block following FC2. Detailed study on the effects of gloss firing temperatures ranging from 1000°C to 1200°C (FC2, FC3, and FC4) for the glazes with 1.0 wt% ZnO (CG1) was also carried out. Finally, verification for the possibility of crystallization occurred during the cooling process was studied using the glaze containing 3.0 wt% CaCO₃ (CG3). The glaze was fired according to FC5 [with crystallization temperature (CT)] and then compared to the ones fired following FC6 (without CT).

| Tab. III. The firing cycles (FC) used for gloss firing and crystallization process |
|----------------------------------------|----------------------------|----------------|----------------|
| FC no.      | Gloss Firing Temp. (°C) | Isothermal Holding Time (min) | Crystallization Temp. (CT) (°C) | Isothermal Holding Time (min) |
| FC1        | 1200                     | 30                           | 1060                      | 180                          |
| FC2        | 1200                     | 30                           | -                         | -                            |
| FC3        | 1100                     | 30                           | -                         | -                            |
| FC4        | 1000                     | 30                           | -                         | -                            |
| FC5        | 1200                     | 1                            | 1060                      | 180                          |
| FC6        | 1200                     | 30                           | -                         | -                            |

Note: Heating rate 5°C/min. Cooling rate from gloss firing temperature to CT is 3°C/min and CT to room temperature is 2°C/min.

Results and discussion

Following FC1, the digital images produced for samples CG0, CG1, CG3 and CG5 are shown in Fig. 1, respectively. It is obvious that at 1200°C of gloss firing temperature with 1060°C crystallization temperature, willemite crystal morphologies appear on each glaze of the substrates except for the CG5 (containing 5.0 wt% CaCO₃). The crystal growth is too dense for the reference glaze (CG0) with 0.0 wt% CaCO₃, whereby the number of crystals growing is very high and they all the crystals overlapping on each other creating a rough glaze surface. Knowles and Freeman [3] stated that the trigonal structures of the willemite and the ability of the crystal to emerge for the tip of their parent fibers at some angle are relevant to the cause of the fibrous morphology of the crystals thus, creating a rough surface. However, after an addition of 1.0 wt% CaCO₃, the crystal starts to be less dense [Fig. 1 (B)]. The image also shows that some crystals started to be distinguishable as an individual spherulite. However, only smaller and non-elongated crystals can be seen for 3.0 wt% CaCO₃ containing glaze (CG3). The crystals in these spherulites are growing from the side of much longer crystals and form various clusters. For the glaze with of 5.0 wt% CaCO₃ (CG5), no crystal can be seen by naked eyes on the sample surface.

It is clear that by manipulating the amount of CaCO₃ addition in to the glaze formulation, especially up to 3.0 wt%, the fired crystal glaze products can be diversified. The glaze surface can be furnished with various shape and size of spherulites morphologies that divulge the artistic effect of a crystalline glaze. The reduction in the number of crystalline phases, as CaCO₃ addition increases, on crystalline glazes is basically due to the changes in glaze fluidity during firing procedure. Other researchers stated that, the crystallization can be achieved with a simple two-steps heat treatment as the nucleation and the nuclei growth steps. In the nucleation step, the mobility of an atom in the glass phase ensures of embryo formation and nuclei stabilization and the latter promotes growth of crystal to a desired size [10-11].
can be observed that, the addition of 3.0 wt% CaCO₃ caused the nuclei to stretch further on all over the substrates surface, thus promotes some spherulites to grow as an individual at different parts of the surface. This behavior is accordance to the statement by Parmelee [1], which reported that nuclei form rapidly in a crystalline glaze melts and its higher fluidity is needed to limit the numbers of willemite. Therefore, the addition of 3.0 wt% CaCO₃ into the glaze batch must have improved the glaze melting at 1200°C firing temperature but its further addition of up to 5.0 wt% caused the glaze to be more fluid and reduce the amount of crystal nucleation site for willemite crystals, thus, retard the crystallization process.

Fig. 1. Digital image of specimens with (A) no CaCO₃ (CG0) as reference glaze, (B) with 1.0 wt% CaCO₃ (CG1), (C) with 3.0 wt% CaCO₃ (CG3) and (D) with 5.0 wt% CaCO₃ (CG5) fired according to FC1.

The presence of willemite crystals (Zn₂SiO₄, ICCD no. 037-1485, hexagonal internal structure (space group R3) with a = 13.9381 Å, c = 9.31 Å) in each glaze undergone FC1 was confirmed using XRD as indicated in Fig. 2. This observation is agreeable with previous studies [4,7,9,12] whereby willemite crystals were formed due to the high amount of ZnO content in silica rich crystal glazes.

Fig. 2. XRD diffraction patterns for reference glaze (CG0) and glaze with 1.0-5.0 wt% CaCO₃ additions (CG1-CG5) fired according to FC1.
According to Fig. 2, the intensities of willemite peaks reduce respectively as the amount of CaCO₃ increases up to 3.0 wt%. Further increment up to 5.0 wt% in the crystal glaze shows no more diffraction peaks because there was no willemite phase detected. This proves that, an addition of CaCO₃ does not promote the growth of willemite crystals but retards them because the diffraction peaks clearly shows reduction of their peaks intensities. Furthermore, willemite crystals do not develop or no longer grow with further CaCO₃ addition up to 5.0 wt% (Fig. 1D). The surface of the glaze was clear from any crystalline structure. On the other hand, it shows that an addition of CaCO₃ into the crystalline glaze batch up to certain limits can retards the willemite crystal growth.

![SEM image of (A) remnant glaze and (B) willemite crystal of CGO fired according to FC1.](image)

Fig. 3. SEM image of (A) remnant glaze and (B) willemite crystal of CGO fired according to FC1.

The morphology of the spherulites growing in the crystalline glaze, as observed by optical microscope, was further confirmed using SEM analysis as shown in Fig. 3. The SEM micrograph shows for two different regions of the glaze surface. The remnant glaze (Fig. 3A) is the surface without crystals and Fig. 3B identified the acicular needle like crystals. The SEM image clearly shows that the willemite crystals are in the form of acicular needle like shape. The grouping of this crystal will create a distinct crystal shape called spherulites [10]. EDX analyses for both the remnant glaze and willemite crystal shown are Fig. 4A and 4B. It is apparent that the composition of the remnant glaze (Fig. 3A) consists of high percentage of Si up to 48.40 wt% and O 35.96 wt%, while the willemite crystals (Fig. 3B) significantly differs from the glaze background because of containing higher amounts of Zn (56.61 wt%).
O (21.24 wt%) and Si (20.79 wt%) elements. The proportions of Zn, Si and O elements in the analysis reflect that the crystal is willemite. The composition would be detected as Zn 28.6 at%, Si 14.3 at% and O 57.1 at% if the crystals truly are willemite crystal of stoichiometric composition. However, by making allowance of possible error when analyzing the willemite crystal, it is apparent that the composition of willemite crystal from the EDX analysis is accordance to expectation.

Fig. 4. EDX analysis of the willemite crystal, (A) remnant glaze (B) willemite crystal of CGO fired according to FC1.

Fig. 5 shows the specific image of spherulites. The blue color of the crystals was the result of CoO (0.05 wt.% CoO) addition. The spherulites pattern resembles a double axe-head shape. In this case, a slightly higher crystallization temperature (1060°C) was used to produce double axe-head shape pattern. These types of patterns were achieved when a lower crystallization temperature was employed, the final shape of the spherulites is more spherical, unlike the one appear when a higher crystallization temperature used causing single bar or double axe-head shape due to the crystal growing range usually lying somewhere between
1010°C to 1187°C [2,4]. The crystal growing temperature for each glaze can be somewhat difficult to predict. Therefore, DTA analysis is required to get the real values.

Fig. 5. Microscopic (20 X) image of double axe-head shape like spherulites for reference glaze (CG0) fired according to FC 1. The blue color was caused by an addition of 0.05 wt% CoO.

Fig. 6. Digital image of flow trial block to indicate fluidity for (A) Reference glaze (CG0), and (B) the glaze with 5.0 wt% CaCO3 (CG5) fired according to FC2. Note that the glaze B is more fluid and flows further.

Fig. 6 shows the comparison between the reference glaze (CG0) and the one with 5.0 wt% CaCO3 (CG5) in terms of fluidity. It is obvious that the glaze (B) with 5.0 wt% CaCO3 flows further down, being 10% more fluid compared to the reference glaze (A). This shows that the addition of 5.0 wt% CaCO3 can influence the glaze to be more fluid and less viscous.

Fig. 7 shows the effects of gloss firing temperatures ranging from 1000°C to 1200°C without isothermal holding at the crystallization temperature (following FC2, FC3 and FC4, respectively) on the specific amount of CaCO3 addition (1.0 wt%). According to the XRD
result, CaCO₃ and orthoclase (feldspar) remained up to 1000°C and then started to disappear with an increase in the sintering temperature up to 1200°C. However, as the temperature increase to 1200°C and above there was no more trace of CaCO₃ and feldspar. This is due to the raw materials already melted at this temperature.

![Fig. 7. XRD diffraction patterns for the glaze with 1.0 wt% CaCO₃ addition (CG1) fired according to FC2-FC4.](image)

![Fig. 8. Digital image of CG3 (with 3.0 wt% CaCO₃) (A) glaze fired according to FC 5, and (B) according to FC 6.](image)

According to the XRD results at 1000°C and 1100°C, peaks for willemite crystals showed high intensities. This is because of these temperatures are still in the range of crystallization temperature (700°C to 1180°C) of willemite crystal as reported by [4-5], which is still in the range of the specified crystallization temperature (1060°C) used in this study. As the temperature increases to 1200°C the diffraction intensities of willemite crystals were decreasing respectively due to the reduction of glaze viscosity and the increase in glaze
fluidity that retards the growth of willemite crystals. Besides that, the glaze melts at 1200°C and the temperature does not promote crystal growth.

![Graph showing XRD diffraction patterns for the glaze with 3.0 wt% CaCO₃ (CG3) fired according to FC 5 (with CT) and FC 6 (without CT).]

In order to check whether the crystalline phase developed at the crystallization temperature (CT) instead of during cooling from gloss firing temperature, a glaze with 3.0 wt% CaCO₃ (CG3) was fired according to FC5 (with CT). It was then compared to the ones fired with FC6 (without CT). The result is shown in Fig. 8. Sample was fired according to FC5 produced a double axe-head shape patterns as seen in Fig. 8A; however, the other sample has none (Fig. 8B). Both samples were analyzed by XRD and the result is shown in Fig. 9. It is obvious that the crystallization of willemite is dependent on the period of isothermal holding at CT rather than during cooling from the peak firing temperature. The peaks intensity of willemite crystals is higher in the glaze with isothermal holding at crystallization temperature (FC5). Therefore, the willemite crystal growth should only be occurring during the isothermal holding at the soaking temperature rather than during cooling from gloss firing temperature.

**Conclusion**

The XRD results prove that the crystalline phases formed on the glaze surface is willemite ones (Zn₂SiO₄). The intensities of willemite crystal in the crystal glaze were reduced respectively with the increase of CaCO₃ content until 3.0 wt% and 1200°C gloss firing temperature. The CaCO₃ in the glaze compositions did not completely react up to 1000°C and started to disappear above this temperature. The willemite crystals started to form during isothermal holding at crystallization temperature instead of during cooling from gloss firing temperature. The SEM image showed that willemite crystals consist of acicular needle shape and align with one and other thus, creating the spherulites morphology. The EDX result
proved that the elements existed within the willemite crystals were high in Zn, O and Si. The crystal glaze formulation developed in this study might be one for the candidates of low temperature firing in crystalline glazes production.

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References