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Effects of different gloss firing temperature on the properties of zinc based crystal glaze

Abdul Rashid Jamaludin, Shah Rizal Kasim, Zainal Arifin Ahmad
School of Materials and Mineral Resources, Engineering Campus,
Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang

Abstract

Ceramic products with crystalline structure on its body give an artistic effect. The usage of zinc oxide which acts as a flux material has a beneficial effect in many colored glazes amongst which is crystalline glaze. Samples are fired at different gloss temperature (1200 – 1250°C) for half an hour and hold for five hours at crystal growth temperature (1060°C). After firing, the morphology of crystalline structure on the ceramic substrate body is identified using visual observation. The phases present are identified through X-ray diffraction (XRD). The results show obvious different spherulites pattern although being hold at gloss firing temperature for half an hour only. As the temperature increase, willemite crystals that consist in the spherulites are also increasing.

Key words: Crystalline glaze, gloss temperature, different temperature

Introduction

Glazes are defined as a thin continuous coating, usually prepared from fused silicate mixtures fusion-bonded to ceramic surfaces by the means of firing [1]. It acts as protective, marking, sealing or for decorative purpose. One of the promising decoration methods for ceramic is using crystalline glaze. The first scientific discussion on the preparation of macrocrystalline glaze seems to have been made by Ebelman during 1847 to 1852; he produced some crystalline glazes around 1850 [1 - 2]. In the United States, the Rookwood Pottery in Cincinnati, Ohio introduced crystalline glaze called “Tiger eye” in 1884 [2].

Crystalline glazes can be defined as devitrified glazes that melt under low or high gloss firing temperature and partially crystallize during controlled nucleation and growth process that also take place during firing procedure in order to form crystalline structure of various compound, sizes and morphology [3]. Two factors that can influence the development of crystalline glaze are the temperature and duration of the firing and the time-temperature cooling period.

The main component ensuring crystallization of these glazes is zinc oxide (ZnO). Furthermore, ZnO is a valuable auxiliary flux in the glaze firing up to about 1050°C [4 - 5]. When a much higher amount is employed and the appropriate cooling cycle (slow cooling) is adopted, decorative willemite (Zn_2SiO_4) crystal as large as several millimeters will appear on the glaze surface [6 - 7]. The formation and size of a crystal are influenced by the rate of cooling. During holding time (isothermal devitrification) and sometimes called aging is applied at the crystal growth temperature or crystallization temperature (Lag, Fig. 1), macro size crystal which is visible to the naked eye will develop for longer holding time.

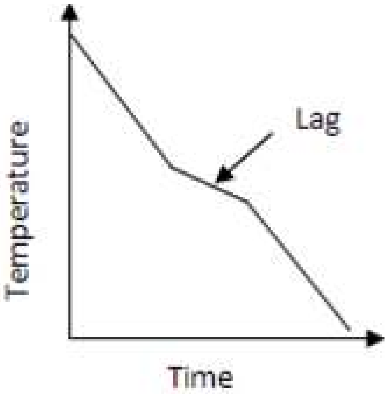

Fig. 1. Lag in cooling curve indicates crystal formation.

When producing crystal glaze, heat treatment cycles have a very strong effect on the concentration, shape and size of crystallites expected to form from original glazes. Gloss firing temperature for crystal glaze are usually high, up to cone 9 (1260°C) of Orton Cone or higher [2]. Besides that, longer holding time of gloss temperature is also adopted up to three hours and sometimes longer. Therefore, the aims of this study is to produce crystal glaze with both the temperature and holding time for gloss firing are reduced and then to investigate the crystallization behavior of this glaze.

Experimental Procedure

The crystal glaze formulas that will be used in this experiment are determined using the Seger Formula calculation techniques. Materials are classified as bases (RO/R_2O), amphoterics (R_2O_3) and acids (RO_2) as required in the empirical glaze formula and will be mixed according to the calculated formula. The mixture will be wet ball-milled for 5 hours using deionized water as medium to reduce the particle size and produce homogenous glaze mixture. After milling operations, the glaze slips were put through 200 mesh (approximately 75 µm) sieves and the sieved material was taken for glaze applications. The glaze mixture will be applied onto the body of ceramic substrate via dipping and brushing. The time of dipping is fixed for ten seconds in order to get the same thickness of glaze layer for every sample and residue of glaze were brushed away. The firing process will be done according to the predetermined firing profile. Finally, beside the visual observation analysis, other techniques such as optical microscope and X-ray Diffraction analysis (XRD) will be conducted to evaluate the quality of the produced crystal glazes.

Results and Discussion

At the beginning of this study, one crystal glaze formulation has been chosen to be use. The Seger formula of the crystal glazes are presented in Table 1 below.

Table 1. The Seger formulas of the glazes

0.044	Na_2O				
0.037	MgO			1.985	SiO_2
0.079	K_2O	0.120	Al_2O_3	0.007	CeO_2
0.145	CaO			0.235	TiO_2
0.625	ZnO				
0.068	BaO				

Table 2 show the heat treatment cycles used for glaze maturing and crystallization process. Photographs of all four different samples are presented in Fig. 2. Four different temperatures have been used as the maturing or gloss firing with the lowest temperature 1200^{o}C which is considered in this study as gloss firing temperature for ordinary glaze. The other gloss temperatures and holding time used for maturing the glazes seemed to be sufficient for the glaze to liquefy. The temperatures also have a positive effect for crystal nucleation as seen in Fig. 2 where three different patterns of crystal growth can be seen.

Table 2. The heat treatment cycles used for maturing and crystallization processes.

Glaze	Gloss firing temperature (^{o}C)	Holding time (h)	Crystallization temperature (^{o}C)	Holding time (h)
CG 1	1200 (ordinary glaze)	0.5	1060	5
	1230	0.5	1060	5
	1240	0.5	1060	5
	1250	0.5	1060	5

Heating rate 5^{o}C/min and cooling rate 3^{o}C/min. After crystallization temperature cooling rate is 2^{o}C/min.

As the maturing temperature increase, the crystal nuclei tends to distributed away from each other thus creating a space between each of them. Holding at crystallization temperature cost them (nuclei) to grow larger and eventually will come in contact with their neighbors as in Fig. 1 (b - d). The longer time adopted at crystallization temperature is to ensure that the crystals produced are large enough too few millimeters and can be distinguished by naked eye.

It was observed that the sample of glaze fired at 1200^{o}C as in Fig. 1(a) showed a satin surface finish like ordinary glaze. However, as the temperature gets higher, the surfaces become less smooth to touch (Fig. 2 (b)) and come with visible macroscopic pattern on the surface of crystalline glaze which is called spherulites. Spherulites were made of a large number of acicular crystals that are perfectly aligned with each other within the silica-rich glaze. The less smooth surface is a result of crowded and overlapped growth of spherulites within the glaze with fibrous morphology taken by the crystals as a consequence of their trigonal structure and the ability of such crystals to emerge from the tip of a parent fiber at some small angle and cause 3-dimensional crystal growth [3].

Many spherical pattern of spherulites start to appear as individual at higher gloss temperature as seen in Fig. 1 (c and d). A relatively wide ring or halo comprising much paler crystals ≈ 5 mm wide was also observed around the spherulites in (c) and a wider ring appear in (d). Creber (1997) suggested that haloes are generated during further cooling when the temperature gets lower from crystallization temperature. From classical nucleation theory, this lowering of temperature has the effect of increasing the rate of heterogeneous nucleation and decreasing the rate of crystal growth forming haloes with smaller willemite crystal [3]. The haloes seen in Fig. 1 (c and d) will have been formed at the end of the heat treatment where a deliberate and steady decrease in temperature of the furnace at 2°C/min. was adopted.

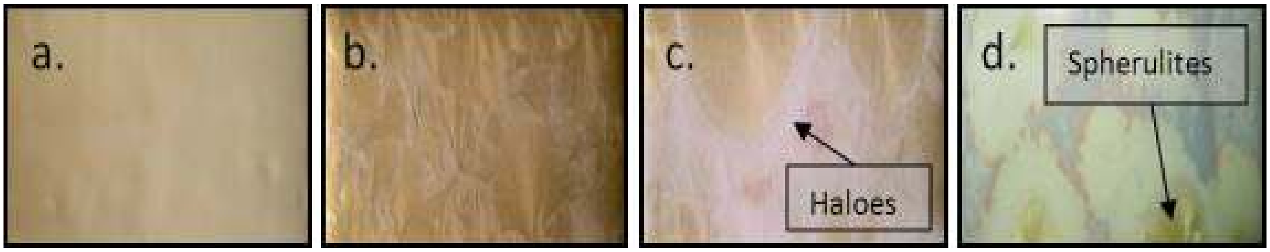

Fig. 2. Photograph of samples with crystalline glaze on the body gloss fired at (a) 1200°C, (b) 1230°C, (c) 1240°C and (d) 1250°C.

The spherulites on the substrate bodies that have been heat treated at different gloss firing temperature were identified by X-ray diffraction (Bruker-AXS) using CuKα radiation (1.5406 Å). An X-ray diffractrometer trace from all three different gloss firing temperature shown in Fig. 3. Form observation, the result show almost similar patterns with sharp diffraction peaks at 2θ under 35°. The sharp diffraction peaks $2\theta < 60^{o}$ for the results are identified as willemite crystal, Zn_2SiO_4 peaks (ICDD 01-085-0453). Willemite crystals are in formed of accicular needle like shape crystal. At lower temperature (1200 – 1230°C), only sharp diffraction peaks are visible. However, several new peaks of willemite crystal started to evolve (in box) and start to grow taller at higher temperature. This show that the amount of willemite crystal increase as the gloss firing temperature gets higher as being state by Lee *et al.* [8]. There are also some unidentified peaks that was obvious at 1200°C and 1240°C.

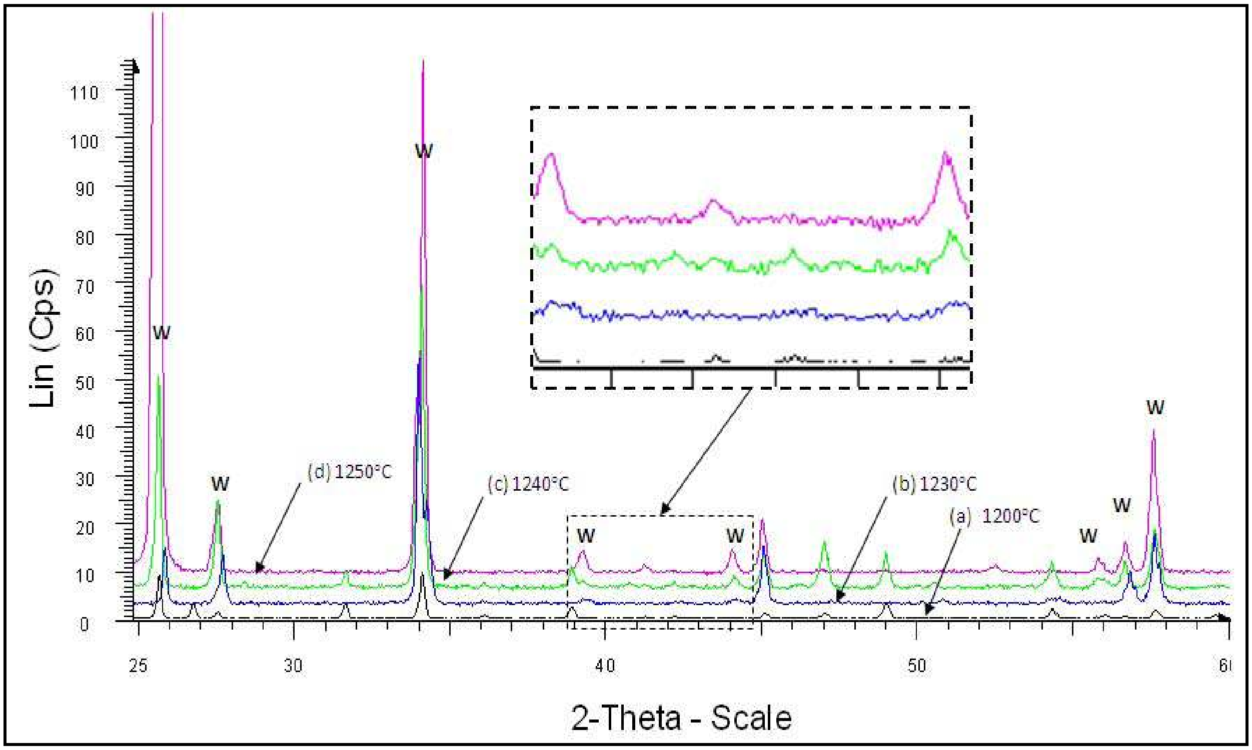

Fig. 3. XRD results showing willemite phase formation in crystal glaze gloss fired at (a) 1200°C, (b) 1230°C, (c) 1240°C and (d) 1250°C (**w**, willemite).

Conclusion

The results indicate that firing conditions strongly influence the phase composition of crystalline glazes. The gloss firing temperatures (1230 – 1250°C) for the period of 30 minutes are sufficient to liquefy the glaze in order for materials transportation mechanism to happen thus facilitates the growth of crystal. The different gloss firing temperatures and coupled with the same crystal growth temperature (1060 °C) and duration (5 hours) produced different pattern of spherulites. However, higher gloss firing temperature is able to reduce the over crowded condition of the spherulites growth. XRD results also indicate that the higher gloss firing temperature the higher the number of willemite crystals formed in the spherulites, thus making the acicular needle shape look tinier and increase in number.

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