



Morphology of Calcium Oxide Added Willemite Crystals

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Crystalline glazes give amazing and spectacular results in ceramic. Their actual chemical makeup is remarkably simple. Two parts frit, one part zinc and one part silica are the constituents needed to make it to workable base glaze. Variations in proportions or addition of other oxides affect the crystal size, shape, colour and number. In this paper we have added 1, 3 and 5 wt % of calcium oxide to basic willemite crystal forming glaze. The samples were examined by scanning electron microscopy for morphological changes and energy dispersive X-ray spectrometer (EDAX-link ISIS 300) attached to SEM was used for chemical analysis.

Key Words: Crystalline glazes, CaO, Willemite, Crystal morphology, Scanning electron microscopy, Energy dispersive X-ray spectrometer.

INTRODUCTION

Crystalline glaze, found in ceramics, contain macro crystals of zinc orthosilicate (Zn_2SiO_4). These are similar to the naturally occurring mineral form of zinc silicate *i.e.*, Willemite. Iron, barium and titanium produce crystals in glazes, but only zinc makes the spectacular crystals of up to three inches or more in diameter¹. The crystalline glaze contains three basic ingredients necessary for crystal growth: zinc oxide, silica (or ground quartz) and a frit which is fused glass that is ground to a fine powder. These three powdered ingredients are mixed with water to form a thick glaze which is then applied to the pot². A crystalline glaze is saturated with oxides usually zinc which combine to form crystals in the glaze whilst it is in a state of flux in the heated kiln. As the kiln is slowly cooled the glaze remains molten long enough for the oxides to combine to form crystals. Zinc oxide combines with free silica to form zinc silicate crystals known as Willemite (Zn_2SiO_4 or $2ZnO \cdot SiO_2$)^{3,4}. The crystals continue to grow until the glaze becomes too viscous for the different oxides to isolate themselves and reform within the matrix of the glaze. Ilmenite, rutile, titanium oxide, calcia, magnesia and zirconium silicate may be used to encourage crystal growth. The glaze should have a low viscosity. If the viscosity is too high, for example by the presence of too much alumina the glaze will not be free flowing enough to allow the oxides to move together to form the crystals. However, if the glaze has too low a viscosity it can run off upright surfaces during the long cooling period. To prevent samples fusing to

the kiln shelf they are usually placed on supports within a catch tray. Macro crystalline glazes are usually fired to at least 1280 °C and then cooled quickly to the crystal growing range usually considered to be 1150 and 1020 °C, soaking (holding the temperature) within this range for periods of some hours and finally cooling naturally⁵⁻⁸.

In this paper we have added calcium oxide to see the effect on viscosity of glaze and hence on crystals morphology. The samples were examined by SEM and EDAX and compared with samples having glaze without any additive.

EXPERIMENTAL

Glaze is formed by combination of 45 % frit and 55 % other raw materials (like Na_2O , K_2O , CaO , MgO , ZnO , BaO , Al_2O_3 , Fe_2O_3 , SiO_2). Alkaline frit was selected for glaze preparation as it forms large crystals. Initially all glaze ingredients (Table-1) in appropriate amount were taken for wet milling in pot mill having dry charge capacity of 4 kg for 6 h. This glaze slurry was then charged into vibro-energy mill for 4 h so that the particle size would be same. The final glaze was then passed through 200 mesh sieve. Three different percentage (1, 3, 5 wt % CaO) were added to final glaze and mixed further for 45 min in pot mill to see the effect of CaO . The glazes were applied onto bisque fired (1000 °C) clay body test tiles using dipping technique for 20 s. This applied a thickness of 100 μm of glaze to prevent from cracking during drying and eventually regional glaze shrinkage problems on the double fired body. Finally all the samples were fired according to firing cycle 1, 2, 3 and 4

TABLE-1
CHEMICAL COMPOSITIONS OF THE RAW GLAZE

Raw materials	Composition (wt. %)										
	Na ₂ O	K ₂ O	CaO	MgO	ZnO	BaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	LOI*
Feldspar	2.00	12.00	-	-	-	-	19.00	-	67.00	-	0.306
Zinc oxide	-	-	-	-	100.00	-	-	-	-	-	0.426
Silica	-	-	-	-	-	-	1.20	-	98.00	-	0.272
Frit	2.60	6.20	8.70	1.60	4.30	-	10.00	-	65.00	-	0.305
Kaolin	-	1.60	-	-	-	-	40.00	1.00	57.00	-	0.507
Calcite	-	-	98.00	1.60	-	-	-	-	-	-	0.615
Calcium oxide	-	-	95.00	-	-	-	-	-	-	-	10 %

*Loss on ignition

(FC1, FC2, FC3 and FC4) (Table-2). The samples were marked as G1, G3 and G5 having 1, 3 and 5 wt % of CaO. Fired samples were examined by SEM. For this the fired sample (1 cm × 1 cm) were coated with a thin film of gold and examined using a SEM with CamScan S6 at 20 kV. An ultra thin Window Energy Dispersive X-ray Spectrometer (EDAX- LINK ISIS 300) attached to SEM was also used for chemical analysis.

TABLE-2
DIFFERENT FIRING CYCLES USED FOR GLAZE

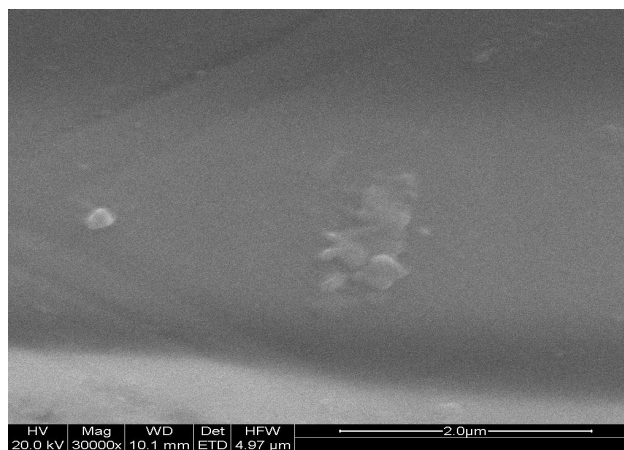
Temperature (°C)	Soaking time (min)			
	FS1	FS2	FS3	FS4
1250	0	0	0	0
1250	10	20	30	40
1075	0	0	0	0
1075	180	180	180	180

RESULTS AND DISCUSSION

Glaze without any colourant produce largest, finest and maximum amount of crystals with smooth surface with first firing cycle⁹. This sample is used for comparing with calcium oxide added samples. After an addition of CaO (G1), the crystal starts to be less dense *i.e.*, the addition of calcium oxide increases viscosity of reference glaze. The glaze having 1 wt. % of CaO when fired according to FC1 produce small crystals, overlapping to each other so no clear sperulite (a group of crystals) is seen but when the soaking time is increased from 10-20 min *i.e.*, FC2 the crystals starts to be less dense but even now with some overlapping at the centre of the sperulites. The similar glaze forms smallest clear sperulite following FC3, having a diameter of 0.5-1.0 cm. On the other hand glaze with 3.0 wt % of CaO shows different results then this, it forms largest sperulites when fired according to FC1. As the soaking time is increased from 20-40 min the glaze starts flowing creating clear glass with out any sperulite at larger area. The glaze with 5 wt. % of CaO create a very small amount of sperulites with FC1 and as the soaking time is increased from 20-40 the number of the sperulites decreases creating a clear glass. Therefore, the addition of 3 wt % CaO into the glaze batch must have improved the glaze melting at 1250 °C firing temperature but its further addition of up to 5 wt % caused the glaze to be more fluid and reduce the amount of crystal nucleation site for willemite crystals, thus, retard the crystallization process. The crystallization is a simple two-steps heat treatment process as the nucleation and the nuclei growth steps. In the nucleation step, the mobility of an atom in the glass phase ensures of

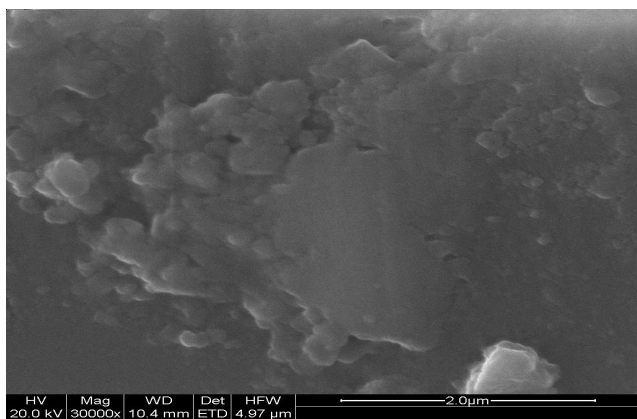
embryo formation and nuclei stabilization and the latter promotes growth of crystal to a desired size⁹⁻¹². It can be observed that, the addition of 3 wt % CaO caused the nuclei to stretch further on all over the substrates surface, thus promotes some spherulites to grow as an individual at different parts of the surface. This behaviour is accordance to the work of Parmelee¹³, 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 wt % CaO into the glaze batch must have improved the glaze melting at 1250 °C firing temperature but its further addition of up to 5 wt % caused the glaze to be more fluid and reduce the amount of crystal nucleation site for willemite crystals, thus, retard the crystallization process.

The SEM photographs of smallest (SEM photographs 1) and largest sperulites (SEM photographs 2) were compared with best sample of reference glaze (glaze without any additive)⁹.



SEM photographs 1: SEM: sample with smallest sperulites (glaze with 1.0 wt. % of CaO fired acc. to FC3)

EDAX analysis of the samples found that the sample without CaO is composed of high percentage of Zn, Si and O with trace of Ca (from calcite, china clay or from any other raw materials). The proportions of Zn, Si and O elements in the analysis reflect that the crystals formed are Willemite⁹. The EDAX of smallest sperulites (Fig. 1) formed by 1 wt.% of CaO fired according to FC3 showed that the crystals have similar composition to willemite having Zn (41.44 wt. %), Si (34.48 wt. %) and O (26.63 wt. %) with an increase amount of Ca upto 1.72 %.



SEM photographs 2: SEM: sample with largest sperulites (glaze with 3.0 wt. % of CaO following FC1)

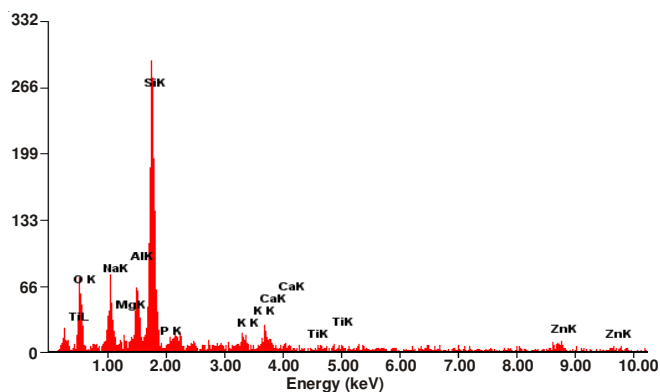


Fig. 1. EDAX of sample having smallest sperulites

The EDAX of largest sperulites with 3 wt. % of CaO following FC1 with 10 min of soaking at peak temperature show a major decrease in Zn percentage to 12.01 wt. % while other remains almost same. It shows that in crystal Zn is replaced by Ca as Ca is increased in crystal 2.73 wt. % (Fig. 2).

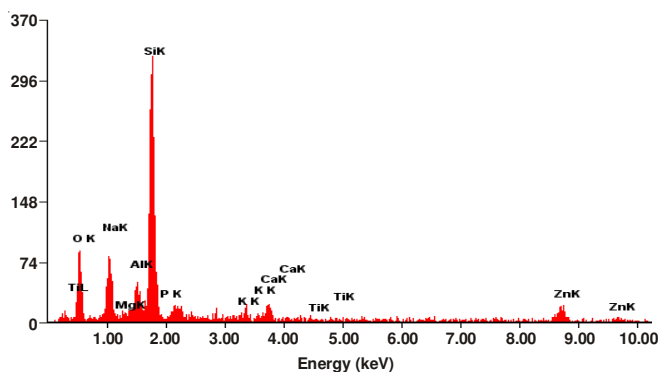


Fig. 2. EDAX of glaze with smallest crystals

Conclusion

Higher fluidity (low viscosity) is needed to form large number of Willemite crystals. Addition of calcium oxide increases viscosity of zinc based crystalline glazes. With the increment of soaking time fluidity of glaze having CaO increases. 1 wt % of CaO added form smallest sperulites with 10 min of soaking at peak temperature. Addition of 3 wt % of CaO form large shiny crystals when given 0.5 h of soaking at peak temperature. More than 0.5 h of soaking at peak temperature for the glaze with 3 wt. % of CaO will cause the glaze to be transparent at large area. The addition of 3.0 wt % CaO into the glaze batch must have improved the glaze melting at 1250 °C firing temperature. More than 3.0 wt % addition of calcium oxide causes reference glaze to be more fluid and hence to form transparent shiny glass containing no crystals. Addition of 5.0 wt % of CaO reduce the amount of crystal nucleation site for willemite crystals, thus, retard the crystallization process.

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