Effect of Firing Cycle and Glaze Variables on Reducing the Number of Pin-hole Defects

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Abstract

Pin-holing, one of the major glazing defects,that tableware ceramic industry in Bangladesh is experiencing. Raw material composition andair trapped between the particles of powdered glaze are the main causes for this glaze relevant defect. A combination of test methods has been developed to characterize and relatebody and glaze raw materialsfor pin-hole growth. It is evident from this research work that the pin-holing defect can be removed by optimizing composition and sintering profile, which in turn yield pin-hole free tableware ceramics with smaller grain size. Tableware ceramic body sintered at 1000ºC (60 min) and 1300ºC (90 min) exhibited appropriate microstructure and coefficient of thermal expansion which meet the requirements for the tableware ceramic. It is found that pin-holing defect depends on the feldspar and quartz content in glaze raw material as well as firing temperature profile, especially soaking time and firing cycle, and the result was satisfactory when the ratio (quartz/feldspar) was ~2.

Keywords:Firing profile optimization,Tableware ceramic, Glaze defects, Pin-hole, Glaze variable, Raw materialscomposition of body and glaze.

1.0 INTRODUCTION

At present, glazing defects are one of the major challenges that the export oriented ceramic industry in Bangladesh is experiencing. The major glazing defect that frequently identified in tableware ceramic industry in Bangladesh is Pin-holing. Pin-holing is a glaze defect in which small dot of depressed areas appear in the glaze surface as a result of gas bubbles in the glaze [1-3]. It may present only on the surface of the glaze or may penetrate to the clay layer. More recently, some research groups tried to modify and optimize firing cycles to reduce Pin-holing defect.

Glaze is a thin layer of liquid suspension of finely ground minerals applied on a surface of bisque fired ceramic ware or on surface of the clay body named as green body. Glaze act as smooth, relatively thin glassy coating of ceramic body which is effectively bonded to its substrate [4]. The glaze interacts with the body, often sinks into the body, and form an intermediate layer between the body and the glaze [1,5]. This buffer layer bonds the body and glaze together. Glazes and ceramic bodies are in close contact and react chemically and physically during firing. Raw material composition, difference in linear thermal expansion coefficient, degradation, and stress relations among the body, intermediate layer, and glaze are the main causes for these glaze relevant defects.Pin-holing and pitting are glaze defects in which the glaze comes out of the kiln with one or more pits in its surface. Pinholes are the smallest of these pits (see Figure 1). All glazes contain volatile materials and will undergo a certain amount of agitation as these burns off during firing. Most pinholes and pits are formed due to this off-gassing. Under-firingcan causeglaze with pin-holing and pitting [5,6]. The matte glazes are more subject to pin-holing and pitting, since they are the glazes made purposefully under-fired.

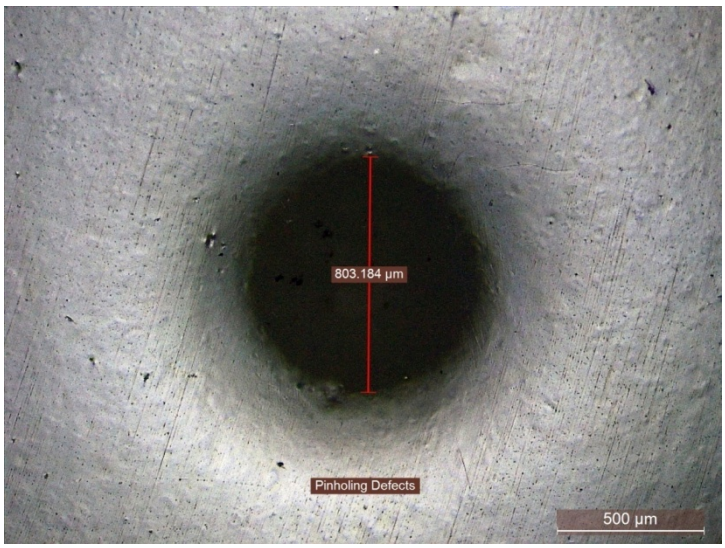

Figure 1.Optical image of Pin-holing defect (50X).

Other contributors to pin-holing and pitting include high levels of zinc or rutile in the glaze. In addition, if the kiln enters into reduction during the early stages of firing, carbon may be deposited on the ware and can contribute to pin-holing and pitting as it later burns off. Perhaps the most common of all glaze defects, pinholes are tiny holes in the glaze surface which penetrate all the way through to the body[4,7]. The most common remedy in low fire ceramics is to ensure that the piece is bisque fired 2 cones hotter than it is glaze fired. Other possible remedies include: a longer firing cycle with optimum soak at the peak temperature, changing the peak temperature, a slower cooling cycle, a thinner glaze coating, using a glaze with more flux, and decreasing the amount of zinc or rutile in the glaze if it is present.Some research groups also change the body and glaze raw materials and their chemicalcomposition in order to get rid of the Pin-holing defect. However, a comprehensiveresearch is so far lacking to find out the root cause for this defect, especially influence of compositional variation and micro structural change due to firing[3,8,9]. In this study weemphasized on characterizing the defective samples with pin-holes, identified thecauses for the defect, and thus implementing remedial measures such as change ofglaze composition and optimization of firing profile.

2.0 EXPERIMENTAL

2.1 Sample preparation

Description of the raw materials, processing techniques and the equipment used to prepare and characterize the tableware ceramic samples are detailed in the following sections. Initially the samples were prepared using traditional industrial recipe which leads to pin-holing defect. A modification of recipe was followed later in an attempt to eliminate the pin-holing defect. Sample preparation and firing were conducted in the industry in order to keep all parameters identical. An overview of the sample preparation steps ispresented in Figure 2.

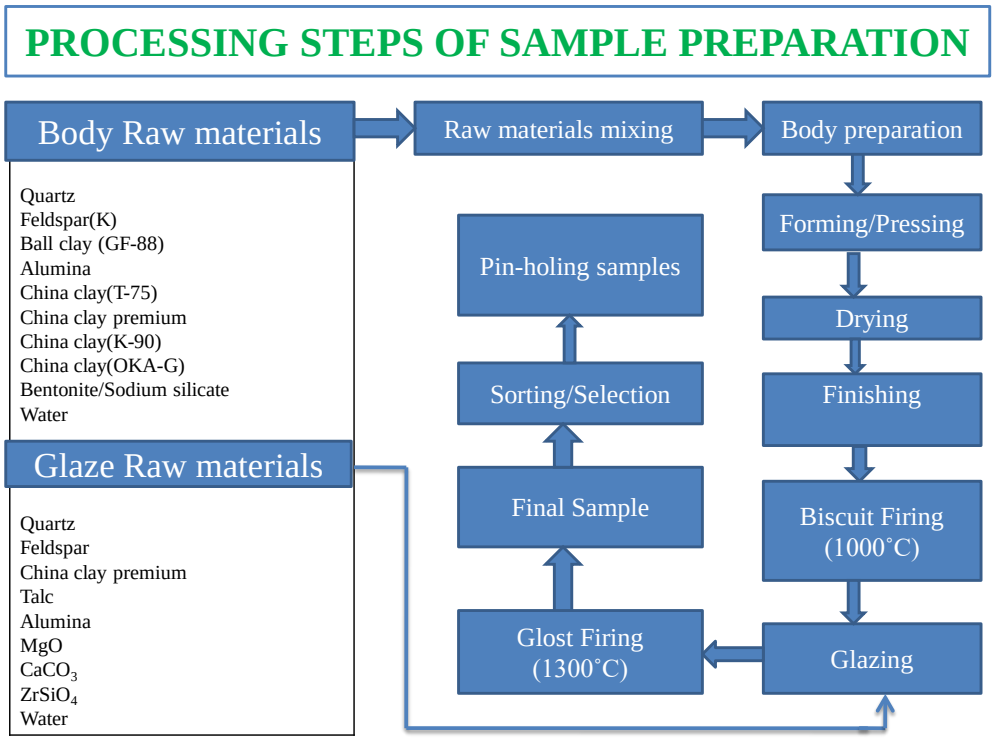

Figure 2.Schematic Representation of the Research.

2.2 Characterization of raw powders

X-Ray Fluorescence (XRF) Spectroscopy:

X-Ray Fluorescence Spectroscopy (XRF) (XRF-1800, LAB CENTER, Sequential X-Ray Fluorescence Spectrometer, Japan) was used to determine the compositional analysis of the as received ceramic body andglaze raw powder.

Field Emission Scanning Electron Microscopy:

Field Emission Scanning Electron Microscopy (FESEM) (JOEL, JSM 7600F, Japan)equipped with an energy dispersive X-ray spectrometer (EDS) was employed to observe the morphology of samples. A coating was applied to all the samples by a JOEL Auto Fine Coater of thin Gold coating (~ 10 nm) for 60 sec.

3.0 RESULTS AND DISCUSSSION

The results of the experimental work are presented and discussed in this section. Tableware ceramics are very sensitive to both firing cycle and composition (ceramic body and glaze). With a slight change in parameters like sintering and firing temperature as well as composition, profuse effect on density, glazing defect, firing defect, forming defect and other properties might perceive. Therefore, in this research work, both parameters were observed carefully.

3.1 Chemical composition analysis of ceramic body and glaze raw materials

Compositional analysis of the body raw powders was conducted by X-ray fluorescence (XRF) spectroscopy. SiO_2, Al_2O_3 and Alkali content in the raw powders were detected as~98.9%. The sample contains 0.38 % iron oxide and

other compoundsare insignificant and can be considered as trace amount(as shown in Table 1). The body composition determines the ultimate firing temperature and also can affect the heating and cooling rates.

Table 1. XRF results of ceramic body raw materials

Material	Composition (%)
SiO_2	74.83
Al_2O_3	19.48
K_2O	3.84
Na_2O	0.75
Fe_2O_3	0.38
CaO	0.27
MgO	0.18
TiO_2	0.09
SO_3	0.06
Rb_2O	0.04
P_2O_5	0.03
Cr_2O_3	0.03
MnO	0.006
ZnO	0.006

Compositional analysis of the ceramic glaze was conducted by X-ray fluorescence (XRF) Spectroscopy. SiO_2, Al_2O_3, CaO, MgO, ZnO and Alkali content in the raw powders were detected as 99.66%. The glazecontains 0.13 % iron and other elements are insignificant (as shown in Table 2). The body and glaze composition were selected in such a way that it ensures the thermal expansion coefficient of the body is slightly higher than that of glaze.

Table 2. XRF results of ceramic glaze raw materials

Material	Composition (%)
SiO_2	72.67
Al_2O_3	10.77
CaO	7.70
K_2O	3.28
Na_2O	0.95
MgO	3.06
ZnO	1.23
Fe_2O_3	0.13
P_2O_5	0.06
TiO_2	0.05
SO_3	0.04
Rb_2O	0.03
Cr_2O_3	0.007
ZrO_2	0.006
MnO	0.005

3.2 Effect of firing temperature and soaking time

3.2.1 Biscuit Firing

Five green samples were prepared using traditional industrial recipe. No change was made in biscuit firing. Both firing temperature and soaking time was same for all five samples. There was no significant change observed among the samples (see Table 3).

Table 3. Relation between firing temperature and soaking time

Sample No.	Temperature (ºC)	Soaking Time (min)	Result/Effect
Sample #1	1000	60	Ok
Sample #2	1000	60	Ok
Sample #3	1000	60	Ok

Sample #4	1000	60	Ok
Sample #5	1000	60	Ok

3.2.2 Glost Firing: Effect of soaking time on sintering at constant temperature

At constant glost firing temperature(1300ºC), lower soaking time results in partially sintered body, whereas higher soaking time results in over-sintered body which causes color fading and bending. Soaking time consist of 90 minutes was found appropriate for desired sintering results and optimum effects. The effect of soaking time and temperature in glost firing is summarized in Table 4 and Table 5 respectively. An optimum firing cycle is a precondition to achieveglazedefect free ceramic tableware. Therefore, emphasis was placed initially to figure out the optimum glost firing temperature and soaking time.

Table 4.Effect ofsoaking time in glost firing

Sample No.	Temperature (ºC)	Soaking Time (min)	Sintering Effects	Result/Effect
Sample #1	1300	60	Slightly sintered	Not ok
Sample #2	1300	75	Partially sintered	Not ok
Sample #3	1300	90	Fully sintered	Ok [Optimum]
Sample #4	1300	105	Over sintered	Color fading and bending
Sample #5	1300	120	Highly over sintered	Color fading and bending

Keeping the soaking time fixed at 90 minutes, at <1300ºC, sintering results were in vain. At >1300ºC, sintering results were in distortion. Therefore, 1300ºC was found suitable as sintering temperature. The optimum firing temperature and time may shift to higher or lower side, should there be any significant change in raw materials.

Table 5.Effect ofsoaking temperature in glost firing

Sample No.	Temperature (ºC)	Soaking Time (min)	Sintering Effects	Result/Effect
Sample #1	1280	90	Slightly Sintered	Not ok
Sample #2	1290	90	Partially Sintered	Not ok
Sample #3	1300	90	Fully Sintered	Ok [Optimum]
Sample #4	1310	90	Over Sintered	Color fading and bending
Sample #5	1320	90	Highly over sintered	Color fading and bending

3.3 Effect of Glaze Composition

Composition of the ceramic tableware body determines the ultimate glostfiring temperature.Both heating and cooling rates depend mostly on what changes occur in the ceramic body and glaze with temperature. However, glaze raw material must be selected based on body composition in order to avoid thermal mismatch as well as requirement of glaze properties. A compatible glaze with optimum firing cycle may also lead to pin-holing defect.In order to eliminate/ reduce pin-holing defect, a compositional variation in glaze should bemade rather than changing the body composition. In this research work glaze composition was altered by changing the ratio of the quartz and feldspar in such a way that wouldyield a surface where pin-holing defect could be reduced.Table 6 lists initial glaze raw material used to prepare the water soluble glaze. Some oxides in the glaze are in oxide form, while others derived from complex oxide minerals.

Table 6. Ceramic glaze raw material composition(quartz to feldspar ratio 2.92)

Sl. No.	Raw Material	Chemical Formula	Content (wt. %)
1.	China Clay	$Al_2O_3.2SiO_2.2H_2O$	8
2.	Quartz	SiO_2	35
3.	Feldspar(K)	$K_2O.Al_2O_3.6SiO_2$	12
4.	Limestone	$CaCO_3$	8
5.	Zinc Oxide	ZnO	2
6.	Zirconium Silicate	$ZrSiO_4$	1
7.	Alumina	(Al_2O_3)	14
8.	Talc	$Mg_3Si_4O_{10}(OH)_2$	20
Total=			100%

It is evident that reducing the viscosity of the glaze would enable the trapped bubbles escape comfortably. Changes in glaze composition may be the key factor for peripheral changes in viscosity. The melting temperature of quartz(SiO_2) is high and increasing the amount of quartz in glaze will accompany undesirable high glaze viscosity. Moreover, bubbles tend to attach themselves with large silica particles and are very difficult to remove. Therefore, it is logical to reduce the amount of quartz in glaze. On the other hand, feldspar is the main fluxing agent in glaze which reduces sintering temperature as well as theviscosity [3-5]. Therefore, by replacing portion of quartz with fluxing agent would decrease the glaze viscosity and thus allow all gaseous components removed from the surface. As a result, pin-holing defect could be reduced. Table 7, Table 8, and Table 9 shows the pin-holing defect outcome obtained when content of quartz in glaze decreased incrementally while fluxing feldspar content increased in the glaze. The pin-hole over the glaze surface wasevaluated visually and minimum defect was observed when the ratio of quartz tofeldsparwas 1.94 rather than 2.36 or 1.61. Although an increased feldspar content (16%) in glazedecreased the pin-holing defect, but causes bending of ceramicware due to low quartz content in glaze which leadsto high thermal expansion andcan be translated as more contraction during cooling. Theextent of residualstresses arising due to thermal expansion mismatch between the body and theglaze cause the tableware to bend [10].

Table 7. Ceramic glaze raw material composition (quartz to feldspar ratio 2.36)

Sl. No.	Raw Material	Chemical Formula	Content (wt. %)	Result/Effect
1.	China Clay	$Al_2O_3.2SiO_2.2H_2O$	8	Extent of pin-holing defect reduced but still exist substantially
2.	Quartz	SiO_2	35-2=33	
3.	Feldspar(K)	$K_2O.Al_2O_3.6SiO_2$	12+2=14	
4.	Limestone	$CaCO_3$	8	
5.	Zinc Oxide	ZnO	2	
6.	Zirconium Silicate	$ZrSiO_4$	1	
7.	Alumna	(Al_2O_3)	14	
8.	Talc	$Mg_3Si_4O_{10}(OH)_2$	20	

Table 8.Ceramic glaze raw material composition (quartz to feldspar ratio 1.94)

Sl. No.	Raw Material	Chemical Formula	Content (wt. %)	Result/Effect
1.	China Clay	$Al_2O_3.2SiO_2.2H_2O$	8	Minimum pin-holes observed
2.	Quartz	SiO_2	35-4=31	
3.	Feldspar(K)	$K_2O.Al_2O_3.6SiO_2$	12+4=16	
4.	Limestone	$CaCO_3$	8	
5.	Zinc Oxide	ZnO	2	
6.	Zirconium Silicate	$ZrSiO_4$	1	
7.	Alumna	(Al_2O_3)	14	
8.	Talc	$Mg_3Si_4O_{10}(OH)_2$	20	

Table 9.Ceramic glaze raw material composition (quartz to feldspar ratio 1.61)

Sl. No.	Raw Material	Chemical Formula	Content (wt. %)	Result/Effect
1.	China Clay	$Al_2O_3.2SiO_2.2H_2O$	8	Bending of sample observed
2.	Quartz	SiO_2	35-6=29	
3.	Feldspar(K)	$K_2O.Al_2O_3.6SiO_2$	12+6=18	
4.	Limestone	$CaCO_3$	8	
5.	Zinc Oxide	ZnO	2	
6.	Zirconium Silicate	$ZrSiO_4$	1	
7.	Alumna	(Al_2O_3)	14	
8.	Talc	$Mg_3Si_4O_{10}(OH)_2$	20	

4.0 CONCLUSIONS

This study suggests that the pin-holing problemobserved in tableware industry could be solvedrapidly with the help of optimizing firing cycle and having right ratio of quartz to feldspar in glaze composition.It was found that tableware ceramic body sintered at 1000ºC (60 min) and 1300ºC (90 min) exhibited appropriate microstructure and well-match between glaze and body. Attempts were made to eliminate or at least reduce the extent of pin-holing

defect by varying the ratio of quartz to feldspar in the glaze and the results found quite satisfactory when quartz to feldspar ratio was ~2. The optimum ratio was obtained empirically and may vary depending on type of glaze used.

REFERENCES

[1] Eppler R. A., Obstler , Understanding Glazes. Ohi, The American Ceramic Society, ISBN 1-57498-222, (2005).
[2] Taylor, John Roberts, and A. C. Bull. "Ceramics glaze technology." (1986).
[3] Kavanova, M., Klouzkova, A., and Jaroslav, K., Characterization of The Interaction Between Glazes and Ceramic Bodies, *Ceramics–Silikáty*, vol. 61, no. 3, pp. (267-275), 2017.
[4] Ceramic Glazes, Cullen W. Parmalee& Cameron G, Harmon, Cahners Publishing Company, Inc, Boston, Third Edition, 1973
[5] JOHN T. JONES, Ph.D, Ceramic processing, Ceramic defect series: (1-10), 2007.
[6] Tunali, A., Investigation of methods of reducing the number of pinhole defects in glossy-opaque floor tile glaze by modifying glaze properties, *Journal of Ceramic Processing Research*, vol. 15, no. 4, pp. (225-230), 2014.
[7] Birlutiu, Adriana, et al. "Defect Detection in Porcelain Industry based on Deep Learning Techniques." 19th International Symposium on Symbolic and Numeric Algorithms for Scientific Computing, Timisoara, 2017.
[8] Jones, J. T., and M. F. Berard. "Ceramics industrial processing and testing, Iowa State University Press" (1993).
[9] Barson, T., "Frit: The Engineered Material," Ceramic Engineering & Science Proceedings, Volume 18, issue 2, 1997.
[10] Cronin, A. P. and Reece, M. J.,"Thermal Stresses in Glazed Substrates",Joinings and Coatings, in 4th European Ceramic SocietyConference Proceedings. Vol. 9.Edited by B. S. Tranching and A. Bellosi.GruppoEditoriale Faenza Editrice, Florence, Italy, pp. 411-8,1995.