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MATERIAŁY CERAMICZNE /CERAMIC MATERIALS/, 62, 4, (2010), 565-568

Effect of Pigments on Crystal Phases in Non-Fritted Matte Glaze

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Abstract

Recently, porcelain with matte glaze, as a unique and attractive coating on ceramic products, has attracted many architects and interior designers' attention. Production of matte glaze was a challenge for sanitary ware manufacturers due to long firing cycle, raw glaze, and single firing condition and being hygienic that is very important. Although, using frit facilitates making matte glaze, its high price and reduction of firing temperature keep manufacturers away from its production. In this investigation, the matte glaze has been designed and produced based on the fact that increasing CaO content in glaze composition induces crystal growth; besides, coloured matte glaze has been investigated, different pigments have various effects on crystal morphology and microstructure that they have been studied by XRD. The surface quality of this glaze has been observed by confocal optical microscope. At the end, standard tests for sanitary ware were passed and confirmed the quality.

Keywords: Matte glaze, CaO, Pigment, Microstructure

WPŁYW PIGMENTÓW NA FAZY KRYSTALICZNE W SZKLIWACH MATOWYCH NIE FRYTOWANYCH

Ostatnio, porcelana z matowym szkliwem, jako unikalną i atrakcyjną powłoką na wyrobie ceramicznym, przyciąga uwagę wielu architektów i projektantów wnętrz. Wytwarzanie szkliwa matowego było wyzwaniem dla wytwórców wyrobów sanitarnych ze względu na długi cykl wypalania, samo otrzymanie surowego szkliwa i spełnienie warunku spiekania jednoetapowego, a także, co jest bardzo ważne, koniecznością spełnienia wymagań higienicznych. Chociaż, potrzeba użycia urządzeń frytujących do wytwarzania szkliwa matowego, jego wysoka cena i obniżenie temperatury wypalania wstrzymują producentów od ich produkcji. W niniejszej pracy opracowano i wytworzono szkliwo matowe w oparciu o fakt, że zwiększenie zawartości CaO w składzie szkliwa wywołuje wzrost faz krystalicznych; poza tym, zbadano zabarwione szkliwo matowe, różne pigmenty mają odmienny wpływ na morfologię i mikrostrukturę faz krystalicznych, co zbadano za pomocą techniki XRD. Jakość powierzchni tego szkliwa obserwowano za pomocą mikroskopu optycznego współogniskowego. Na koniec, przeprowadzono standardowe badania wyrobu sanitarnego i potwierdzono jego jakość

Słowa kluczowe: szkliwo matowe, CaO, pigment, mikrostruktura

1. Introduction

Using coloured glazes for interior designs are increasing every day, on the other hand, coloured matte glaze in various colours make an outstanding change in interior design. In this paper, matte glaze has been studied for sanitary wares. Economic analysis and bench marking shows that architects and interior designers are interested in using matte glaze.

For the first time Ch.F. Beans could produce matte glaze by increasing alumina in composition of glossy glaze for pottery industry in 1903, afterward the microstructure of glossy, semimatte and matte glaze were studied by Stall in 1912 [1]. Matte glaze was produced by using RO group in 1923. Pans developed matte glaze theory with microscopic images; he also declared that mattness is due to formation of 3 different crystals of calcium, alumina and zinc-barium [2]. In 1963, American ceramic research center produced fritted and non-fritted matte glaze on porcelain surface [1].

Although many investigations has been done on matte glaze, it has not been studied this kind of glaze on sanitary ware surfaces yet. Crystal phase has to form during firing and cooling, if these crystals are small, the glaze surface will be smooth enough for using in sanitary ware industry.

Unfortunately, many or most of the matte surfaces out there are simply underfired glazes, they are not melted enough. A true matte has a specific chemistry that does not happen easily by random material blending because the vast majority of materials are silica-dominant and thus by nature produce glossy glazes. In addition, crystal mattes that are discovered by chance invariably craze on the body. A true matte is one that is both matte and still functional, that is, it is hard, fits the clay body, does not cutlery mark, is resistant to leaching, etc. A true matte will usually fire higher and often still be matte.

In this investigation, matte glaze has been produced using more than necessary amount of CaO in glossy glaze. A microcrystal mesh can form on the surface during cooling and it scatters light like little prisms. Low amount of CaO improves glossiness of glaze while higher amount leads to crystalinity of glaze [3]. Matteness in calcium included glaze is due to

formation of crystals such as anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$), wollastonite ($CaO{\cdot}SiO_2$) and gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) [4].

In this paper different coloured matte glazes were studied, moreover the microstructure of these glazes has been investigated by confocal microscope, XRD analysis has been also used for detecting crystal types.

2. Experimental

The chemical analysis of sanitary ware body which was used for this research is shown in Table 1.

Table 1. Chemical analysis of sanitary ware body.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2
57.67	32.33	1.11	0.64	0.36	0.11	0.98	1.06

First of all, raw materials of body were prepared in a ball mill with specific particle size and composition, afterward it is prepared in a high speed mixer to set its rheology properties, at the end, it is transferred into low speed mixer for final rheology settings and aging. The prepared slip with density of 1900 kg/m^3 and thixotropy of 35 after 1 minute was transferred into plaster moulds to form a sanitary ware, and then the wet ware is demoulded and stayed in casting unit for a day. Afterward it is moved into dryer to become dry and being ready for inspection and surface finishing unit. Dried ware is ready for glaze spraying.

To fit thermal expansion coefficient of glaze and body, an engobe was used with chemical analysis shown in Table 2.

Table 2. Chemical analysis of engobe.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	ZrO_2	BaO	ZnO
55.6	20.8	0.64	4.4	0.27	1.94	1	0.5	4	2.2	1

The engobe slip has been applied on dried sanitary ware surface with density of 1530 kg/m^3 and fluidity of 320 gallenkamp degree, for two times.

Matte glaze was sprayed on this surface; the chemical analysis of the calcium base matte glaze is shown in Table 3.

Table 3. Chemical analysis of matte glaze.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	ZrO_2
47.3	9.45	0.1	17.5	0.1	2.15	2.6	0.03	6.18

This chemical analysis is coming from raw materials such as calcium carbonate, feldspar, zirconia and kaolin. These materials were mixed together in a ball mill with specific composition. Particle size of the glaze after milling is 0.2-0.3 % coarser than 45 μm and 73 % finer than 10 μm. Afterward the rheology of glaze was fixed at density of 1770 kg/m^3 and fluidity of 175 degree of gallenkamp in high speed mixer with special additives, and then it is sprayed on engobed surface.

Glazed wares were fired in a long time cycle of a 106 m tunnel kiln at 1200°C for 14.25 h, firing curve has been shown in Fig. 1, this diagram is a common firing curve of sanitary ware and it is as the same as firing curve for glossy glazes.

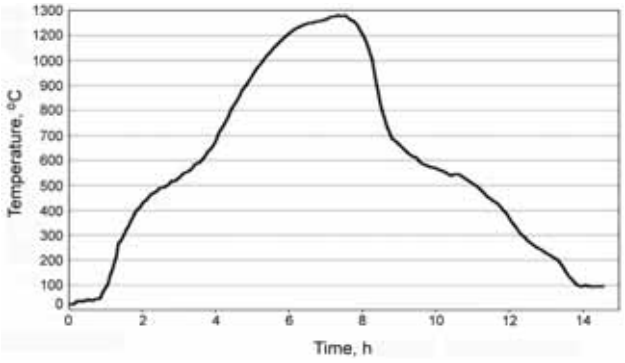


Fig. 1. Firing curve.

3. Results and discussion

Fig. 2 shows the matte glaze sanitary ware product, complex design and dimension of this product confirm the proper fitness of glaze and body.

Fig. 2. A sample of matte glaze on sanitary ware product.

Regarding to the definition of matte glaze, the glossiness of a matte surface is less than 30 g.u. by gloss meter of incident beam 60°. Glossiness numbers of matte glaze in different colours confirm the mattness of the glaze; on the other hand different colours show different glossiness number. Glossiness of samples has been measured by gloss meter (Picogloss 500 MC) by incidence beam 60°. Results have been indicated in Table 4.

Table 4. Glossiness of coloured matte glaze measured by gloss meter (Picogloss 500MC).

Colour	Black	Brown	Blue	Pink	Green	Yellow	White
Glossiness (60°) g.u.	18	15	17	3	14	7	11.5

Data given in Table 4 indicate that different pigments affect crystal formation in matte glaze.

For better analysis of body and glaze fitness of expansion coefficient, test of thermal and humidity shock has been carried out by autoclave. As it is anticipated the glaze has been matched with sanitary ware body completely. This test analyzes thermal shock and humidity resistance of the body according to ASTM C554 [6]. Samples were placed in autoclave under pressure of 5 bar for 1 h. If the thermal expan-

sion coefficient of body and glaze are matched properly, no hairline cracks have to be seen after 1 hour on the surface. Results confirm proper thermal expansion of body and glaze.

Samples have been tested for chemical resistivity according to ASTM C650 and Table 5. Results show that chemical resistance of this glaze is acceptable for using in sanitary ware.

Table 5. Chemical resistance test according to ASTM C650.

Chemical material	Concentration [%]	Duration [h]	Temperature [°C]
HCl	20	48	15-21
NaOH	5	0.5	60
H_2SO_4	3	16	100

Although crystal phase is more likely to corrode exposing to chemicals comparing to glass phase, this glaze is resistant to corrosion due to thin layer of glass on crystal surface, therefore crystals are not exposing to corroded environment directly. Results of chemical resistance test confirm this theory.

Surface hardness of product has been measured by Mohs indenter according to ASTMD1474. The hardness of different samples is between 6 and 6.5 which is a proper range of surface hardness for sanitary wares.

Crystal types were analyzed by XRD (Siemens D500). X- ray diffraction pattern of yellow matte glaze is seen in Fig. 3.

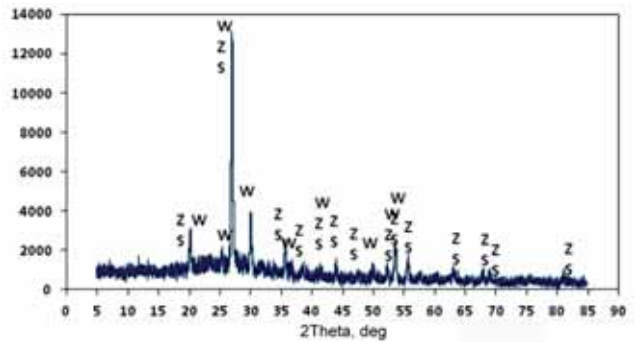


Fig. 3. X- ray diffraction pattern of yellow matte glaze: W – wollastonite, $\frac{Z}{S}$ – zirconium silicate.

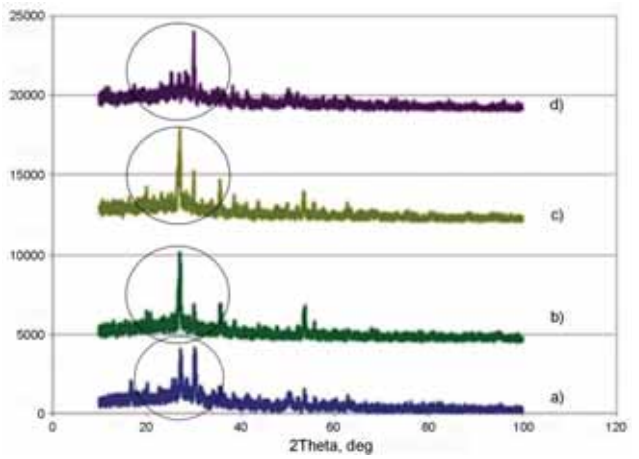
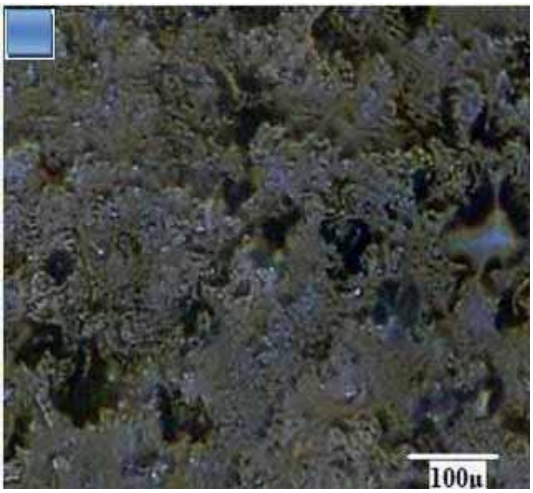


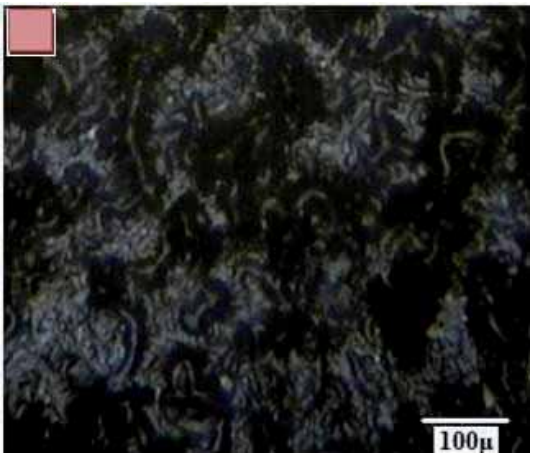
Fig. 4. XRD analysis of different coloured matte glazes: a) blue, b) green, c) brown, d) pink.

X-ray pattern shows the presence of wollastonite and zirconium silicate crystals. It is important to know that the ratio of these two crystals in X-ray pattern is not representing of these two phases in the glaze. XRD pattern in Fig. 4 is just showing existence of crystal phase due to low depth of penetration of X-ray.

XRD analysis of different coloured matte glazes has been depicted in Fig. 4, as it can be seen, different colours have different patterns, so pigments affect crystal type and its morphology, as it has been displayed in Fig. 5.



a)



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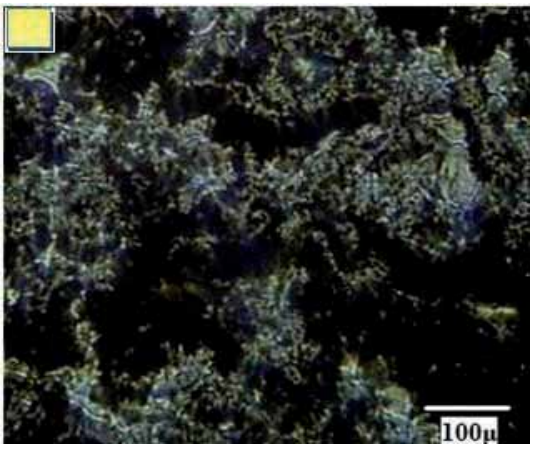

c)

Fig. 5. Microscopic images of different coloured matte glazes: a) blue, b) pink, c) yellow.

Microscopic images of 3 different colours have been shown in Fig. 5. Dendritic morphology of wollastonite phase is clearly observable, as it can be seen; pigments affect microstructure and crystal distribution of matte glaze. These observations confirm differentiation of glossiness of matte glaze in different colours.

4. Conclusions

In this paper, with respect to decorative use of matte glaze for interior design, a matte glaze matched with porcelain body of sanitary ware has been designed. Chemical resistivity of the glaze is acceptable for using in sanitary ware due to formation of thin layer of glass on outer surface of glaze. The mattness of glaze has been measured by gloss meter; different colour of matte glaze has shown different glossiness. This observation has been analyzed by XRD and confocal microscope. Results proved that pigments of coloured matte glaze affect crystal morphology and its distribution. Calcium base of this glaze leads to formation of wollastonite crystal in the layer of glaze. Zirconium silicate crystals also have been seen in X-ray diffraction pattern of the glaze.

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Received 18 April 2010; accepted 12 May 2010