Thermochimica Acta 588 (2014) 75–80

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

The role of firing process on bubble formation in a glaze layer of sanitary ware

Jiyuan Li[a,b], Jinsheng Liang[a,*], Fei Wang[a], Lijuan Wang[a]

[a] Institute of Power Source and Eco-materials Science, Hebei University of Technology, Tianjin 300130, PR China
[b] School of Materials Science and Engineering, Tianjin Chengjian University, Tianjin 300384, PR China

ARTICLE INFO

Article history:
Received 26 November 2013
Received in revised form 11 March 2014
Accepted 21 March 2014
Available online 29 March 2014

Keywords:
Glaze
Bubble
Cleanability
Start of melting temperature
Firing process

ABSTRACT

Glaze is composed of glassy phase, pores and a small amount of crystal phase. The glazed product is endowed high technological properties such as low water absorption, good cleanability, high bending strength and abrasion resistance, excellent chemical and soil resistance. Nevertheless, surface degradation might lead to opening of closed bubbles in glaze thus diminishing the cleanability. As a result, a study of bubble formation in glaze layer would favor the improvement of mechanical property and cleanability of final products. In this paper, glaze slurry was prepared by milling for 30 min, then applied to green bodies and dried for later use. The same glaze was fired in hot stage microscope to measure melting behavior. Two characteristic points were obtained: start of melting temperature of 1184 °C; half sphere temperature of 1220 °C. The firing curves applied to glaze can be designed according to the characteristic points, and then the dried samples were fired. The bubbles in fired glaze were observed by 3D depth of field microscope. Microhardness was performed using Vickers hardness tester. A solution was proposed to decrease bubbles and increase microhardness via changing firing process. The results showed the formation of bubbles in glaze was determined by firing process.

1. Introduction

Sanitary wares are materials made from two components: supporter which is usually ceramic material; and a layer of glaze which covers the raw body and plays both decorative and functional roles. The two roles are mutually combined and very important for commercial products. Further more, the two roles are completely determined by the surface properties of glazes [1–3]. Thus, improving the surface quality of glaze layer has a great influence on the performance of final ceramic products.

Usually, there are several ways to improve the surface quality of glaze layer, especially improving the easy cleaning ability, in ceramic technology [4–13]. Two methods are described here. One method is to coat photocatalytic TiO_2 film onto the glazed surface, followed by re-firing process at low temperature [4–10]. The formed coatings in the above method, exposed to UV light and rinsed with water, can endow the surface with easy-to-clean properties. However, the short lifetime of the TiO_2 coating resulting from its low wear abrasive and scratch resistance is a major disadvantage of this technology. The other method to decrease soil attachment is to create a double glaze layers onto product to ensure a smooth surface [11,12]. In this method, a second transparent layer is applied on the opaque glaze in order to keep the white, opaque appearance of the glaze with the enhanced cleanability of a smoother surface.

It is well known that glaze is composed of a dominant amorphous phase, closed bubbles and a small amount of crystalline phase. The existence of bubbles will decrease the mechanical property of glazed surface, due to weak wear abrasive and scratch resistance resulting from more bubbles. And the surface degradation usually leads to the change of bubbles from closing to opening, then forming micro-scale holes, which then reduces the cleanability of glazed surface [13–16]. So we have to find an effective way to decrease bubbles in glaze layer for easy-to-clean ceramic products with high quality.

In this paper, the role of firing process on the bubble formation of a glaze layer was intensively studied in order to find a good way to produce easy-to-clean ceramic products. Firstly, thermal behavior of raw glaze was performed by Seiko TG–DTA thermal analyzer. Secondly, firing schedule was designed based on the key temperature detected by hot stage microscope (HSM). Then, the influence of firing process parameters on the bubble formation and surface quality was further investigated.

---

* Corresponding author. Tel.: +86 022 26582575.
E-mail address: liang_jinsheng@sina.com (J. Liang).

http://dx.doi.org/10.1016/j.tca.2014.03.024

2. Materials and methods

Based on previous research [17], a typical raw material was chosen as the following (wt%): kaolin, 4.3; feldspar, 37.8; dolomite, 6.5; calcite, 10.8; talc, 2.2; quartz, 36.8 and zinc oxide, 1.6. And the chemical compositions of raw glaze were found to be (wt.%): SiO_2, 64.66; Al_2O_3, 9.02; CaO, 8.2; MgO, 2.13; K_2O, 4.6; Na_2O, 1.32; ZnO, 1.6; Fe_2O_3, 0.14; ignition loss, 8.31. In our experiment, a batch of raw material (200 g) was mixed with water (33 vol%) and carboxy methyl cellulose (0.3 wt.%) as additives in a planetary ball mill, and then were milled for 30 min using alumina balls as grinding media. The resultant slurry was sieved to 80 μm. The glaze particle size distribution was analyzed using a OMEC LS-C(I) laser diffractometer. A few slurries was dried in oven at 110 °C for 2 h to obtain glaze powder. Different thermal analysis was performed on raw glaze powder, using a Japanese Seiko DTA unit in air atmosphere. The tests were carried out at a heating rate of 10 °C/min in platinum crucibles with calcined alumina as reference.

Sequently, glaze powder was mixed with absolute alcohol, shaped in a cylindrical mold (φ 2 mm × 3 mm) by uniaxial dry pressing and heated in HSM from room temperature to 1400 °C at a heating rate of 10 °C/min. The CCD camera projects the cylinder-shaped sample image through a quartz window onto the computer. The image analysis system automatically records and analyses the sample geometry during heating. A professional HSM software is used to calculate the decrease percentage of the heated image height compared to the initial height.

Green bodies, with initial sizes of 65 mm × 65 mm × 7 mm, were prepared by slip casting process, then dried at 110 °C for 24 h in an oven. The glaze slurry was applied to green body in a dip-coating process and dried. Dried samples were fired in laboratory kiln at three different firing cycles (given in Fig. 1). The microstructure of glazed surface was measured by 3D depth of field microscope (VHX-600E, Olympus). Microhardness was performed on glazed surface by MHV-3000 Vickers hardness tester. For each case a mean of 10 measurements was taken.

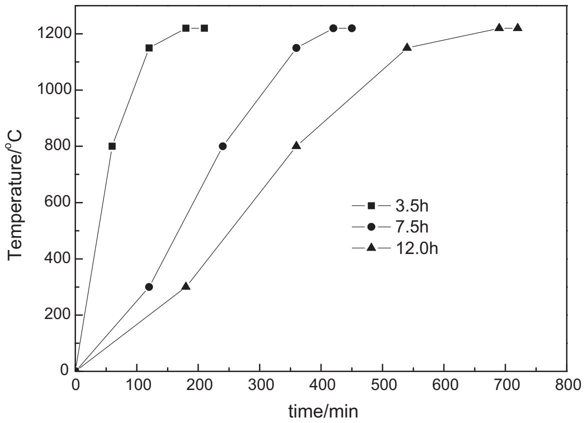

Fig. 1. Different firing cycles applied to the glazes: (a) 3.5 h, (b) 7.5 h, (c) 12.0 h. The top temperature was 1220 °C and hold for 30 min.

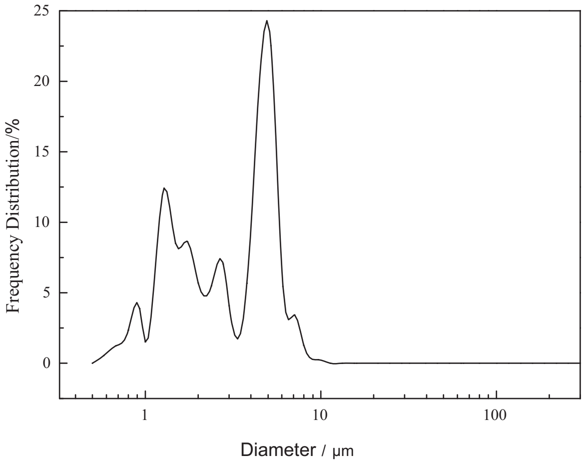

Fig. 2. The particle size distribution of glaze slurry.

3. Results and discussion

It is known that the particle size distribution of glaze has a significant impact on the glazed surface quality, due to its influence on the smoothness, gloss and cleanability of final products. Furthermore, the particle size distribution also has a great impact on the packing efficiency, which significantly changes the size and shape of pores, the shrinkage behavior of raw glaze and the microstructure of final products [18]. As is indicated in Fig. 2, it can

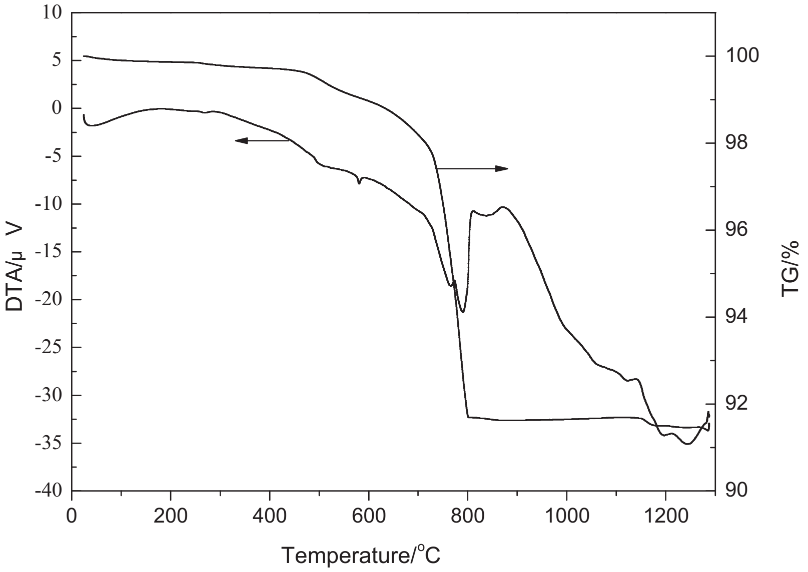

Fig. 3. Thermal analysis curves of raw glaze.