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Influence of surface crystallinity on the surface roughness of different ceramic glazes

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ABSTRACT

Surface smoothness is an important characteristic of ceramic glazes as it influences chemical resistivity, glossiness and stainability of glazes. Surface crystallinity of zirconia-based and titania-based glazes (as two common opaque glazes), calcium-zinc based matte glaze and also two transparent glazes with different compositions were studied in this work. Degree of surface crystallinity measured by stereological methods using scanning electron microscopy (SEM) images showed that transparent glaze has the minimum degree of crystallinity (2.1%) and the maximum amount (25.4%) was obtained for matte glaze. In addition, X-ray diffraction (XRD) was used to characterize the glaze mineralogy. Optical surface profiler showed that the smoothest surface belongs to titania-based opaque glaze ($R_a = 0.0157$ μm) and transparent glaze ($R_a = 0.0168$ μm). In contrast, the roughest glaze surface corresponded to the matte glaze ($R_a = 0.2772$ μm). The results suggest that surface roughness is influenced by crystallinity of surface, but degree of surface crystallinity is not the only parameter that can influence the surface roughness. The most important factor is the morphology of the crystals grow and their protrusion from the surface.

1. Introduction

Surface cleanability is an important concern in production of traditional ceramics (such as tile, sanitary ware and tableware). Although smoothness of glaze layer improves cleanability, there are still some issues (such as soil adhesion and stain susceptibility) which need to be considered [1–3]. Adhesion of soil on glazed surfaces and their cleanability depends on chemical composition, phase composition, and roughness of the surface [2]. Thus, surface quality improvement of glaze layer has a great influence on the performance of final ceramic products [1]. Several attempts have been done in order to improve the cleanability of ceramic products and, in general, they are categorized into two different groups: (1) Methods focusing on applying additional coating such as sol-gel functional coatings or the application of a transparent glossy layer [2–6]. These methods are not very interesting for producers due to the additional costs which second layer may impose. So far, they have been mainly used as coatings on windows [7,8] where they don't experience a great deal of chemical or mechanical attack [9]. (2) Another method is to reduce the causes of hard cleanability by modification process which is of particular interest in the related industries [10–12]. Partyka and Lis examined the effect of zircon grain size on the glaze roughness, glossiness and whiteness. Their results showed that decrease of zircon grain size can considerably improve the glaze whiteness and glossiness; however the roughness increased due to the protrusion of zircon crystals on the glaze surface [11]. L. Hupa et al. studied chemical durability, soiling and cleaning properties of fast-fired raw glazes with the focus on the phase composition and topography of glaze surface. Results showed that average surface roughness, R_a, increases with increasing crystal content and decreasing gloss value, moreover, soiling and cleaning degree of traditional glaze surface consisting of different crystalline phases embedded in a glassy phase depends rather on surface micro- and macro-roughness than on chemical composition of the phases in the surface [1,2]. However, chemical durability is closely related to the crystalline phases in the surface. Wollastonite and pseudowollastonite in the surface lead to surface pitting in alkaline detergent solutions typically used for cleaning of every-day life surfaces [1].

Generally, glaze is composed of a dominant amorphous phase, closed bubbles and a small amount of crystalline phase [13,14]. There are such a wide variety of glaze compositions due to wide range of firing temperatures (ranging between 800 °C to 1400 °C [16]) and the need for a variety of surface features (bright or dull, opaque or transparent, glossy or matte, thick or thin) [17]. These terms are differenced by their optical behavior: glossy glazes are very smooth, smooth on the scale of the wavelength of visible light (390 nm–750 nm), thus any bumps, pits, or undulations on the glaze surface are smaller than

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Table 1
Chemical compositions of commercial glaze samples (%wt) analyzed by ICP-MS. *.

No.	Glaze type	Na_2O	K_2O	ZnO	MgO	CaO	ZrO_2	Al_2O_3	TiO_2	B_2O_3	SiO_2	Fe_2O_3	BaO
1	Opaque-Zirconia based	1.04	4.82	7.36	0.45	8.99	14.41	14.00	0.06	5.15	46.25	0.27	0.00
2	Matte- Calcium & Zinc based	1.49	2.68	12.56	0.98	22.27	5.58	2.77	0.06	4.22	44.09	0.13	0.00
3	Opaque-Titania based	0.70	4.62	5.50	0.98	8.09	0.89	13.14	16.99	3.25	45.65	0.12	0.00
4	Transparent	1.36	4.09	6.04	0.65	16.95	0.082	16.56	0.04	6.34	43.29	0.18	1.70
5	Transparent	2.01	3.56	3.02	0.48	13.29	0.096	10.00	0.10	4.83	60.93	0.20	3.74

*Whole Rock Analysis, Acme Analytical Labs, Vancouver, B.C. Canada.

approximately 390 nm, and then if the light's wavelength is larger than the bump, we won't be able to see the bump. Conversely, the protruding crystals in matte glazes are larger than this and therefore scatter the light. It scatters the light because it doesn't have the super-smooth surface of a gloss glaze [18]. The formation condition of crystalline phase is critical in determining how to control the quantity of crystalline phase, which consequently controls the surface quality of the glaze (gloss, matte or satin surfaces) [19,20]. Normally, glazes without any crystals on the surface possess a better surface smoothness, so they have better cleaning tendency [21]. In this case Stull diagram specify a safe area where formation of any crystals is prevented in glaze layer by controlling the ratio of SiO_2:Al_2O_3. However, his work focused on glazes fired at cone 11 [22].

Glossy glazes naturally have better surface smoothness compared to matte glazes due to the lack of crystallinity on the surface, but this research shows that amount of crystals on the surface is not the only factor contributing to surface roughness. Due to X-ray penetration depth, analysis of the surface crystallinity is difficult. To augment the XRD results, image analysis was performed on SEM images using commercial software (Image J, 1.44p). Since glaze surface roughness is the main variable controlling the cleanability, this research is an attempt to analyze the effect of crystallinity and morphology on surface roughness to improve cleaning tendency of glazes without incurring additional manufacturing costs associated with incorporating a second glaze layer.

2. Experimental

Commercial frits were used to produce five glazes: zirconia-based and titania-based opaque glazes, matte glaze and two transparent glazes as shown in Table 1. Chemical analysis of glazes (frit + kaolin) was measured by ICP-MS technique at Acme Analytical laboratory. Samples were prepared via fusion using lithium borate glass. A batch of 100 g from each frit was mixed with 5.66 g kaolin and 40 cm^3 water in a fast milling device using alumina balls for 12 min. After measuring and setting the rheology of glaze slips, they were all applied on the same wall tile body. Samples were fired in fast firing roller kiln at 1040 °C for 40 min according to the firing curve shown in Fig. 1.

Surface of the samples was studied by scanning electron microcopy (SEM) using a TESCAN VEGA2. Due to non-conductivity of the samples, 10 nm Au—Pd layer coating was deposited using a sputter coater prior to SEM-EDX analysis. All images were analyzed by ImageJ 1.44p Software. Phase analysis of the crystals formed on the glass matrix was carried out with X-ray diffraction (XRD) using an X'Pert PRO MPD device with Cu K_α ($\lambda = 0.154$ nm) at 30 KV and 10 mA, using a continuous scan mode over a range of $2\theta = 5–70°$.

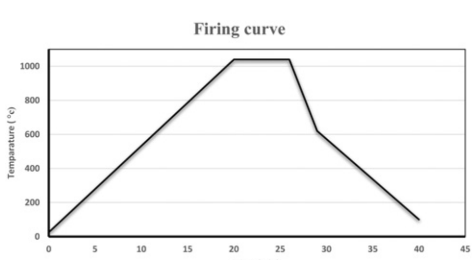

Fig. 1. Temperature profile for heat treatment cycles.

The glaze surface roughness was measured by optical interferometry (NewView 5032, Zygo Corporation, Middlefield, CT). To this end, the optical interferometer analyzed the interference pattern of reflected white light from the surface of a sample by focusing on the fringes (the interference pattern from the reflected light) and allowing the head of the instrument to scan in the z-direction to collect the data. For this study, the interferometer was set up using the 5× Michelson objective and a 1.0× zoom. The surface roughness data was collected using the extended scan option which allows a scan length of 75 to 5308 μm. To develop statistically significant results, stitching application was used to analyze a larger area, randomly selected, on the glaze surface. The software associated with the optical interferometer (MetroPro™, Zygo Corporation, Middlefield, CT) allowed for a stitching application which means several images were collected in sequence and then were stitched together to analyze a larger area. Surface roughness measurement was done on the different areas of each sample, in a way that for each sample at least three R_a and RMS results were measured. Data were analyzed by one-way ANOVA method with 95% confidence interval to check the reliability of collected data and to see if it is possible to differ samples in terms of roughness. Results showed that samples have different mean values of R_a and RMS, but almost the same trend of R_a and RMS is clearly deduced by the comparison of mean values.

3. Results and discussion

Chemical compositions of the glazes are presented in Table 1. As can be seen, chemical compositions of Sample 1 and Sample 3 are almost the same and they are just different in terms of opacifiers i.e. ZrO_2 and TiO_2. Besides, since the amount of opacifiers in Sample 4 and Sample 5 are trivial, both of them are deemed transparent. Fig. 2 shows the result of SEM and image analysis together for different glazed samples. SEM study of the glazed samples was performed in back scattered mode. Since surface crystals of glazes have a high color contrast compared to matrix glass phase in SEM images (due to the high molecular weight differences), therefore it was possible to use ImageJ Software for counting the number of crystals, measuring area of crystals in a specified field (SEM image field) or degree of crystallinity and average size of the crystals [23]. Images were analyzed with ImageJ 1.44 Software. This software uses pixels instead of grid of lines that may be superimposed on the microstructure. It is necessary to calibrate the dimensions of the pixels with a scale of images, so that the accurate size of the field being examined can be measured, and consequently precise area scanned will be known in μm^2.

One of the basic stereological counting measurements is point count (P_p). The point count is the ratio of the number of points in the feature of interest to the total number of points in the grid [24,25]. Most image analyzing softwares such as ImageJ use P_p (point fraction) to measure A_A (area fraction). In another word, by increasing the number of grid points (pixels in computer) the term of A_A can be assumed to be identical to P_P