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Research Article

Influence of kaolin to temperature characteristics of ceramic glaze

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ABSTRACT

Inorganic additives are often added to adjust the rheological properties of the ceramic glaze suspensions. However, additives will change the chemical compositions of the ceramic glazes and thus their temperature characteristics, including melting temperatures. The most common glaze suspensions are a mixture of frits and kaolin. The kaolin is used as an anti-thixotropy agent to regulate the rheology of the glaze suspensions. However, the kaolin contains aluminum oxide (Al_2O_3) and silica oxides (SiO_2), which will change the properties of the ceramic glazes, especially their melting temperature. Studying the influence of kaolin on the melting temperature range of ceramic glazes is always a task that ceramic factories often have to perform. In the methods of studying glaze melting temperature, using heating microscopy (HM) to study the continuous change of glaze with firing temperature by analyzing image data gives quick information quickly and brings high economic efficiency. In this study, based on data analysis obtained from HM, the authors proposed an empirical equation to determine the melting point of glaze depending on the chemical composition of added kaolin with a different concentration in the range of 6 - 12% (6, 8, 10, 12% by mass composition). An empirical estimation is also given that each percent (%) by weight of kaolin will increase the melting temperature of ceramic glaze by 2°C. The research results are a premise for the application of HM to investigate thermal properties such as flocculation temperature, softening temperature, spherical temperature, hemisphere temperature, and melting temperature of glaze and bone ceramic.

Key words: glaze, kaolin, frit, heating microscope, melting temperature, empirical formula, Seger's formula

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INTRODUCTION

Heating microscopy (HM) is a thermal analysis technique that combines the best properties of thermal analysis and optical microscopy [1,2].

By analyzing the visual observations directly from the HM (height H, width D of the test speciments, contact angle α between the specimens and the base), it is possible to monitor the change of the specimens with the heating temperature to 1500^{o}C

The HM method was used to investigate critical phenomena related to the heating of frits and ceramic glazes [1,3].

Today, this instrument is used in both industry and research in the traditional and advanced ceramic industries. It is a convenient tool for studying the melting temperatures of ceramic glazes [4–6].

Using HM has shown a good effect in the research results on changing ceramic glazes in rapid firing. Some of the studies can be mentioned such as investigated of BaO content based on the SiO_2 – Al_2O_3 – CaO – MgO – ZnO– (BaO) at 1220°C [4], investigated on glaze containing ZnO and CoO, CuO and Fe_2O_3 affecting crystal formation on the surface [7], the influence of oxides on the thermal expansion coefficient of ceramic glazes [8], thermal properties of the mixture of raw materials and frit samples [9], the crystallization temperature range of frits [10], the melting temperature of the mold powder increases when silica and alumina are added to the original composition [11], etc. In the above studies, the conclusions are based on the visible results; the relation of chemical composition to the coefficient of glaze thermal expansion is only found in the study of Z.B. Öztürk [8].

Kaolin is a fine-grained material with the main mineral component kaolinite ($Al_2O_3.2SiO_2.2H_2O$), commonly used as a stabilizer for glaze suspensions in ceramic technology. The kaolin is mixed with a frit finely ground to make the glaze suspension. When heated to high temperatures (400 - 600^{o}C), the kaolin will decompose [3,12], and the decomposition equation is as follows:

$Al_2O_3.2SiO_2.2H_2O = Al_2O_3.2SiO_2 + 2H_2O$ (1)

Thus, the content of SiO_2 and Al_2O_3 in the original glaze increases and influences the melting temperature of the glaze.

Determining the effect of kaolin on the melting temperatures of ceramic glazes is essential in ceramic factories.

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In this study, the temperature characteristics of glazes were determined using an HM instrument. Assuming that the characteristic temperatures of the glaze (determined by the HM instrument) depend on its chemical composition, it is possible to establish an equation describing the relationship between the characteristic temperatures and its chemical composition.

Each kaolin component mixed with frit will get a corresponding equation. According to the added kaolin components, temperature-composition equations can be established. Solving this system of equations will obtain an equation describing the relationship between the melting temperature and the chemical composition in the range of the investigated composition. Thanks to this equation, it is possible to calculate the characteristic temperatures by chemical composition without repeating the experiments on the HM instrument. The equation coefficients also indicate the influence of oxides on the characteristic temperatures of the ceramic glaze.

EXPERIMENTAL METHODS

The glaze sample

Glaze samples were prepared by mixing frit and kaolin in proportions of 6 – 12% wt. kaolin, 88 - 84% wt. frit, and adding 5% wt. water by dry weight. Additives such as 0.5% wt. CMC (Carboxyl Methyl Cellulose) and 0.5% wt. STPP (Sodium Tripolyphosphate) were added to each mixed sample. These mixtures were ground in a ball mill to obtain the suspensions with 0.5% wt. residue of 45 μm sieves.

The kaolin and frit chemical compositions were analyzed using XRF (ARL ADVANT'X – Hãng Thermo).

The rheology of glaze suspensions (from a mixture of frit, kaolin, additives, and water) was determined using a Ford cup. The glaze suspension is poured into a Ford cup with a volume of 100ml. Underneath, there is a small hole 4mm in diameter for the glaze suspension to flow out. The viscosity of the glaze suspension was determined by noting the time to empty the cup[6,8].

The glaze suspensions were dried to a powder with a moisture content of 7 – 8% wt. The samples were prepared from these powders. The samples were pressed into a cylindrical block with a height of H_0 = 3mm and a diameter of D_0 = 3mm (Figure 1) using a specialized tool according to DIN 51730 (1998-4). The cylindrical glaze sample allows simultaneous investigation of the size variation of the glaze by height and radius.

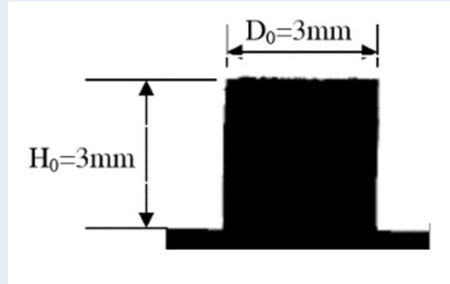

Figure 1: Cylindrical sample

Study of the glaze characteristic temperatures be the HM

The Leica HM instrument (Hess Instrument) investigated the shape changes during heated glaze samples under the same conditions: air atmosphere. The heating rate was 60^{o}C/min to 500^{o}C. Over 500^{o}C, the heating rate was 10^{o}C/min until the experiment stopped. An image of the enamel specimen is taken when the contact angle changes by 12% wt., the changes in surface area are 5% wt., or the change in form factor is 5% wt.

The characteristic temperature points are determined according to DIN 51730 (1998-4)/ISO 540 (1995-03-15).

- Sintering point (T_{sinter}): the temperature corresponding to 5% wt. contractions of the initial sample height.
- Softening point (T_S): the temperature for which round edges were visible (H = 3/4 H_o).
- Ball point (TB): the temperature for which the probe appeared like a sphere (H =D).
- Half ballpoint (T_{HB}): the temperature for which the height is half of the base (H = 1/2D).
- Melting point (T_M): the temperature for which the sample is melted down to 1/3 of its initial height (H = 1/3H_0).

The equations describing the temperature composition relationship

The temperature characteristics had been determined from the HM instrument. The relationship equations between the characteristic temperatures and the glaze composition were established for each different kaolin ratio.

Consider the melting temperature (TM) as a function of the variables xi that are the component oxides. Make and solve a system of first-order equations according to experimental data to determine the general equation of the dependence of the melting temperature on the composition of oxides.

THE RESULTS AND DISCUSSIONS

Calculation of the glaze suspension systems according to Seger's formula

The composition of the glaze suspension is shown in Table 1. The chemical composition of the glaze suspension is shown in Table 2. Table 3 is the composition of the glaze suspension converted to mole compositions.

The chemical compositions of the glazes in tables 2 and 3 were calculated, excluding LOI (losses on ignition). Chemical composition is converted to mole fraction and write the glaze formula according to Seger's formula [7,9]. The glaze formula written according to Seger is presented in Table 4.

In the composition range of 6–12% of kaolin added to frit, if only considering the influence of SiO_2 and Al_2O_3 oxides from sample F-6 to F-12, the increase in SiO_2 content is 0.1%, while the increase in Al_2O_3 is 0.1%. 0.77%.

The melting temperatures

Table 5 is the results of thermal microscopy analysis of the samples.

The effect of kaolin content on softening temperature is complex and uneven. The softening, sphere, semisphere, and melting temperatures are increased as the kaolin content increases. Therefore, only after the chemical dehydration of kaolin (above 600^oC), the SiO_2 and Al_2O_3 oxides show a clear influence on the temperature properties of the glazes.

The temperatures of the sphere and hemisphere increased gradually in the range of 3-5^oC. The melting temperature of the F-8 is only 1^oC higher than F-6, but F-10 vs. F-8 is 18^oC, F-12 vs. F-10 is 4^oC.

The temperature range changes from semisphere - melting, the sample height is decreased to the minimum. The process corresponds to a sudden decrease in the viscosity of the liquid phase. The glaze is completely transformed to the liquid phase, capable of spreading evenly on the surface of the material to be glazed. This temperature is the temperature needed to determine the actual glaze melting temperature.

With the glaze system studied, when increasing kaolin from 6% to 12%, the difference in melting temperature is 845 - 822 = 23 (^oC). Thus, when the kaolin content increases by 1%, the melting temperature of glaze increases by about 2^oC.

We can calculate the melting temperature (T_m) of these glazes according to empirical equation:

$T_m = 2.53.10^3 n_S - 6.37.10^3 n_A - 3.97.10^3 n_B$ (2)

Where: n_S, n_A, n_B – The ratio of the mole fractions of the SiO_2, Al_2O_3 and B_2O_3 oxides respectively when compared to the total number of moles of the oxides $RO + R_2O = 1$; T_m: melting temperature (^oC); n_S - molar fraction of SiO_2 (mol.%); n_A - molar fraction of Al_2O_3 (mol.%); n_B - molar fraction of B_2O_3 (mol.%); ($2.53.10^3$), ($-6.37.10^3$) and ($-3.97.10^3$) are the influence coefficients of SiO_2, Al_2O_3, and B_2O_3 and are calculated from Tables 4 and 5.

Wood liquefaction samples at different soaking times were determined functional groups by FT-IR method. FT-IR spectrums of samples were presented in Figure 2. FT-IR spectrum showed that the samples all had functional groups such as: CH_n (2929, 2850 cm^{-1}), C=O (1700cm^{-1}), C=C (1598 cm^{-1}), C-C (1513 cm^{-1}), CH_2 (1452 cm^{-1}), CH (1371 cm^{-1}), OH (1257 cm^{-1}), C-H (1092, 815, 754 cm^{-1}) (Table 4) [2,3].

CONCLUSIONS

The effects of kaolin on the temperature characteristics of the glazes are as follows:

- After the kaolin decomposes, the composition of SiO_2 and Al_2O_3 oxides in the glaze increases, which will increase the softening temperature, the temperature of the sphere, the hemisphere, and the melting temperature of the glaze samples.

- With the glaze composition studied, when the kaolin content increased by 1%, the melting temperature of the yeast increased by about 2^oC. With the empirical formula, we can consider the influence of each oxide on the melting temperature of the glaze. This formula can be used to calculate the melting point of the same glaze without retesting.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

AUTHOR'S CONTRIBUTION

The authors confirm contribution to the paper as follows: study conception and design: Do Quang Minh, Kieu Do Trung Kien; data collection: Nguyen Vu Uyen Nhi; analysis and interpretation of results: Huynh Ngoc Minh; draft manuscript preparation: Kieu Do Trung Kien. All authors reviewed the results and approved the final version of the manuscript.

Table 1: Compostion of the glaze suspnesions

Raw materials	The glaze suspension systems (% wt.)			
	F-6	F-8	F10	F-12
Frit	94	92	90	88
Kaolin	6	8	10	12
CMC	0.5	0.5	0.5	0.5
STPP	0.5	0.5	0.5	0.5
H_2O	33	33	33	33

Table 2: Chemical composition of the glazes suspensions

Oxides	The glaze suspension systems (% wt.)			
	F-6	F-8	F10	F-12
SiO_2	47.53	47.63	47.72	47.81
TiO_2	0.03	0.03	0.04	0.05
Al_2O_3	2.5	3.27	4.04	4.82
B_2O_3	26.47	26	25.52	25.04
Na_2O	7.13	7.01	6.88	6.76
K_2O	0.02	0.03	0.04	0.05
BaO	7.13	7.00	6.87	6.74
ZnO	6.11	6.00	5.89	5.78
CaO	0.01	0.01	0.02	0.02
MgO	0.02	0.03	0.03	0.04
Li_2O	3.05	3.00	2.94	2.89

Table 3: Chemical composition of the glazes suspensions (number of moles)

Oxides	The glaze suspension systems (number of moles)			
	F-6	F-8	F10	F-12
SiO_2	0.79	0.79	0.79	0.80
Al_2O_3	0.03	0.03	0.04	0.05
B_2O_3	0.38	0.37	0.37	0.36
Na_2O	0.12	0.11	0.11	0.11
BaO	0.05	0.05	0.05	0.05
ZnO	0.08	0.08	0.07	0.07
Li_2O	0.10	0.10	0.10	0.10

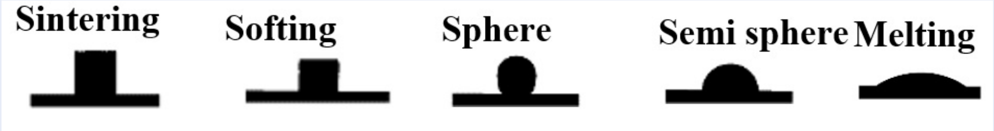

Figure 2: Temperature characteristics (table 5)

Table 4: The glaze formula according to seger

F6		
0.34 Na_2O 0.28 Li_2O 0.14 BaO 0.24 ZnO 1	0.09 Al_2O_3 1.09 B_2O_3	2.26 SiO_2
F8		
0.32 Na_2O 0.29 Li_2O 0.15 BaO 0.24 ZnO 1	0.09 Al_2O_3 1.09 B_2O_3	2.32 SiO_2
F10		
0.33 Na_2O 0.30 Li_2O 0.15 BaO 0.22 ZnO 1	0.12 Al_2O_3 1.12 B_2O_3	2.39 SiO_2
F12		
0.33 Na_2O 0.30 Li_2O 0.15 BaO 0.22 ZnO 1	0.15 Al_2O_3 1.09 B_2O_3	2.42 SiO_2

Table 5: The results of thermal microscopy analysis

Glazes	Temperature characteristics (^oC)				
	Sintering	Softing	Sphere	Semi sphere	Melting
F-6	540	629	670	756	822
F-8	530	645	676	761	823
F-10	522	645	678	764	841
F-12	530	650	681	770	845

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