

Evaluation of the steger method in the determination of ceramic-glaze joining

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Abstract

The lack of compatibility between the glaze surface and the ceramic substrate is one of the major causes of defects in ceramic processing. When no compatibility in the thermal expansion behavior exists between these two parts of a ceramic tile, defects like chipping, curvature and cracks can occur. Some methods have been developed to study these events, particularly the stresses between glaze and substrate, like the superposition of dilatometric curves, the glazed ring method and the Steger method. In this work the Steger method was compared to the dilatometric method in order to determine the factors that cause a perfect coupling (fit) between the glaze surface and ceramic substrate.

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1. Introduction

The classical evaluation of glaze-substrate coupling is based on the difference between the thermal expansion of the glaze in comparison with the substrate [1–5]. Their respective dilatometric curves are analyzed simultaneously in order to infer the stress state to which the glaze is submitted. The stress state can determine the origin of certain defects typical in the ceramics industry, like cracks, chips and curvatures. This classical approach results in some errors, because measuring the dilatometric curves of the glaze and substrate occurs separately in a dilatometer [6]. The interactions between the glaze and the substrate at the interface are not taken into account. A more precise evaluation requires the use of an instrument that is capable of measuring the stress at the interface caused by glaze-substrate interaction. The GST device (glaze stress tester) uses the Ste-

ger method to determine the residual stresses between glaze and substrate. In the Steger method, the specimen is already glazed and errors derived from the exclusion of the interface in the analyses are avoided, a typical problem in the dilatometric tests.

When two regions show different expansion rates, coefficient stresses arise in order to balance the differential expansions or contractions. In ceramic materials this behavior is important in the cooling stage. The equilibrium state presents two situations, because the glaze is firmly adhered to the ceramic substrate; the substrate contracts more than the glaze, causing glaze compression, or the glaze contracts more than the substrate, causing glaze tension. If the expansion were the same for glaze and substrate the incurred stress would be null [7–9].

A glazed surface under compression turns the specimen convex; under tension, the glazed surface turns the specimen concave. In a nonstress state the specimen remains plane. Although the coupling state between a glaze and its ceramic substrate can be estimated by the comparison of their thermal expansion coefficients, the behavior is not so simple. During firing the glaze selectively reacts with the substrate, forming an interface between both that can considerably affect the stresses acting on them as a whole. The composition of the

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glaze changes due to reactions with the substrate in function of the volatilization of certain elements (B, K, etc.) [10,11].

At the same time, the substrate texture, due to changes in its porosity, and mineralogical composition, such as quartz dissolution and phase formation, are modified. These transformations change the mechanical and thermal properties of the substrate and, consequently, the existing stresses. In fast firing processes the thermal expansion of the glaze during the cooling stage is considerably different from the coefficient measured in a quasi-static dilatometer. The phases formed during fast cooling are different from slow cooling, moreover, the glaze and substrate temperatures are not equal during industrial cooling due to differences in thickness and thermal gradients. Finally, in a fast firing process the cooling rate is very different in comparison with a dilatometric test [7].

The Steger method is based on the measurement of the curvature variation in the central part of a previously fired glazed tile. Curvature is related to the stress state of the specimen. The specimen is a piece of the ceramic substrate (30 cm length) with a glazed surface (15 cm length), where glaze thickness must be controlled because it determines the stress state of the system. The specimen is submitted to a temperature program, wherein it is heated to 900 °C at a 5 °C/min heating rate and cooled to ambient temperature, and the curvature is measured by the displacement of a sensor perpendicular to one end of the specimen [12].

The coupling temperature corresponds to the nonstress state. At this point the glaze presents such a low viscosity that any change in the substrate dimension promotes a stress relief. A base line is determined, above which the load is compressive and below which the load is tractive. This point is denominated the effective coupling of the glaze, corresponding to the same coupling temperature used in the dilatometric method [10].

Regarding glaze and body characteristics, the first studies attributed crazing and shivering primarily to differences in the thermal expansion of the glaze and body [13,14]. Also, glaze-body reactions influence the glaze fit. Since early observations, many papers have been published suggesting methods of controlling glaze-body fit by changes in the batch composition. Stull and Howat in 1914 [13] presented a classic study of the control of properties of porcelain glazes by the adjustment of the alumina and silica content on a molecular basis.

Many investigators have proposed expansion factors for the various ceramic oxides for calculating the coefficient of thermal expansion of glazes [14]. But the method of calculating thermal expansion from the factors cannot be relied on to give absolute values [15]. The calculated values are not applicable throughout the cooling range in which glazes are rigid and therefore must be used with considerable discretion. Increases in the molecular equivalents of alumina or decreases in the molecular equivalents of silica increases the thermal expansion. However, the changes in the silica content have a more pronounced effect than the changes in alumina. There was a net decrease in expansion when silica and alumina were increased together in constant ratio because of the relatively large changes in the silica content [13].

The proper glaze fit increases the strength of the glazed object and improves its resistance to thermal shock. The capacity of a glaze to withstand stresses set up by unequal expansion or

contraction of the glaze and body depends on its tensile strength, elasticity, thickness, and adherence to the body [14,15].

Finally, Kingery [16] stated that some factors could affect the thermal stress resistance of ceramic materials as glaze thickness and shape, where the temperature drop for a given heat flow is directly proportional to glaze thickness and increased thermal stresses occur; heat flow properties, that are different if steady-state or transient conditions are considered, where a small glaze layer presents poor thermal stress resistance; coefficient of thermal expansion, where for any given temperature distribution, the thermal stresses are directly related to the thermal expansion; elastic properties, where as the temperature increases, there is a decrease in E due to grain-boundary relaxation, and at still higher temperatures, plastic or viscous flow takes place; strength, where on cooling, the most dangerous thermal stresses are tensile, on heating, either shear or tensile stresses may be most dangerous; finally interface properties, where no one material property or condition can be taken as a uniform criterion. In general, composition changes which give rise to high strengths also increase E.

2. Materials and methods

Samples of a transparent glaze were prepared according the ASTM C 372/94 standard for dilatometric tests. The samples were fired in a single firing process used for ceramic tiles. For the Steger tests, the samples were prepared using ceramic substrates glazed and fired in the same single firing process used for the dilatometric test samples. The samples were cut in 30 cm × 3 cm rectangles with a central glazed area (15 cm) 3 mm in thickness. The linear expansion coefficient of the substrate was $73 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$; the expansion coefficient of the transparent glaze was $67 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ with a melting point of 770 °C. Ten specimens were prepared for the dilatometric test and for the Steger method. The substrate used in this experiment was a typical grés product for single firing process. The glaze used was an industrial boron glaze, also for single firing process and the glaze thickness was constant for all samples. Glaze, body, glazing, firing and thickness glaze were all maintained constant.

The Steger method consists to heat the glazed specimen to 900 °C and cool it to room temperature at 5 °C/min heating/cooling rate. The measured curvature during heating or cooling is associated to the stress state between the substrate and the glaze. The Steger specimen is adjusted to the equipment – a controlled electrical furnace – with one edge clamped and the other free to bend. The curvature is measured by an LVDT (linear variable differential transformer) sensor and the signal is sent to a computer that calculates de stress state of the specimen.

3. Results and discussion

Table 1 shows the results for the dilatometric method. The standard deviation for the expansion coefficient was $0.4 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ and 1.1 °C for the glass transition. The variations were probably caused by sample preparation, however, the confidence limit for both standard deviations was 95%, suitable for the purposes of this study. Regarding the melting point, the standard deviation was 6.3 °C, a higher value. Since the

Table 1
Dilatometric tests for the transparent glaze

Sample	α ($\times 10^{-7} \text{ }^\circ\text{C}^{-1}$)	Glass transition ($^\circ\text{C}$)	Melting point ($^\circ\text{C}$)
1	56.1	613.2	719.3
2	55.5	616.0	721.3
3	56.1	614.4	726.2
4	56.6	614.7	706.3
5	55.9	615.4	716.8
6	55.6	614.3	715.3
7	56.6	617.2	705.8
8	56.0	615.0	716.8
9	55.9	615.1	717.8
10	55.8	614.1	712.3
S.D.	0.37	1.1	6.3

software used to determine the melting point uses the minimum derivative function to calculate T_m , signal noises present a strong influence on the mathematical treatment of the curves and consequent increases in the associated error. The derivative function amplifies the signal and minimum variations in the temperature curve are identified as the melting point of the curve.

It is possible to minimize this effect on the melting point temperature using the onset temperature of the curve, that is, the intersection of prior and posterior tangents to the melting point. This function is used to determine the glass transition temperature (Fig. 1).

Regarding the Steger method, Fig. 1 shows the coupling temperatures of a transparent glaze applied over a single firing substrate; 10 specimens measured under the same conditions. The differences among measurements are clear, most probably due to variations in glaze thickness during sample preparation. When the glaze thickness is altered, the stress state also demonstrates change. Moreover, as the chosen glaze thickness was very thin, in order to simulate industrial conditions, the test resolution was diminished. The temperature where the nonstress state occurred could not be determined.

When the glaze thickness is increased, the resolution of the test also increases. Consequently, the dispersion of the results diminishes (Fig. 2). The thicker glaze layer can be explained by the higher resolution and reduced dispersion can be explained by

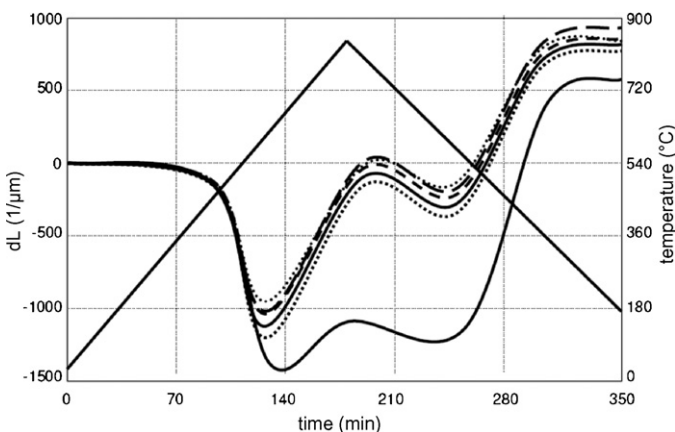


Fig. 1. Measurement of the displacements (stresses) for a transparent glaze applied over a single firing tile.

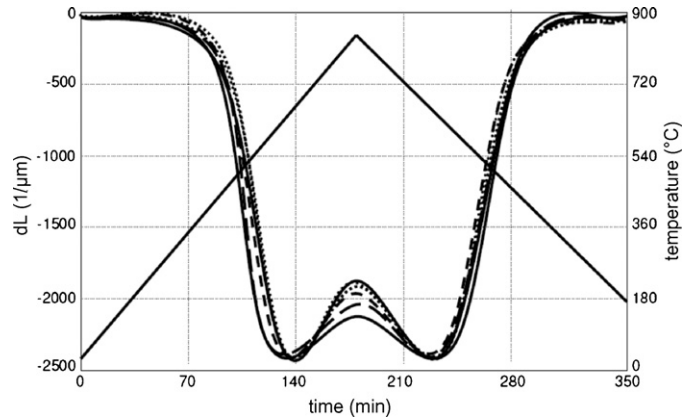


Fig. 2. Stress curves for a thicker layer of transparent glaze applied over a single firing tile.

improved sample preparation; a more constant glaze thickness. The glaze studied was under compression at ambient temperature, a desirable condition for ceramic tiles in order to avoid cracks.

An important aspect is that no hysteresis occurred in the test (Fig. 2). Both the heating and cooling curves are similar. Hysteresis depends on the heating and cooling rates, glaze formulations and interface reactions. As the heating and cooling rates were very slow ($5 \text{ }^\circ\text{C}/\text{min}$), glaze crystallization occurred in the cooling stage, modifying the glaze characteristics and the stress state. Thus, the glaze formulation is very important, since the degree of crystallization obtained is a function of glaze composition and cooling rate.

Interface reactions can change the characteristics of the glaze-substrate system, promoting some hysteresis. In this study the nonstress temperature was approximately $829 \text{ }^\circ\text{C}$, where the glaze viscosity was so low that no influence on substrate contraction or expansion over the glaze occurred. The coupling temperature using the dilatometric method was approximately $762 \text{ }^\circ\text{C}$ (data not shown).

A number of factors may be involved in the development of stress in a glaze layer; chief among these factors is the ratio of volume changes in the body to volume changes in the glaze. If a body and its attached glaze layer have a common area of contact at high temperatures, then any tendency during cooling of either to depart from the size of their common results in stress formation, and if carried far enough, rupture occurs in one or the other member. Other factors, such as strain temperature of the glaze, rate of cooling, especially through the annealing range of the glaze, and glaze thickness and its strength and elasticity have modifying influences on glaze fit. Diffusion, vaporization, and glaze adherence may also be important [17].

The introduction of surface compression is a well-established technique for strengthening of glasses and ceramics [18]. The presence of layers of surface compression inhibits failure from surface flaws. Surface compression is also likely to enhance the thermal shock and contact damage resistance of these materials, like the incorporation of an outer layer having a lower coefficient of thermal expansion as in glazing. The thickness of glaze application has considerable influence on glaze fit. Schurecht [19]

found that in thermal-shock crazing tests, a mat glaze 460 μm thick crazed after three quenchings, and the same glaze at 89 μm thickness first crazed after 25 quenchings.

4. Conclusions

The difference between the coupling temperatures measured by the Steger (829 °C) and the dilatometric methods (762 °C) showed significant differences between the test methods. The dilatometric method analyzes the expansion of glaze and substrate coefficients separately, with no analysis of the interface effects. The Steger method (GST) takes into account the interface effects. The coupling temperature is higher when compared with the dilatometric method, probably due to chemical–physical interactions between the glaze and substrate at the interface. When the tests are run separately with the glaze and substrate, these interactions are not considered.

Finally, regarding the precision of the methodologies, the GST test presents reduced dispersion of the results. Sample preparation is fundamental in the GST test method: to improve the accuracy it is necessary a thicker glaze layer than usually used in the industrial glazed tiles. Also, due the slow heating some reactions can occur between the substrate and the glaze, mainly crystallizations, causing difficulties in the cooling analysis.

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