Viscosity and thermal evolution of density and wetting angle of a commercial glaze by means of hot stage microscopy

F. M. Stábile[a,*], M. Piccico[a], M.F. Serra[a], M. Rafti[b,c], G. Súarez[a,c], N.M. Rendtorff [a,c]

[a] Centro de Tecnología de Recursos Minerales y Cerámica CETMIC (CICPBA-CONICET La Plata), Cno. Centenario y 506, Gonnet, Argentina.
[b] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas INIFTA (UNLP-CONICET La Plata), 64 y Diag 73, La Plata, Argentina.
[c] Departamento de Química, Facultad de Ciencias Exactas, UNLP, 47 y 115, La Plata, Argentina.

Abstract

In the present work we attempt to describe the results of the thermal behavior analysis of a commercial glaze obtained in a thermal microscope developed by the research group. At the same time, the density and the wetting angle of the glaze with an alumina surface was evaluated. Particularly the sintering temperature, the sphere, semi-sphere and fusion temperatures were also determined. These present characteristic viscosities. Afterward, by means of the de Vogel-Fulcher-Tammann equation, the viscosity as a function of temperature was estimated.

In the first part the developed equipment is described together with the image analysis carried out for the in-situ cylindrical samples (2,5 mm of height and diameter). The thermal cycle was up to 1200ºC with a heating rate of 5ºC/min. The developed equipment presents the following characteristics: some problems with the temperature evaluation, it was slightly affected by air currents and difficulties for achieving an adequate parallelism. On the other hand, the potentialities of the equipment for development and study of the thermal behavior of glasses was established.

* Corresponding author. Tel.: +54-221-484-0167 Int. 107; fax: +54-221-471-0075.
E-mail address: mstabile@cetmic.unlp.edu.ar

1. Introduction

A glass is a molten inorganic product that has cooled down to a rigid state without experiencing crystallization (Shelby (2005)). Considering only their main technical properties, common glass can be described as an amorphous inorganic product, consisting predominantly of silica (a typical soda-lime glass is formed by approximately 70 wt. % of SiO_2, the rest is mostly Na_2O and CaO), hard, brittle, transparent, high chemical resistant and deformable at high temperature.

Traditional porous ceramics are often seal off through the application of a glass cover that is usually applied in powder form (for immersion or vaporization of aqueous dispersions) and is then melted in a second heat treatment (Matthes (1990)). If the vitreous coat fits properly to the ceramic body it is known as glazed ceramic. In addition, this cover is usually of high chemical and mechanical resistance. This cover is often modified by the addition of colorants (oxides or inorganic pigments), other modifiers or opacifiers.

Ceramic glazes are manufactured from glass frits obtained by casting melts of homogeneous inorganic mixes of mainly siliceous composition accompanied by alumina and alkaline and alkaline-earth oxides (Matthes (1990)).

The thermal behaviour of the glazed ceramic is of technological importance. Thermal expansion coefficient is of particular interest, whose detaching forms crackle defects; so as wettability, whose detaching generates nodulization defects. Knowledge of the complete viscosity curves allows knowing temperatures of technological interest, such as workability temperature, to which glass can be shaped by the action of an external force; the practical melting temperature, allowing the rise of gases generated by reaction in the production of glass in economically viable times, among other temperatures of practical interest (Shelby (2005)). The high temperatures viscosity of glaze is also important because its detaching produces the coating to drip and uneven coating thickness. Another important property is the glass transition temperature, which is generally defined as the point that separates the behaviour of the glass between a solid and an undercooled liquid. The knowledge of this temperature is useful in practice, since that annealing of glass is done near glass transition. Annealing is a process of essential importance that prevents cracks that occur as a result of internal stresses generated during cooling of glass.

The viscosity of a glass has an exponential dependence with temperature. Some glasses have Arrhenius type behaviour, associated with an activated mechanism for viscous flow. But in the majority of the cases, the activation energy of viscous flow is not constant and varies with temperature. For this reason, the most commonly used model to describe this dependence is the Vogel-Fulcher-Tamman model (VFT) (Fulcher (1925)), which adjusts very well the experimental data, although care must be taken to calculate viscosity near glass transition temperature by using this model, since the viscosity is overestimated in the vicinity of this point.

High temperatures measurements of viscosity (η) of glass involve high complexity and expensive equipment, such as high temperature rotational viscometers, with platinum rotors and crucibles (Shelby (2005)). Another employed method is the fiber elongation (Shelby (2005)), in which viscosity measurement is based on the deformation speed of a glass fiber by applying a constant traction force, compared with a standard glass fibber of known viscosity. There is however a cheaper alternative which is based on determining the temperatures at which a small piece of glass made up from compact glass powder is deformed and acquires certain geometries, which have fixed viscosities. This method also allows obtaining information with an efficient use of time, since only one experiment needs to be carried out.

Scholze (1962) was the first to define characteristics geometries that adopts a pill of compact glass powder when subjected to a heating cycle. In this way, characteristics points were defined, such as first shrinkage, maximum shrinkage, deformation, sphere and flow; and in turn assigned fixed values of viscosity. Pascual et al. (2001) established a method for calculating the viscosities of the mentioned characteristic geometries and compared them with values obtained by a high-temperature viscometer. In a later work, more precise viscosity values of the same geometries were obtained, and, in addition, the sphere point viscosity was determined which had not been taken into account before (Pascual et al. (2005)).

In the present work, we were able to establish the temperatures of the defined geometries of fixed viscosities calculated in the mentioned work of Pascual et. al. (2005); in addition to other relevant measures, by means of a hot stage microscope (HSM) developed in CETMIC, using MatLab® for image processing. The viscosity-temperature points were adjusted to the VFT model to obtain the complete curve of viscosity as a function of temperature.

The fact that the test is done on a continuous form is an improvement, which allows not only to identify the corresponding temperatures to the fixed viscosity points, but also allows to construct continuous curves, through which thermal behaviour of glass of different compositions could be studied.

1.1. Objective

The main objective is to explore the capabilities of a hot stage microscope (HSM) developed by CETMIC, in particular we intend to obtain the thermal behaviour of a commercial alkaline glazing widely used in the local ceramics industry. The evaluation of sintering curve, thermal evolution, the dimensions of the test piece, the shape factor and wetting angle will be assessed continuously. Finally, viscosity of the glaze as a function of temperature was estimated in the range of technological interest (900 - 1400°C) by applying the VFT model previously described.

2. Experimental procedure

The studied material is a commercial transparent alkaline glazing (Q92, CRECER POLES S.A., Argentina) recommended for limestone slab in double firing between 1020 and 1040°C. It has a maximum particle size of 74 μm (#200).

Fusibility test was carried out on a hot stage microscope developed by CETMIC (HSM). Figure 1 shows schemes of the developed equipment, which consists of simultaneous attachment of a tube furnace with a silicon carbide heating element and a temperature controller with a digital VGA camera (640 x 480 resolution), registering the evolution of the temperature of the sample taken with a platinum thermocouple on the surface of the sample. The thermocouple is independent of the oven programmer. The computer registers temperature and images simultaneously, so both can be correlated. Image analysis allows obtaining characteristic temperatures of the sample that have defined viscosities (fixed).

The kiln cycle consisted of a 5°C/min heating rate. The dimensions of the cylindrical sample of compacted commercial glazing powder were 1.5 mm in diameter and 2.5 mm in height. The images were taken every 10 seconds. The sample holder was made of sintered alumina.

2.1. Images analyses

The experimental information produced, consisting of captured images at the same time that a linear temperature ramp was applied, allows recording morphology changes of the sample.
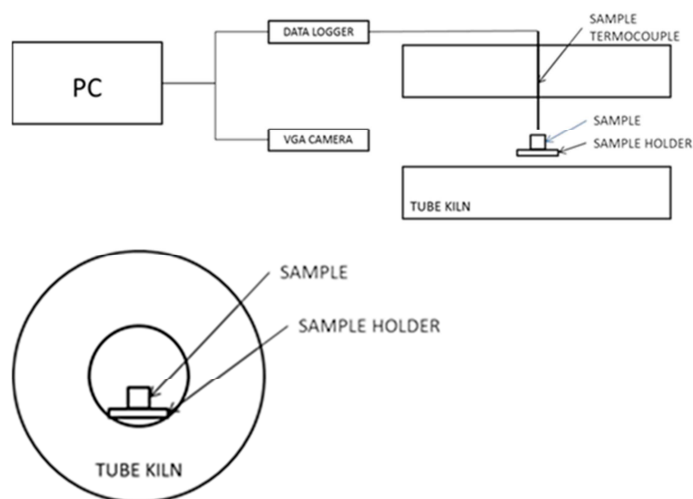

Fig. 1. Schemes of the hot stage microscope (HSM) developed by CETMIC. Parallel cutting and cross sectional area of the kiln tube.

In particular, the evolution of the contact angle and transverse area with temperature, that will then be used to determine the viscosity through Vogel-Fulcher-Tammann model (VFT). The software was developed for this purpose using commercial MatLab ® platform, where both image processing and numerical calculations can be made conveniently. The procedure consists of the following steps: 1) .mov format video files are converted to an images sequence of with consecutive names (in our case was free software VirtualDub, available at (http://virtualdub.com). 2) cross-sectional area of the specimen and the spatial coordinates of three points of interest for each image are determined: a) the highest point, b) a point further away from the center of the sample where the material contacts the support c) a point located on the surface of the sample slightly above the previously mentioned point (see Fig. 2). Using the points a, b, and c the contact angle and the area of a semicircle of equal radius to the height are calculated, necessary to determine the so-called shape factor (ratio between the area of the image and the calculated assuming a circular).
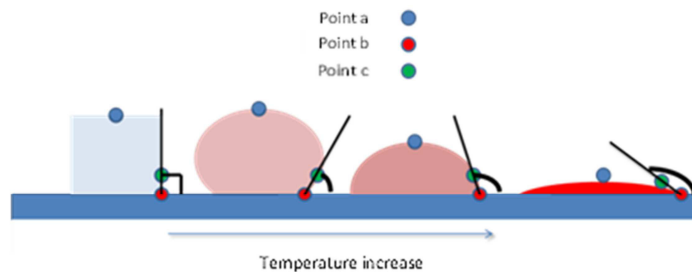

Fig. 2. Scheme corresponding to the image analysis conducted for the calculation of contact angle.

2.2. Definition of characteristics points and geometries of the sample

The points can be defined on the basis of the calculated values of the size and shape of the sample as a function of temperature, and the characteristic geometries where the viscosities have a constant value (see Table 1).

First shrinkage and end of shrinkage: Both are extracted from the curve of relative density as a function of temperature. The relative density is calculated as the ratio between height and square area (h/A^2). First and end of shrinkage corresponds to the temperatures of 10 and 90 per cent of densification, respectively.

Deformation: It is defined as the temperature at which the shape factor changes 1.5 % with respect to the first image.

Sphere: Several criteria must take into account to determine the point corresponding to this geometry. Firstly, the relationship between height and width must have been at least one time between 0.9 and 1, but should not be less than 0.85. In addition, the shape factor should be at least 0.8.

Hemisphere: The temperature at which the height-width ratio is equal to 0.5.

Flow: At this point, the height of the sample is equal to 1/3 the hemisphere height.

According to VFT model, viscosity (η) takes values as a function of temperature according to the following relation:

$$\log \eta = A + \frac{B}{(T - To)} \tag{1}$$

where *A*, *B* and T_0 are the fitting parameters and *T* is the temperature measured in K.

3. Results

Table 1 shows the images corresponding to the fixed viscosities points, through which VFT equation could be adjusted. Figure 3 shows the logarithm of viscosity as a function of temperature. In this figure, the points corresponding to the hot stage microscope (HSM) and the least squares fit with the VFT model function (Equation 1) are shown. Flow point was not reached because of the working temperature range. These points allow adjusting the parameters A, B and T_0 by using the method of least squares (Equation 1). Temperature values are shown in Table 1. Viscosities obtained are comparable with literature (Matthes (1990)) which shows the potential of the technique and equipment developed by the work team.

Table 1 Experimental images of the fixed viscosities points extracted from Pascual et. al. (2005).

Characteristics points	Nº	HSM images	η (Poise)
First shrinkage	1		$10^{9,1}$
End of shrinkage	2		$10^{7,8}$
Deformation	3		$10^{6,3}$
Sphere	4		$10^{5,4}$
Hemishere	5		$10^{4,1}$
Flow	6	>1200ºC It was not reached	$10^{3,4}$

3.1. Continuous commercial glaze thermal behaviour

In the second part of the work, continuous curves of the commercial glaze properties as a function of the temperature are shown. Curves were built according to the methodology described above. In some cases, it was necessary to perform a smoothing (Fast Fourier Transform (FFT) with a cut-off frequency of 0.03). Sources of noise come mainly from the oscillation of the heating system of the oven, which had a frequency of a few seconds in the circulating current in the heating element, and from the camera resolution. These curves have an interesting potentiality to compare the performance of two similar materials.
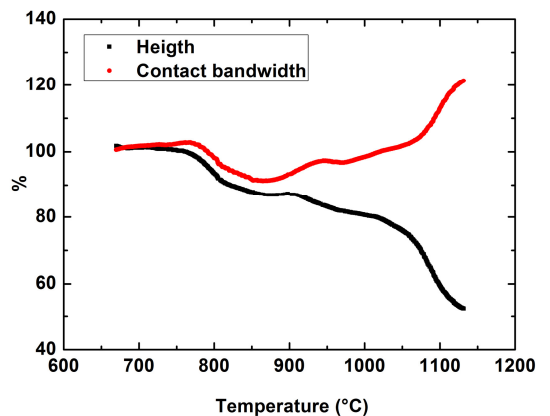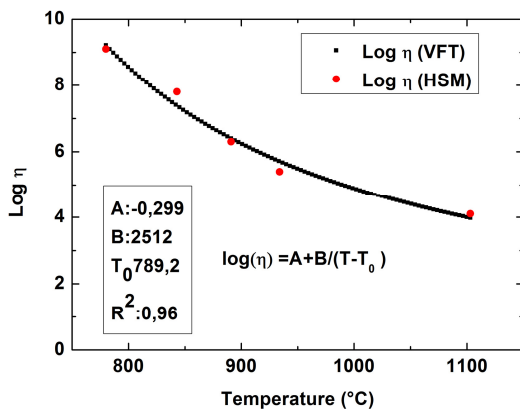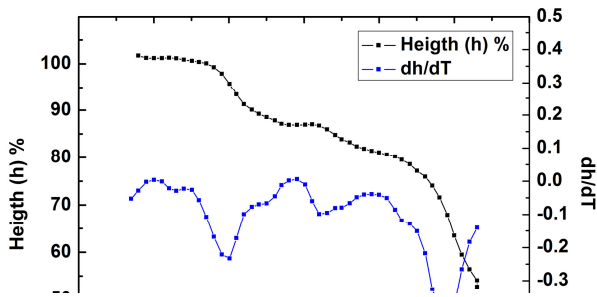
Fig. 3. Log (η) curve as a function of temperature. Experimental (HSM), calculated (VFT) and the values of the adjustment.
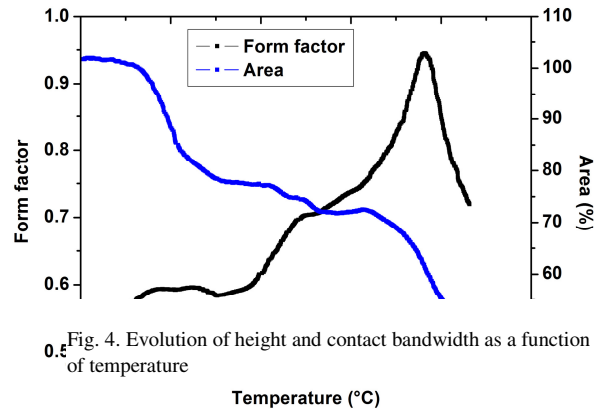

Fig. 4. Evolution of height and contact bandwidth as a function of temperature

Fig. 5. Evolution of height and its derivative as a function of temperature.

Fig. 6. Evolution of area and shape factor as a function of temperature.

The present work shows the behaviour of a commercial glazing. In particular, Fig. 4 shows the evolution of the height (the maximum distance between the base and the upper border of the sample image (dot "a" in Fig. 2)). Jointly, we graph the contact bandwidth of the sample as a function of temperature.

It is clear that the curves evolve softly with temperature and present some inflection points and changes of curvature that correspond to fusion of the compact subjected to heat treatment. These distinctive features could be used to compare the behaviour of two materials. By way of example, Fig. 5 shows the evolution of the height along with the derivative (easily calculable); which allows identifying the inflections temperatures.

Figure 6 shows the evolution of the area and the shape factor of the image with temperature. Two temperature ranges can be seen where changes are well marked, and an intermediate zone with a minimum change with respect to area measurement. The first change between 750 and 850°C coincides with sintering process, where the pill densifies. It can also be seen that this process is carried out without major changes in the initial form of the sample, fact which is confirmed by an almost unchanged shape factor in this temperature range.

Then, up to about 1000°C, area changes are not important. At the same time, there are notable changes in the shape factor. In this zone, the sintered pellet begins to deform, progressively losing its original cylindrical shape, taking an increasingly rounded silhouette up to achieve the morphology of a drop, coincident with the sphere temperature. The cohesive forces are sufficient as not to alter too much the dimensions of the pill. In the zone of higher temperatures (1000 - 1150°C), area values suffer a major fall.

The shape factor is rising up to a maximum and then decreases. This is because the formed drop has a decreasing viscosity as a result of the temperature increase, and therefore has greater fluidity, which makes that the drop spread more and more on the substrate ceramic. That is to say, the drop is changing its form from a truncated sphere, to the hemispherical form (where the value shape factor reaches its maximum value); and finally, becoming a silhouette of spherical cap increasingly squashed with temperature.

The graph of Fig. 7 was obtained by calculating values inversely proportional to the volume of the pill as a function of temperature, taking into account the range where the initial form is not altered (without major shape factor changes). In this way is possible to determine the first shrinkage and end of shrinkage, which are identified in the figure.

Figure 8 shows the evolution of the contact angle calculated by means of the points shown in schematic form in Fig. 2. Behaviour is gradual and well defined. In a first stage it remains around the 80°, then it increases almost linearly while the shape of the test piece tends towards the spherical drop, corresponding to higher liquid-liquid affinity interactions. The behaviour then presents a maximum peak (corresponding to the form of quasi-sphere or truncated sphere).
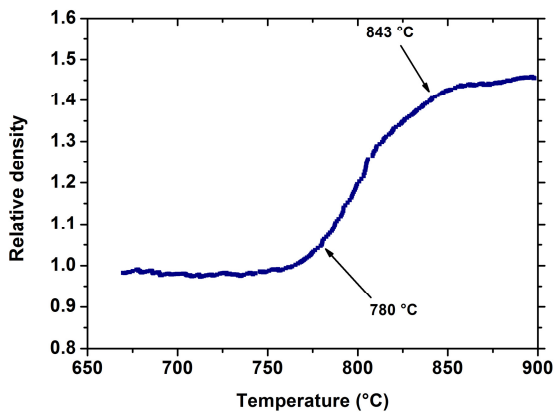
Fig. 7. Thermal evolution of the relative density of the glass powder compact before deformation.
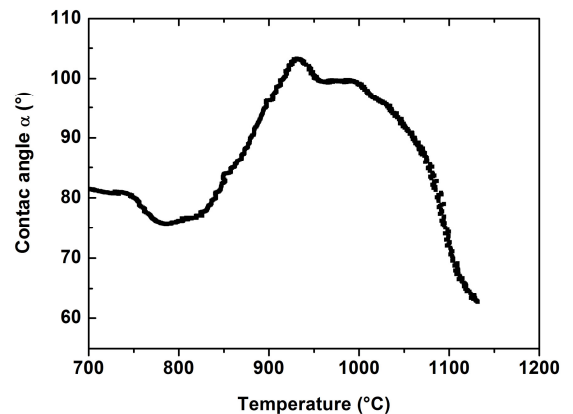
Fig. 8. Evolution of contact angle as a function of temperature.

From this temperature the contact angle also decreases gradually, i.e. the liquid "wets" increasingly the substrate (sintered alumina), then the angle returns to the perpendicular value (90°), decreasing gradually in a supposedly asymptotic way up to the total wet, where liquid - solid interactions are more akin to the fluid-fluid ones (angle 0°). However the single trial was carried out up to 1200° C, where the angle reaches the value 60°.

4. Conclusion

The present work shows a broad characterization of the thermal behaviour of a commercial glaze with a hot stage microscope developed by the working group, into the temperature range of technological interest.

Taking into account the definitions of characteristic geometry points adopted by the compact glass powder pill with temperature, using the graphics obtained by digital image processing, the temperatures corresponding to the above geometries could be obtained. Fixed viscosity points were used to make a regression using the VFT model, resulting in a rather good fit of the experimental values ($R^2 = 0.96$).

The source that induced a greater error in the measurements was due to the resolution of the camera, since the lower the amount of pixels that forms the image being measured, the higher the dimension changes evidences, which causes that the curve of pill dimensions values have a notorious oscillating behaviour (noise). In addition, the power control of the kiln made that at low temperatures heating was not compensated, so that the control came in resonance (oscillatory behaviour of power) and caused a periodic change of dimension by the effect of the changing radiation. The fact that we were able to estimate the viscosity of a glass at a temperature range of technological importance by means of a single experiment is very much appreciated, enabling to evaluate this behaviour as a function of the most diverse variables of processing, in particular chemical composition. In addition, it is possible also to carry out dynamic behaviour studies of the interactions between a substrate and any melt that are particularly important in the evaluation of refractory materials performance for fusion furnaces.

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