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Determination of the activation energy for densification of porcelain stoneware

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Experimental porcelain stoneware has been formed by slip casting and sintered by rate controlled dilatometry. Shrinkage has been measured at various constant heating rates up to 1300 °C by dilatometry. A kinetic field for stoneware firing has been set up by connecting points of equal density on the sintering rate curves to determine the activation energy for densification and to calculate optimum firing cycles. The activation energy for densification has been calculated from the slope of the isodensity curves. It has been observed that the activation energy increases with progressive sintering i.e. 470-497 kJ/mol for the intermediate sintering stage (1100-1225 °C) accounting for most of the densification. The abrupt shrinkage and low activation energy values during the intermediate sintering stage suggest a viscous flow mechanism of densification. The final sintering stage responsible for a reduced densification rate showed a lower 313 kJ/mol activation energy.

Key words: Activation energy, Densification process, Dilatometric behavior, Constant heating rates.

Introduction

Porcelain is a highly vitrified ceramic material produced from a body formulated by mixtures of clay, quartz and feldspar. The main phase composition of a porcelain body is constituted by a heterogeneous glassy matrix and needleshaped mullite crystals together with some quartz grains and closed irregular shaped pores. Mullite crystals, which are derived from the solid-state decomposition of the clay reacting with feldspar, are endowed with excellent mechanical, creep, thermal and chemical properties. Because of the complex interplay between raw materials, processing routes and the kinetics of the firing process, porcelains represent some of the most complicated ceramic systems [1-3]. Densification at higher temperatures is rate-controlled by the strong dependence of melt viscosity on temperature and by the solubility of solids in the liquid phase, mainly free quartz. On the other hand, it can be said that quartz dissolution is the slowest process during firing of such products, and it helps to maintain a higher melt viscosity, even with an increase in the temperature, which prevents pyroplastic deformation. A maximum firing temperature can be defined by the coarsening and solubility of gases filling the closed pores accompanied with a more or less pronounced expansion, called bloating [3, 4]. On the whole, the magnitude of physicochemical transformations can vary considerably, depending on the characteristics of the raw materials employed and the complex interplay between them. Zanelli et al. [4] concluded that the firing shrinkage is not proportional to the amount of liquid phase, but rather depends essentially on the viscosity of the liquid phase, which exhibits limited changes in composition with time, seems to be mainly affected by temperature. Calculations for the activation energy by Dannert et al. [5], show values of about 870 kJ/mol which are considerably higher than those corresponding to the viscous flow as the rate controlling mechanism of densification (200-500 kJ/mol). They assumed that the speed of solution or diffusion in the liquid phase determines the shrinkage rate. The maximum densification temperature and soaking time should be emphasized as other important parameters useful; to optimize firing cycles and this information can be derived from kinetic fields. Thermogravimetry and differential thermal analysis can be used to study the kinetics of the phase transformation using constant heating rate experiments. Such methods allow a measure of the length change of a sample subjected to a controlled temperature. Dilatometry can advantageously be used to study the kinetics of densification at several temperatures leading to determination of the activation energy by using nonisothermal and isothermal experiments. In general, the equation for the densification rate can be separated into temperature and density as follows [6, 7]:

$$\rho' = \frac{d\rho}{dt} = A \frac{e^{-Q'RT}}{T} f(\rho) \tag{1}$$

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where $\rho' = dp/dt$ is the instantaneous rate of densification, *R* is the gas constant, *T* is the absolute specimen temperature, *Q* is the activation energy, f(r) is a function of density and *A* is a material parameter that is insensitive to ρ . The complication in the determination of *Q* lies in the fact that densification rate ρ' changes not only with temperature, unambiguous estimates of *Q* are possible only if ρ remain constant [7]. Densification rates may be written as:

$$\rho' = \frac{d\rho}{dt} = \frac{d\rho}{dT}T'$$
(2)

where T', is the heating rate, and is held constant during the experiment. Substituting Eq. (2) into Eq. (1), and taking logarithms we obtain:

$$ln\left(TT'\frac{d\rho}{dt}\right) = -\frac{Q}{RT} + ln[f(\rho)] + lnA$$
(3)

A plot $\left(TT\frac{d\rho}{dt}\right)$ vs l/T would give a value for Q provided that data points are taken at a constant value of ρ .

In the present investigation special attention has been paid to the shrinkage behavior during the intermediate stage of sintering, where most densification occurs [4]. The shrinkage behavior and the kinetics of densification using constant heating rate experiments, should help to establish the appropriate firing cycle for industrial compositions.

Materials and Methods

Triaxial industrial compositions of porcelain stoneware were prepared out of clay, feldspar and alpha quartz (50 : 40 : 10 wt%) and made into a slurry by mixing in a porcelain jar. The chemical composition of the green body was : 66.62 wt% SiO₂, 24.76 wt% Al₂O₃, 0.63 wt% Fe₂O₃, 1.03 wt% TiO₂, 0.29 wt% CaO, 0.12 wt% MgO, 3.18 wt% Na₂O and 3.26 wt% K₂O. Rectangular 120 × 25 × 10 smm samples were cast into paster molds and dried at 100 °C. The dried samples were subsequently fired in an electric muffle furnace with a heating rate of 10 K·minute⁻¹ and 0, 0.5, 1 and 2 hours soaking time.

Phase characterization was defined by thermal analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM). 10 mg samples were run in DTA measurements by a DSC instrument (Model Q600 simultaneous DSC/ DTA/TGA, New Castle, DE, TA Instruments). The heating rate was 10 K minute⁻¹ to 1300 °C, with a nitrogen gas flow of 100 cm³minute⁻¹. X-ray diffraction analysis used a Siemens D5000 with Cu Ká radiation 1.54 at 20 kV. Microscopy samples were previously polished to a mirror surface by standard techniques and etched in 5% HF solution in order to dissolve the glass and reveal the phases. SEM examination was done using a scanning electron microscope, (Jeol JSM-6400, 15 kV acceleration voltage). Energy dispositive X ray spectroscopy (EDX) (Bruker AXS Inc. XFlash 4010) microanalysis was performed simultaneously with microstructural observations in order to distinguish the various phases. The bulk density and apparent porosity was measured by the Archimedes method according to ASTM designation C 373-88. The elastic modulus of the ceramic bodies was determined by a grindosonic method according to the ASTM designation C 1259 -98, test method for dynamic Young's Module.

The shrinkage behavior was mainly assessed by in-situ measurements in a Theta dilatometer Model 3230, the heating rates used were 12.5, 15 and 17.5 K minute⁻¹, from 25 to 1300 °C. The time-dependent density was calculated from the following expression:

$$\rho = \left(\frac{L_f}{L_{(f)}}\right)^3 \rho f \tag{4}$$

where L_f is the final length of the specimen, $L_{(t)}$ is the time-dependent-length, and ρ_f is the final density as measured by the Archimedes method.

Results and Discussion

Activation energy for densification

XRD patterns of specimens at 25 °C and 100 °C in Fig. 1(a), basically show the mineralogical composition of the raw materials i.e. showed quartz (Q), Anorthoclase (A) and kaolinite (K) as common crystalline phases. Kaolinite becomes progressively less crystalline by dehydroxylation to give rise to metakaolinite at around



Fig. 1. XRD patterns of porcelain stoneware at increasing vitrification temperature.

500 °C, according to the endothermic peak at 494 °C in the DTA measurements. A spinel-type phase change appears at 990 °C and most vitrification takes place within the 1100-1225 °C range, coincident with the intermediate stage of densification. Glass forms at 1100 °C from heating sanidine previously transformed from anorthoclase. Fig. 1(b) shows melting of sanidine in the range 1150-1200 °C as well as the appearance of mullite at 1150-1300 °C. Quartz starts to dissolve at 1150 °C reaching the (101) peak minimum at 1300 °C corresponding to maximum quartz dissolution.

Fig. 2 shows linear shrinkage versus temperature of ceramic bodies, at different heating rates (12.5, 15 and 17.5 K minute⁻¹). The curves show a similar shape and are generally shifted to higher temperatures with an increase in the heating rate. A three stage sintering process including initial, intermediate and final steps are seen on the curves, as reported in the literature [4]. A negligible shrinkage is observed during the initial sintering step, up to 1100 °C. In this temperature interval, $\alpha \rightarrow \beta$ quartz transforms at 580 °C and metakaolinite (amorphous phase) converts into spinel-type and mullite structures around 980 °C [8, 9]. Fig. 3 shows SEM images of an etched polished section of ceramic bodies sintered at 1250 °C and 1300 °C. Fig. 3(i) shows acicular mullite, quartz, granular (primary) mullite, which is seen to form in the clay particles subsequently becoming seeds for acicular mullite growth as discussed also by Schneider and Komarneni [10]. In the intermediate stage of sintering, most densification starts by the K₂O-Al₂O₃-SiO₂ eutectic formation (1100 °C), and judging by the shrinkage extent of the dilatometric curve densification develops into a fully vitrified body up to 1225 °C. Glass first forms at 1100 °C from heating sanidine previously transformed from anorthoclase in accordance with XRD analysis. At high temperature, silicon and aluminum ions from the quartz and clay mineral precursors



Fig. 2. Dilatometry data for experimental stoneware sample sintered up to $1300 \,^{\circ}$ C at constant heating rates (12.5, 15 and 17.5 K minute⁻¹). Note most of the shrinkage takes place at the intermediate sintering stage coincident with vitrification which gives rise to an endothermic peak on the DTA curve at about 1200 $^{\circ}$ C.



Fig. 3. SEM images showing microstructure of a triaxial ceramic body. i) HF etched sample at 1250 °C disclosing porcelain phases: secondary mullite (SM) and quartz (Q). ii) Large rounded pores are visible at a higher temperature (1300 °C) for the onset of bloating (B).

are dissolved into the glassy phase, thereby increasing its viscosity and thus, the densification rate will decrease. The final sintering stage starts at about 1225 °C, in which the liquid phase becomes progressively less viscous and is able to eliminate large pores. Fig. 3(ii) shows large rounded pores within the microstructure due to the onset of bloating in specimens fired up to 1300 °C.

Fig. 4 shows instantaneous densification for three heating rates, it can be seen that at the slowest heating rate, the maximum densification occurs at 1224 °C. The curves also show incipient densification at 1050 °C during the initial sintering stage. An Arrhenius plot was used to estimate the activation energy for densification. Isodensity lines were constructed by connecting points of equal density on the sintering rate curves at different heating rates. From the slope of the isodensity lines the activation energy for densification has been calculated, within the 253-497 kJ/mol range. As densification develops the activation energy changes significantly, as seen on Fig. 5 increasing from 253 kJ/mol to a maximum of 497 kJ/mol, for the intermediate sintering stage and decreases back to 313 kJ/mol for de-densification. By reference to Fig. 6 the phases that appear at the lowest level of activation energy correspond to an increasing concentration of mullite within the glassy phase, and dissolving feldspars. By contrast, at the higher level of the activation energy, we find that quartz has considerably dissolved into the glass. At 1250 °C quartz keeps dissolving and the intensity of mullite decreases, implying that silicon and aluminum dissolves into the glass which can increase the glass viscosity that may in



Fig. 4. Densification and densification rates of porcelain (12.5, 15 and 17.5 K minute⁻¹). *Note:* the increment in the maximum temperature point at higher densification rates.



Fig. 5. Activation energy calculated for progressive densification.



Fig. 6. Thermal phase evolution during intermediate and final sintering.

turn cause the rise in activation energy for densification. This results agrees with the literature for similar triaxial systems that report a 470-497 kJ/mol activation energy level corresponding to a viscous flow sintering mechanism in which the reaction of clay precursor with glass limits densification [4,11].

Physical properties

Fig. 7 shows the variation of the bulk density and Young's modulus with temperature and time. The density is seen to depend critically on time, at 2 h the density reached a 2.39 g/cm³, value compared to 2.22 g/cm³ without soaking. Similarly, the Young's modulus values correspond to a 72.40 Gpa maximum and a 45.80 Gpa without soaking. Such optimum values in physical properties correspond to maximum vitrification as found above by dilatometry and SEM. Fig. 8, shows the optimum firing profile i.e. bulk density and linear shrinkage achieve a maximum value, for the experimental porcelain by using a 1250 °C maximum temperature and 120 minutes dwell time, with a heating rate of 10 K minute⁻¹. From the above results it can be anticipated that very short soaking times may lead to incomplete reactions in the porcelain bodies with the presence of a high proportion of clay and feldspar relics in the vitreous matrix; Also, an insufficient viscous liquid phase may be formed. Regarding faster heating rates, phase transitions at 450-600 °C and 900-1200 °C should be considered to avoid defects in the material.

Concluding remarks

The calculated activation energy for densification has been found to vary significantly within the intermediate sintering stage where most vitrification occurs. The lowest level of activation energy 253 Kj/mol⁻¹ is coincident with a feldspar-clay derived porcelain glassy matrix. The 497 kJ/mol highest activation energy value corresponds to silicon and aluminum enriched phase and therefore a high viscosity porcelain. These activation energy values are comparable to those reported in the literature (200-400 kJ/mol) for



0 min 48 30 min 60 min 44 120 min 40 1170 1200 1230 1260 1290 1320 1140 Temperature ^oC

Fig. 7. Temperature and time variation of the bulk density and Young's Modulus during intermediate sintering.



Fig. 8. Porcelain optimum firing profile. Maximum bulk density and shrinkage are reached after 1250°C and 2 h firing.

a viscous flow rate controlling mechanism of densification. Kinetic fields and the thermal behavior helped to optimize the 1250 °C and 120 minutes firing cycle for a high shrinkage and high bulk density.

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