Shrinkage prediction during non-isothermal sintering in the presence liquid phase: New kinetic model, Part I

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ABSTRACT

The thermal behavior of porcelain stoneware compositions during the sintering was investigated by hot stage microscopy, HSM, and dilatometric tests. The experiments were carried out with a commercial porcelain stoneware composition as a reference, STD, and a modified composition in which 10.0 wt.% of potassium-feldspar in STD mix was replaced with the same content of nepheline syenite. In order to evaluate the effect of technical factors on shrinkage, the specimens were prepared at different milling time and forming pressures. According to HSM results, the increment in milling time of modified composition causes the improvement in dimensional stability. Also, the non-isothermal variation in shrinkage is accurately described by a new semi-theoretical model. The value of dimensionless factor, m, shows that the diffusion mechanism is a function of milling time and the forming pressure cannot change dimensionless factor. The model successfully predicted the shrinkage of bodies sintered in presence liquid phase.

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1. Introduction

Sintering in the presence of liquid phase is a method for rapid densification of ceramic compositions such as porcelain and porcelain stoneware bodies. The structural changes are quite complex, but these variations can be grouped into two major categories. The first category consists of changes which occur as a result of liquid phase flow while the second category is associated with chemical reactions, occurring during the heat treatment. The liquid phase has the potential to diffuse into the pores due to fluidity at high temperatures [1,2]. The exact mechanism providing densification is viscous flow. This phenomenon leads to significant textural changes, mainly concerning porosity, pore size distribution and morphology [3,4]. Other phenomena observed during the sintering are the structural change due to crystallization of new particles and elongation of mullite [5,6]. The final characteristics of product are controlled by the glassy and crystalline phase composition [7,8], alkali oxide content [9], porosity and pore size distribution [10].

Generally, the reactions occurred in ceramic body during the heat treatment have a complex origin. Ceramic body undergoes some transformations during firing which can be listed as: losing humidity and crystal water of clay components, forming Al–Si spinel and amorphous silica around 980 °C [11], softening and

melting of fluxing agents. In correspondence to this point, the fluxing agents start to melt, wetting and forming a continuous liquid layer around the particles [12,13]. When the body is cooled, the viscosity of liquid phase increases until the product becomes rigid [14].

Hot stage microscopy, HSM, is a standard, well-known technique in the ceramic fields [15,16]. Traditionally, the instrument has been mainly applied to assess thermal behavior, particularly to determine the dimensional stability of compact materials. The small cylindrical sample is produced by pressing in a die at room condition normally without addition of binders. The sample is placed on a small ceramic plate with the longitudinal axis coinciding with the vertical direction. For non-isothermal experiments, the furnace of instrument is heated to the maximum temperature normally with constant rate. By observation of changes in height of sample during the heat treatment and taking photographs at pre-defined time intervals, it is possible to ascertain the expansion–shrinkage of ceramic powder. HSM enables to monitor the thermal behavior from room temperature up to softening and melting points. The main application of this technique is to study the sintering and melting behaviors of different ceramic substrates as reported by a number of researches [17–19].

Fast firing is the dominated technology for manufacturing porcelain stoneware bodies. The time is reduced to reach an optimal stabilization of the body [19,20]. The size of the products grows quickly. For example, the request of market has increased for porcelain tiles above one meter in size. Thickness is down to the minimum, to save the costs of manufacturing and transportation

[21,22]. Regardless, the smoothness of the surface, geometrical perfection is a must. The products are mechanically squared to give better arrangement indoors and outdoors. In order to improve the dimensional stability, the thermal shrinkage should be controlled. In some cases, the tendency of the ceramic body to deformation appears in the edges of product. This problem is normally observed in the bodies with high shrinkage [23]. The only type of body that can be dimensionally considered stable during the lifetime is the completely sintered body, characterized by a lack in open pores. In the bodies with low porosity, the maximum shrinkage corresponding to zero water absorption turns into great technological importance. It describes the tendency of body to form the closed pores within a given temperature range. In fact, an abundant vitreous phase with a sufficiently low viscosity flows and causes rapid deformation of the material during the final stage of sintering. The body composition and firing cycle should be designed to avoid the expansion of gas isolated into closed pores [24]. The problem, however, can be successfully tackled by studying the dimensional stability by HSM. To solve deformation problem due to expansion of isolated gas during firing the additional investigation by dilatometry technique becomes indispensable.

Sintered ceramic bodies, like porcelain ware, undergo a viscous flow sintering, where the driving force is mainly given by the surface tension of the liquid phase and the speed of the process is controlled by the viscosity of the liquid phase [25]. The viscosity of liquid phase decreases exponentially as the temperature rises according to Arrhenius law, accelerating the sintering process. On the other hand, the low viscosity causes increase the material tendency to deform under its own weight. The measurement of thermal stability is particularly important for bodies that have to be completely sintered because during the final stage of sintering they develop an abundant vitreous phase with a sufficiently low viscosity to cause rapid deformation. In some cases, the higher deformation speed is found at the maximum temperature reached inside the kiln. In other cases, the deformation due to expansion of isolated gas occurs when the fluxing agent content exceeds than critical values [26]. At higher temperatures the tendency to deformation falls as the vitreous phase dissolves other mineral components such as quartz due to increment in viscosity.

Sintering in the presence of liquid phase is broadly defined as a densification of a relatively loose mass of compacted particles to a denser body. Sintering of porcelain stoneware body causes both the pore size and porosity to decrease until minimum value [15]. The Tammann temperature of the solid, 0.4–0.5 of the melting point, is considered to be the temperature below which sintering does not occur to any appreciable extent [27]. Liquid phase transformation occurs in three steps. In the initial step, the liquid phase is formed around 980 °C between the particles and grows in high temperatures [16]. In the second step, the fluxing agents are melted and contacted with the large number of small particles. In this stage, capillary pressure produced in the inter-particles push the liquid phase into the open pores. In the final step, the liquid phase flow is blockaded by the isolated gas and closed pores remain in the body. The pores whose volume may be inaccessible for the liquid phase are associated to form macro pores [10]. A simple model for the shrinkage, S, of compact glass particles was proposed by Frenkel [28]. In this model, various geometric and physical parameters have been interrelated, precisely.

$$S = \frac{3\gamma}{2a\eta}t \tag{1}$$

where a is the uniform diameter of glass spheres and t is the isothermal sintering time. An important result of this approach is that the shrinkage rate is proportional to surface tension/viscosity ratio, γ/η, which depends on temperature. In the initial stage, viscous flow produced by the driving force of surface tension causes neck

growth. Sintering occurs rapidly when glass heated to softening point. Thus, the mass transport process can be identified via the kinetics of the shrinkage.

The shrinkage measurement technique is applied to a variety of sintering data and discussed in terms of simple model [29]. The shrinkage model is generally presented by

$$S = kt^b \tag{2}$$

where k is a constant that includes temperature dependency, and b is the mechanism-characteristic exponent which is dependent on the mass transport process. The chemical composition of liquid phase plays effective role in mass transfer in the sintering [18,30]. Nepheline syenite was found to decrease the viscosity of liquid phase, which produces enhanced shrinkage rate. The use of 10.0 wt.% nepheline syenite in porcelain stoneware composition allows obtaining the maximum densification rate. Higher percentage has negligible effect on densification rate [29].

The results presented in this investigation deal with two porcelain stoneware compositions. The first contains illitic–kaolinitic clay, potassium and sodium feldspars. This composition, denoted as a reference body, is normally used by industries for manufacturing porcelain stoneware bodies. The second is a modified composition that contains 10.0 wt.% nepheline syenite replaced with the same amount of K-feldspar. The aim of present study is to understand the structural changes, i.e. dimensional stability and shrinkage of two compositions during heat treatment. Therefore, the shrinkage data of reference composition is necessary to compare the behavior of modified mix during the thermal process, and then understand the sintering mechanism. The effects of technical parameters on sintering process are evaluated by HSM and dilatometeric techniques. After studying the densification of reference and modified compositions, it seems useful to understand the role of milling time and forming pressure on shrinkage behavior.

2. Theoretical approach

The theoretical procedure that is proposed here for prediction of shrinkage in non-isothermal sintering is based on creeping flow in spherical coordinate. In Fig. 1 the motion of active materials, containing crystalline and liquid phases, is described, schematically. The pore was located at the center and the active materials diametrically diffuse into the pore. The active solid enters diametrically by capillary forces. According to the presented approach, the shrinkage can be described as a following equation by considering $z^3/(1+z^3) = (\varepsilon_0^{1/3} - S/1 - S)^3$:

$$F(z) - F(z_0) = F(T) \tag{3}$$

$$F(z) = \frac{1}{2}\ln\frac{(z^3+1)}{(z+1)^3} - \sqrt{3}\tan^{-1}\left(\frac{2z-1}{\sqrt{3}}\right) \tag{4}$$

where $F(z)$ is the shrinkage function and $F(z_0)$ is the value of $F(z)$ when $S = 0$. Also ε_0 is the initial total porosity of ceramic body. $F(T)$ which is the absolute temperature, T, dependency function can be presented by

$$F(T) = \frac{A_0(T - T_0)}{6\beta}\left[(T - T_0)^m \exp\left(-\frac{E_a}{R_g T}\right)\right.$$
$$\left. + 2(T - T_0)^m \exp\left(-\frac{2E_a}{R_g(T + T_0)}\right)\right] \tag{5}$$

where A_0 is a frequency factor, E_a is the activation energy and R_g is the gas constant. In this equation β is heating rate and T_0 is the temperature in which shrinkage is zero. Also, m is an adjustable constant. The kinetic parameters and the adjustable constant can be