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Effects of technical factors on dimensional stability of porcelain stoneware body during sintering process: Isothermal kinetic study, Part II

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ABSTRACT

The effect of technical factors on dimensional stability of porcelain stoneware bodies during the isothermal sintering was investigated by measuring linear shrinkage. Different milling times and forming pressures were considered in the preparation of specimens. The sintering process was isothermally carried out at different soaking times. It was observed that the presence of nepheline syenite in the composition negatively affects the dimensional stability range. In order to improve the dimensional stability of modified composition, the milling time should be increased up to 12 h. It was found that the pressure drastically influences the thermal shrinkage and dimensional stability range. The increment in pressure is able to reduce the defects of microstructure. In the next step, a modified kinetic model was applied to analyze the shrinkage variation. The heterogonous diffusion of liquid phase into the pores was confirmed from the computation of a dimensionless factor and calculation of average rate constant.

1. Introduction

Porcelain stoneware body is a ceramic product with great of interest in different building fields [1]. The properties that make porcelain stoneware body as a superior ceramic material are the absence of open pores and high bending strength [2]. While the numerous sizes of porcelain stoneware bodies were manufactured by companies, the composition, body preparation condition and fast firing profile substantially control the size and microstructure of final product [3]. The quality of porcelain stoneware products is directly related to the regularity and uniformity of dimensions. For this reason, the dimensional differences and irregularities in curvature alter or disturb the harmony and flatness of surface covered by ceramic body. The importance of dimensional uniformity is evident because it affects the regularity of design and flatness of surface [4].

Different factors affect the manufacturing process of porcelain stoneware bodies [5]. The isothermal sintering yields a dense ceramic body with minimum porosity, corresponding to maximum shrinkage [6] while the closed pores remain in microstructure after sintering process [3]. The viscosity of liquid phase, influenced by the kind of fluxing agent like feldspars and sintering cycle, is able to drastic affect the shrinkage as well as dimensions of final product. The changes in mixing ratio of fluxing agents and particle size distribution also affect the shrinkage and water absorption of body, consequently [7,8].

Nepheline is a major component of several igneous rocks called nepheline syenite. The basic difference among these rocks is the amount and type of feldspars. In nepheline syenite, feldspars are the most important phase and potassium is invariably observed in natural samples. The chemical analysis of nepheline is more like $Na_3K(AlSiO_4)_4$. Nepheline syenite is actually a mixture of 55 wt.% albite, 25 wt.% potassium feldspar and only about 20 wt.% nepheline, approximately. In comparison to pure feldspars, the advantages of nepheline syenite are: (i) the high content of potassium and sodium, $K_2O + Na_2O$ is about 9–12 wt.% in feldspars whereas it is larger than 14 wt.% in nepheline syenite, (ii) the low melting temperature, potassium-feldspar always contains other phases such as quartz, which shift the melting point to higher temperatures, and (iii) the high content of Al_2O_3 and low content of SiO_2, in feldspar Al_2O_3/SiO_2 is about 0.2 whereas in nepheline syenite this ratio is 0.5 [9]. Therefore, the use of nepheline syenite in the composition of different ceramic products such as electrical porcelain and china ware bodies reduces the firing temperature

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due to increasing the alkali level in the glass phase. Unfortunately, nepheline syenite has not been used in the production of porcelain stoneware bodies and the detailed studies do not exist about nepheline syenite effect on the dimensional stability of product. The enhanced sintering rate is observed in bodies containing nepheline syenite [10]. The superior mechanical properties are reported for body prepared with 10.0 wt.% nepheline syenite. From the mechanical point of view, the use of nepheline syenite in composition appears to be most adequate in comparison to bodies prepared only with feldspars [11]. On the other hand, the increment in content of fluxing agent increases the shrinkage and accelerates the deformation in final stage of sintering mainly due to expansion of hot gas into the isolated pores [12].

One of the major considerations that should be taken into account in manufacturing porcelain stoneware bodies is the dimensional stability range. The sintering temperature and soaking time should be adjusted to achieve a product with minimum tolerance in shrinkage [13]. Deformation after reaching maximum shrinkage, rapid expansion, occurs in porcelain bodies during the sintering. According to the well known over-firing theory, deformation is a function of hot gas pressure exerted on the isolated pores [14]. The increment in hot gas pressure and reduction in active material resistance increase deformation rate. During the firing of porcelain stoneware body, fluxing agent particles react with SiO_2 released meta-kaolin to form eutectic liquid at 980 °C in which the amounts of alkali materials is high [15]. Also, the content of silica is low in liquid phase in this condition [16]. The rapid deformation is observed in the bodies containing high amounts of alkali oxides or low level of Al_2O_3/SiO_2 [17]. The resistance of active material is significantly improved when quartz dissolution becomes rapid, causing an increase in the liquid phase viscosity [8].

The firing profile of a porcelain stoneware body may be divided into three parts, representing structural changes that occur with temperature and time [3]. During pre-sintering section, the green body is a rather fragile and brittle. The loss of absorbed water, burning of organic materials, dehydroxylation, allotropic transformation, metakaolin decomposition and forming amorphous silica as well as melting of fluxing agents are carried out in this section as temperature is increased up to maximum value, maturing temperature. The sintering process is completed in maturing zone, isothermal section, by development of liquid phase in the second step of firing profile. The viscosity of liquid phase decreases as the maturation temperature rises. The melted phase loses its viscous characteristics at glass transition temperature [18]. The third division is cooling, below the glass transition temperature, where the body is a relatively strong and brittle. In design of isothermal section of fast firing profile, the thermal expansion data should be considered in first step and then it can be modified by dilatometery [10] and hot stage microscopy data [16]. This procedure establishes the shape of firing profile for porcelain stoneware body [18]. The isothermal sintering region should be separately designed according to shrinkage-expansion data. The irreversible thermal expansion data are used in final sintering stage, before cooling step. The critical region on the isothermal sintering section is identified by dimensional stability data. The ceramic body can be damaged by hot gas pressure if the reliable dimensional stability range is not identified, correctly. It is important to experimentally determine the adjustable sintering temperature and soaking time to avoid deformation because the behaviors of ceramic compositions are substantially different in the isothermal sintering section. Though, the dilatometery [18] and hot stage microscopy [19] data are useful in design of firing profile, the dimensional stability range should be determined empirically if it is not available for a new composition. In summary, due to oscillation of temperature in the industrial kilns, the dimensional stability range should be considered for complete maturation.

Squaring is commonly conducted by abrasive materials [3,4,20]. This process is machining of product to achieve well-defined sizes. Porcelain stoneware bodies are brittle materials and squaring cost is indirectly related to shrinkage and dimensional stability. When the dimensional stability range is not considered, especially for the bodies with high shrinkage, it is impossible to avoid squaring because the interest sizes cannot be achieved only by firing process.

The fluxing agent type, milling time and forming pressure should be optimized to achieve a dimensional stability during the sintering of porcelain stoneware body. These factors essentially influence the quality of product through the change of amorphous and crystalline phases, porosity and pore size distribution. In this investigation, a commercial porcelain stoneware body composition has been selected as a standard mix, STD, and a modified body composition has been formulated by introducing 10.0 wt.% nepheline syenite, as a partial substitution of a typical potassium feldspar. The previous studies presented by authors have indicated that the substitution at a level of 10 wt.%, improves the rheological [21,22] and mechanical [11] properties. The novelty of present study is the determination of dimensional stability range for standard and modified compositions. The next part of work evaluates the effect of milling time and forming pressure on dimensional stability range and the optimum condition for the sintering of modified body was described. Finally, the variation in linear shrinkage during the isothermal sintering was analyzed by a modified kinetic model.

2. Isothermal kinetic approach

In order to evaluate the isothermal sintering rate, the linear shrinkage variation was analyzed by a model presented, previously [23]. Eqs. (1) and (2) were used to correlate the experimental data. The principles of this model was related to motion and momentum transfer of viscous flow. According to the presented theory, the shrinkage, S, can be described as a modified equation by considering $z^3/(1+z^3) = [({\varepsilon_0}^{1/3} - S)/(1-S)]^3$. The required initial condition is the total porosity, ε_0.

$$F(z) - F(z_0) = at^b \tag{1}$$

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

where t is soaking time. Also, $F(z)$ is the shrinkage function and $F(z_0)$ is the value of $F(z)$ when $t = 0$. z is an intermediate variable that relates the shrinkage to $F(z)$. a and b are the constant parameters of model and can be calculated by using linear regression method. In order to better understand the effects of technical factors on the thermal shrinkage, the average rate constant should be calculated. By use of empirical methods [24], k_a which is the average rate constant can be represented by:

$$k_a = \frac{1}{6}k(S) + \frac{2}{3}k(S) \tag{3}$$

where

$$k(S) = 3ba^{\frac{1}{b}} \cdot \left(\frac{1}{S} - 1\right) \cdot \left(\frac{\varepsilon_0^{\frac{1}{3}} - S}{1 - \varepsilon_0^{\frac{1}{3}}}\right) \cdot \left[\left(\frac{1-S}{\varepsilon_0^{\frac{1}{3}} - 1}\right)^3 - 1\right]^{\frac{1}{3}} \cdot [F(z) - F(z_0)]^{\frac{b-1}{b}} \tag{4}$$

For compact powder, the shrinkage depends on temperature and the variation of k_a can be related to absolute temperature by Arrhenius equation:

$$k_a = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{5}$$