Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Feature article

Pyroplastic deformation of porcelain stoneware tiles: Wet *vs.* dry processing

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ARTICLE INFO

Article history:
Received 27 February 2016
Received in revised form 7 August 2016
Accepted 13 August 2016
Available online xxx

Keywords:
Pyroplastic deformation
Porcelain stoneware tiles
Vitreous phase

ABSTRACT

Several batches of porcelain stoneware were formulated by partial replacement of coarse Na and Na-K feldspars (standard batch) with quartz in two different grain sizes, micronized K-feldspar or a mixture of these components. Everyone was processed (laboratory scale) by wet and dry routes to compare: sintering curve, microstructure, phase composition and viscosity of the liquid phase at high temperature. Pyroplasticity index was determined by 3-point bending test. Results indicate that finer the quartz particles, more they dissolved in liquid phase, increasing viscosity and reducing deformation. Micronized K-feldspar increased the sintering kinetics (causing deformation). However, when K-feldspar was combined with quartz, densification rate was improved without compromising integrity of tile. About dry route, microstructural heterogeneity turned as fundamental to prevent Pyroplastic deformation. As conclusion, pyroplastic deformation occurs by different mechanisms in samples prepared by the two processing routes and bodies prepared via dry route are less likely to undergo pyroplastic deformation.

1. Introduction

Porcelain stoneware tiles have a high added value and a wide market acceptance owing to their excellent technical and aesthetic characteristics. To ensure their high technical performance, their porosity should be very low, which is achieved by manufacturing a product with a high degree of vitrification after firing [1]. The mechanism involved is viscous flow sintering, which requires the formation of a large amount of liquid phase during the thermal cycle, *i.e.*, from 50 to 80% [2,3]. During the firing reactions, the ceramic tile must retain its geometrical features as it moves on the refractory rollers of the furnace, but this has become increasingly difficult due to recent innovations in porcelain stoneware, such as the production of thin tiles with large dimensions, highly rectangular shapes, and in the case of fast thermal cycles [4,5]. In any case, the manufacturing of this type of product, *per se*, exacerbates the tendency for pyroplastic deformation, *i.e.*, deformation of the ceramic body during the thermal cycle due to its own weight, causing it to lose its original shape [6,7]. Porcelain stoneware tiles have traditionally been producing by the wet route [1,8]. However, growing concerns for the sustainability of ceramic tile production have opened the way for a new, dry processing route involving lower water and energy consumption and hence environmental benefits [9,10]. Nevertheless the pyroplastic behavior of dry-processed porcelain stoneware is still unknown. It is believed that modifying the properties of the liquid phase formed during firing may improve the shape stability of the ceramic body, thereby contributing to minimize this problem. Therefore, in this work, starting from a standard ceramic batch, some raw materials were substituted and changes in particle size were made, aiming to promote a modification in the amount of skeleton grains and the composition and viscosity of the liquid phase. These variables are considered key factors to reduce the firing deformation in porcelain-like materials, as pointed out in a previous work [11]. The effect of such changes has now been investigated also in batches produced by the dry route. The objective is to shed light on the dependence of pyroplastic deformation on both microstructure and composition in porcelain stoneware tiles.

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.08.015
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Please cite this article in press as: L.R. dos Santos Conserva, et al., Pyroplastic deformation of porcelain stoneware tiles: Wet *vs.* dry processing, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.08.015

2. State of the art

Pyroplastic deformation is attributed primarily to the volume and nature of the liquid phase and to the porous structure in which this phase is contained [7,12]. This phenomenon has been widely studied in ceramic tableware [7,13,14] and sanitaryware [15,16]. In a broad study, Airey and Birtles [17] defined a general pattern of behavior represented by three stages, the first of which involves slight deformation due to the breakdown of the metakaolin structure. Most of the deformation associated with the shrinkage of the ceramic body and the high mobility of the liquid phase with low viscosity then occurs in the second stage, during heating and after formation of the liquid phase. Lastly, in the third stage, when shrinkage no longer occurs, the tight particle packing reduces deformation to a very slow and almost constant rate, increasing the viscosity of the liquid due to the dissolution of particles that alter its chemical composition and forming crystalline phases that reinforce the structure [2,12,13,17]. It should be kept in mind that ceramic tableware is sintered in considerably longer cycles (2–3 h) than those applied to porcelain tiles, which are fired in about 40–60 min [1,8].

The amount of liquid phase formed during firing is determined mainly by the amount of flux and the threshold temperature [2,13]. These aspects, which are essential for the development of the final microstructure of porcelain tiles, result in the desired technical characteristics. Rambaldi et al. [18] suggested that pyroplastic deformation begins at 990 °C through movements in low-viscosity regions that are formed from the alkali-rich and silica-poor eutectic liquid, but the ratio between the amount of liquid phase formed during firing and the pyroplastic deformation is not clear.

A liquid of very high viscosity is undesirable because of the low kinetics of densification, while low viscosities cause problems such as increased closed porosity and/or pyroplastic deformation. According to Restrepo and Dinger [19], highly viscous liquid phases increase the nucleation and growth rates of secondary acicular mullite crystals, which strengthen the structure of the system, reducing deformation. Another factor that determines the characteristics of viscosity is the ratio of sodium to potassium alkalis. Many studies show that increasing the Na_2O/K_2O ratio decreases the viscosity of the liquid phase [18,20,21]. Although there is a clear relationship between viscosity and the Na_2O/K_2O ratio, the same does not hold true of its interrelationship with pyroplastic deformation.

The main difficulty in identifying the processes that control deformation rates at high temperatures is the complexity of the microstructure resulting from the low mobility of the components and from their incomplete equilibrium. Although many reactions and interactions occur between the constituent powders, the microstructure retains a remarkable heterogeneity. Porte et al. [22] demonstrated that the liquid phase can be seen as a viscous suspension of fluid and particles and that, at a given temperature, the higher the particle content in the viscous suspension the higher its viscosity. Moreover, considering the feldspar-kaolin-quartz system, each component consists of a particle phase (crystalline) and a liquid associated with this phase. The particle size and morphology of each of the crystalline phases, as well as the chemical composition of the three liquids associated with them, differ from each other, resulting in microsystems with very different viscosities.

3. Experimental procedure

3.1. Batch design and preparation

Six batches typical of technical porcelain stoneware were formulated, using the proportions reported in Table 1. The standard composition (STD) contains both sodium and potassium feldspars with relatively coarse particle sizes; 10% of which was substituted by other types of raw materials with a different particle size distribution. Such substitutes were micronized potassium feldspar (median particle diameter, d_{50}, 3 µm and specific surface area, SSA, 4.0 $m^2 g^{-1}$), fine-grained (<74 µm) quartz (d_{50} 1.8 µm and SSA 1.3 $m^2 g^{-1}$) and micronized quartz (d_{50} 1.7 µm and SSA 2.3 $m^2 g^{-1}$).

Table 1
Batch formulation of porcelain stoneware bodies: C = coarse-grained, F = fine-grained, M = micronized.

Raw materials (% wt)	STD	QF	QM	KM	QFKM	QMKM
Kaolin	25	25	25	25	25	25
Ball Clays	12	12	12	12	12	12
Bentonite	4	4	4	4	4	4
Talc	4	4	4	4	4	4
Zircon	3	3	3	3	3	3
Na Feldspar C	26	21	21	21	21	21
Na-K Feldspar C	26	21	21	21	21	21
Quartz F	–	10	–	–	5	–
Quartz M	–	–	10	–	–	5
K Feldspar M	–	–	–	10	5	5

Table 2
Chemical composition of the fired porcelain stoneware bodies.

% wt	STD	QF	QM	KM	QFKM	QMKM	e.u.
SiO_2	66.98	69.42	69.42	66.10	67.75	67.75	±0.25
TiO_2	0.31	0.31	0.31	0.31	0.31	0.31	±0.01
ZrO_2	2.06	2.05	2.05	2.05	2.05	2.05	±0.02
Al_2O_3	22.44	21.25	21.25	23.11	22.18	22.18	±0.20
Fe_2O_3	0.85	0.83	0.83	0.83	0.83	0.83	±0.02
MgO	1.89	1.73	1.73	1.73	1.73	1.73	±0.02
CaO	1.35	1.05	1.05	1.06	1.06	1.06	±0.02
Na_2O	3.39	2.68	2.68	2.98	2.83	2.83	±0.02
K_2O	0.70	0.63	0.63	1.79	1.21	1.21	±0.02
P_2O_5	0.03	0.03	0.03	0.04	0.04	0.04	±0.01

e.u. = experimental uncertainty.

The chemical composition of batches is shown in Table 2. These compositional changes enabled us to investigate the effects of chemical, mineralogical and physical characteristics (particle size) on pyroplastic deformation. In the remaining ceramic batches, each substitution relative to the STD was aimed at altering either the properties of the liquid phase or the body microstructure, or both, in order to evaluate their effects on firing deformation. Thus, once dissolved in the melt, quartz increases the viscosity of the liquid phase and its dissolution is fostered by a smaller particle size (and wider SSA). The use of potassium feldspars decreases the Na_2O/K_2O ratio and also helps to increase the viscosity of the liquid phase. It is believed that modifying the properties of the liquid phase, in order to stabilize the ceramic body during firing, could contribute to minimize the problem of pyroplastic deformation.

Preparation of the samples was performed with two granulation techniques: the wet and dry routes. The wet route technique involves replicate in laboratory as close as possible the processes employed in factories, where the grinding uses water and deflocculant and then water is removed from slurry through atomization. In dry route, the grinding of the raw materials is carried out without addition of water, which is added only at the granulation stage through micro granulator equipment, which forms spherical granules facilitating flowability of powder. These techniques are described next.

All batches underwent the wet processing: raw materials were ball milled with the addition of 50%wt of water and 0.6%wt of deflocculant (sodium silicate) adjusting the milling time to obtain a residue between 0.5 (minimum) and 2.0% (maximum) retained on a #325 mesh (45 µm) sieve. The suspensions were oven dried at 110 °C and granulated with the addition of 6.5%wt water.

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