Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Soda-lime-silica-glass/quartz particle size and firing time: Their combined effect on sanitary-ware ceramic reactions and macroscopic properties

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ARTICLE INFO

Keywords:
Ceramic reactions
Recycling waste soda-lime-silica glass
Firing time
Particle size

ABSTRACT

This paper describes how soda-lime-silica (SLS) glass particle size in combination with firing time and quartz particle size influence sanitary-ware ceramic reactions (mullite/glass formation rate and activation energy), and affect some relevant ceramic bodies' macroscopic properties (water absorption, WA; linear thermal expansion, α; linear shrinking, LS). The study is focused on the system kaolinite, quartz (d_{50} = 28 and 4 µm), Na-feldspar and SLS-glass (d_{50} = 35, 23 and 16 µm). SLS-glass in partial replacement of Na-feldspar accelerates the mullite formation rate and the same effect is achieved by decreasing the quartz-d_{50}, which leads to a higher reactivity of the starting slip and to a lesser vitrification grade. In general, mullite formation rate increases with a decrease in SLS-glass-d_{50}. Secondary mullite occurs more abundantly and better shaped in samples with small quartz and SLS-glass d_{50}-values. The technological properties here considered exhibit a complex dependence on SLS-glass/quartz particle size and firing time; in general, they result more sensitive to the former than to the latter. The issues of this work show that one can (i) notably tune WA−α−LS as a function of SLS-glass/quartz particle size and firing time cycle, and (ii) achieve a 30–90 K lowering of firing temperatures (curbing CO_2-emissions), making it possible to tailor a reuse of SLS-glass as a function of final ceramic targets.

1. Introduction

A significant volume of ceramics, representing one of the most important classes of materials, is manufactured by heating mixtures of clay, kaolinite, quartz and feldspar up to ~ 1500 K [1].

Because of the large amounts of natural raw materials involved and the high temperatures required, the ceramic industry significantly impacts upon the environment, in terms of CO_2 emissions and huge energy requirements (*i.e.* in the European Union annual ceramic production of 50 Mt pieces per year the CO_2 emissions reached 1 Mt/y [2]).

In such a view, the ability to replace, even in relatively small amounts, the natural raw materials producing wastes can have particular advantages in terms of effective refuse disposal and reduction of CO_2 emissions. An attractive approach is the use of alternative materials such as industrial scrubs, electronic wastes (cathode ray tube TVs and monitors) and silica rich wastes from bottle banks [3–9].

Souza et al. [10] showed the feasibility of using glass cullet from bottle banks (*i.e.* "soda lime silica" glass, hereafter SLS-glass) in ceramic slips. In a more recent study, Marinoni et al. [11] proved that SLS-glass can partially replace the traditional fluxing agents (Na-feldspar) in vitreous sanitary-ware slip, up to about 7–11 wt%. The results attested that the introduction of SLS-glass: i) influences the mechanism of mullite growth, ii) accelerates the sintering kinetics at lower temperature and iii) facilitates the densification process, thus reducing the firing time and yet resulting in final products with acceptable technological properties.

A full understanding of the ceramic reactions in the presence of SLS-glass is a fundamental step in its exploitation and requires that the effects of SLS-glass particle size in combination with the heating time-temperature parameters be duly explored. Moreover, it is also important to take into account the coupled effect resulting from the quartz particle size, *i.e.* the other main SiO_2-carrier commonly occurring in ceramic mixtures and potentially competing with SLS-glass as a silica provider/taker. These topics are still modestly explored despite the fact that they are a key to improving the level of exploitation of SLS-glass in

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http://dx.doi.org/10.1016/j.ceramint.2017.05.126
Received 29 December 2016; Received in revised form 2 May 2017; Accepted 16 May 2017

Please cite this article as: Marinoni, N., Ceramics International (2017), http://dx.doi.org/10.1016/j.ceramint.2017.05.126

a variety of ceramic processes, especially in sanitary-ware production.

The roles of both grain size of quartz [1,12] or feldspar [13] as well as of microstructures [15] in commercial porcelain processes have already been investigated. In particular, Stathis et al. [12] studied how the grain size of quartz affects the bending strength in porcelain. Alves et al. [13] analysed instead the effect of the feldspar particle size on the formation of pores as well as on strain resistance in the middle (green compact) and final product. Last, Romero and Pérez [14] reported a review of the relation between the microstructure and technological properties of porcelain stoneware.

Furthermore, in the case of sanitary glazes, an adequate selection of the grain size of raw materials leads to an improvement of whiteness and gloss as well as a decrease in the surface roughness [15–18].

However, to date, little is known on the influence of particle size on sanitary ware vitreous ceramic reactions. Bernasconi et al. [19,20] showed that the grain size of quartz and feldspar affects the evolution of the phases upon heating, water absorption and volume thermal expansion of the glass. The effects of the feldspar particle size on the glass-mullite reaction energy in the Na-feldspar-kaolinite system were investigated by Diella et al. [21].

Therefore, the aim of the present study was to investigate the role of (i) the particle size of the starting SLS-glass and quartz (using the d_{50}-parameter as a marker), and (ii) the soaking (firing) time (t-interval) in the production of sanitary-ware-like ceramics. Industrial slips were prepared by mixing kaolin, quartz, Na-feldspar and SLS-glass to form conventional sanitary-ware compositions (clay: filler: flux 50:25:25). Following the results of [11], the present investigation is focused on a T of 1413 K, and on the exploration of a wide t-interval (20–240 min). Note that no higher T's were considered because they would simply accelerate the reactions of the ceramic processes, thus restricting the t-interval to explore in detail.

Mullite and amorphous phase contents in the final products as well as their growth rates *versus* soaking time were studied by means of X-Ray Powder Diffraction (XRPD) using the Rietveld Method. The phase composition and the macroscopic observables have been related to t and quartz-/SLS-glass-d_{50}. In particular, special attention was paid to the trends of the crystalline and amorphous phase content *versus* SLS-glass's d_{50} and soaking time, rather than to their absolute values.

The morphology of mullite crystals was investigated by Scanning Electron Microscopy (SEM). Finally, reference technological properties, such as water absorption, linear thermal expansion and shrinkage were measured to assess the achievable level of compatibility of the designed ceramic material with performance improvement and requirements for wholesale production/marketability.

The obtained results contribute to:

(i) Understanding fundamental ceramic reactions as a function of the SLS-glass/quartz morphologic properties. Attention is paid to the relationship between SLS-glass/quartz particle size, soaking time, mullite/ceramic-glass formation rates and activation energy, which control the equilibrium of mullite *versus* glass and drive formation of ceramics;
(ii) Curbing CO_2-emissions by being able to reduce the firing temperature since the SLS-glass acts as a ceramic reactions booster;
(iii) Getting an insight into how SLS-glass/quartz particle size in combination with soaking time change reference macroscopic properties. This aspect provides a basis for maximizing, in terms of volume and technology type, the recycling of cullet glass in sanitary-ware production.

Points (ii) and (iii) open interesting vistas to sanitary-ware technology developments ever more responsive to environmental safeguards and sustainable production policies.

Table 1
Starting compositions in wt% of the samples under investigation, in terms of raw materials.

Set of slip	Sample ID	Sample description		
		Quartz (Q) d_{50} (μm)	Glass (G) d_{50} (μm)	
Slips without glass (50% kaolin, 25% quartz; 22% feldpsar)	*CQ*	28	–	Slip with coarse quartz (reference slip)
	ffQ	4	–	Slip with very fine quartz
Slip with glass in partial substitution of feldspar (50% kaolin, 25% quartz; 15% feldpsar; 7% glass)	*CQ-CG*	28	35	Slip with coarse quartz and glass with variable grain size
	CQ-fG	28	23	
	CQ-ffG	28	16	
	ffQ-CG	4	35	Slip with very fine quartz and glass with variable grain size
	ffQ-fG	4	23	
	ffQ-ffG	4	16	

2. Material and methods

2.1. Material

In the present investigation two sets of sanitary-ware slips were prepared (Table 1). The former consisted of two slips with the same mineralogical composition (mixture of kaolin, Na-feldspar and quartz), but differing from one another in the quartz d_{50}. The latter contained six batches composed by kaolin, Na-feldspar, quartz and SLS-glass in partial substitution of Na-feldspar, differing from each other in quartz and SLS-glass particle sizes. The used sample labeling shows the presence of quartz (Q) and SLS-glass (G), either accompanied by a prefix that identifies its particle size (coarse, fine and very fine: *C*, *f* and *ff*, respectively), *i.e.* *CQ*, *ffQ*, *CQ-CG*, *CQ-fG*, *etc.* Note that the symbols *CQ*-G and *ff*Q-G are here used to indicate blends containing SLS-glass, without specifying its d_{50}, along with coarse quartz or very fine quartz, respectively.

The raw materials were provided by Minerali Industriali (Novara, Italy). Na-feldspar, kaolin and quartz were natural samples, treated by magnetic ventilation to separate out impurities, accessory phases and contaminations, as already described in previous study [21]. SLS-glass comes entirely from the recovery of glass cullet collected from primary beneficiation plants and was already described in [11]. The particle size distributions of quartz and SLS-glass were measured by laser-light scattering using a Master-sizer S of Malvern Instruments Ltd.

In particular, a total of 76 slips were prepared. The components of mixtures were blended together in bi-distilled water, and then cast into 1 cm in diameter/5 cm in height cylindrical molds. The dried mixtures were eventually fired in an Elite Thermal System Ltd, BRF14/box furnace at a heating rate of 5 °C/min to the two maximum firing temperatures explored, 1413–1443 K. The treatments lasted 20, 40, 60, 80, and 240 min (60, 80, 150 and 240 min for samples composed of coarse and fine quartz and without SLS-glass, used as reference), followed by a cooling inside the furnace (about 12 h). Some experiments at 1443 K were performed for a comparison with those at 1413 K. Each experiment was repeated 3–4 times to guarantee reproducibility, and the results here shown are the average values of the measurements on such sets (with error that ranges from 0.5 to 1 wt% as calculated from XRPD).

2.2. X-Ray Powder Diffraction (XRPD)

CuKα powder data were collected on a PANalyticalX'Pert Pro