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Properties related phase evolution in porcelain ceramics

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Abstract

Porcelain represents one of the most complex ceramics, formulated from a mix of clay, feldspar and quartz are sintered to conform a glass-ceramic composite. Two porcelain stoneware compositions were studied. Chemical–physical and microstructural analyses were accomplished in order to determine the relationship between the microstructure and the mechanical–technical properties of these stoneware tile products. The phase evolution, in particular the formation and growth of mullite has been investigated. The mechanical improvement in which the glass phase is dominant, it is shown to be influenced mainly by the stresses set up in the glass matrix, induced by the quartz grains which have higher expansion coefficients than that of the glassy phase, rather than the amount or size of mullite.

Keywords: Porcelain; Mullite; Mechanical properties; Stoneware tile

1. Introduction

In the last decade, the growth rate of the global production of porcelain stoneware tiles has increased more than other ceramic products because of its excellent mechanical properties and superior aesthetic performance.[1,2] At present ceramic tiles are already been marketed with characteristics and performance features that make them products whose applications go far beyond traditional tile uses.[3,4] As examples in this sense stoneware tiles as technical ceramics are used given their optimal technical performance features in high transit areas, antifog and self-cleaning applications, building facades, photovoltaic supports, etc. In some of the new engineering applications there is a clear tendency to reduce the tiles weight to lightening building and this requirement implies to increase the stoneware tile mechanical properties.

Porcelain stoneware tiles are highly vitrified ceramic materials[5] with a very compact structure (water absorption <0.5%, ISO 13006), low porosity and high technical performance, especially as regards the modulus of rupture, chemical and frost resistance and resistance to deep abrasion. Produced primarily from clay, feldspar and quartz mixtures they are heat-treated to form a heterogeneous glassy matrix with quartz grains and small crystallization of mullite.[6]

There are two major approaches that have been developed in order to explain the strength of porcelains. One of the oldest, is the mullite hypothesis, first proposed by Zoellner,[7] posits the strength of a porcelain body as solely dependent on the interlocking of mullite needles. Later versions[6] of these hypotheses have indicated that the strength increases with the increase of mullite content. At higher temperatures, the mullite needles coarsen, leading to a smaller number of larger needles. The larger needles do not interlock as efficiently as the smaller ones, and a decrease in strength resulted. So both the composition and the sintering process must be adequate to generate the correct amount of properly sized mullite needles in order to achieve the desired strength. On the other hand the porcelain composite complexity required to take into account the different crystalline phases present in the material. The matrix reinforcement hypothesis, where the difference in thermal expansion coefficients between the matrix, a glassy phase, and dispersed particles, such as quartz, or crystalline phases formed during the firing process, such as mullite, produces strong compressive stresses on the glassy phase. Such induced “thermal” compressive stresses due to thermal expansion mismatch lead to strength improvements in the porcelain bodies.

The aim of this work is to study the evolution of the crystalline phases of the two compositions prepared with different contents of glass formers and its influence on the mechanical

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reinforcement. The mechanical improvement[8] in which the glass phase is dominant, it is shown to be influenced mainly by the stresses set up in the glass matrix, induced by the crystalline materials which have higher expansion coefficients than that of the glassy phase, rather than the amount or size of mullite.

2. Experimental procedure

Two standard commercial porcelain stoneware tile compositions denoted A and B were prepared. The chemical compositions of both samples in wt% of equivalent oxides were reported in Table 1. B composition was design with a higher content on glass former cations on the base of a glaze material addition.

To prepare the batches standard industrial quartz, kaolinitic clay, feldspar and glaze as raw materials with ratio 9/41/50/0 for A composition and 27/15/51/7 for B composition were ball milled for 30 min in a porcelain jar with alumina balls using water as media and 0.2 wt% of sodium tripolyphosphate as dispersant. After the milling step, PVA and PEG-400 organic additives were added to help pressing of samples. Slips were oven dried at 60 °C for 24 h, crushed and passed through a 500 μm sieve. The resulting powders were moistened up to ∼6 wt% water, hand granulated and uniaxially pressed at 45 MPa into 8 mm × 3 mm tiles. A total of five tiles for each composition were prepared to ensure the reproducibility of the measurements. Specimens were fired in a laboratory electrical furnace simulating an industrial fast firing process in an air atmosphere involving basically: an average heating rate of 25.6 °C/min, a soaking temperature of 1220 °C hold 0.1 and 1 h, and a furnace cooling step.

The products were characterized in terms of compositional, microstructural, technological and electrical properties. The crystalline phase compositions were quantitatively determined by X-ray powder diffraction by using a Siemens Kristalloflex equipment. X-ray fluorescence attempted chemical analysis in a Philips MagiX spectrometer. Water absorption and bulk density were quantified measuring the dry weight, the water-saturated weight and the weight suspended in water, according to ISO 10543-3. The modulus of rupture was measured with a three-points flexural method ISO 10545-4 using a Universal Instron machine. A Leco Hardness Tester using a Vickers indenter determined the microhardness and toughness. The surface roughness, expressed as R_a, average roughness, was determined with a Taylor Hobson instrument. Differential thermal and thermogravimetric analyses, DTA–TG, have been used to study the kinetics of phase transformation processes and chemical reaction mechanisms up to 1250 °C with at a heating rate of 10 °C/min. The microstructure of the polished, chemical etched and gold coated surfaces was also investigated by using a field emission scanning electron microscope, FE-SEM, Hitachi S-4700. Porosity was evaluated on polished surfaces by using image analysis. Impedance spectroscopy measurements were performed on platinum electroded discs by using an Impedance Analyzer HP-4294A in the frequency range of 100 Hz to 10 MHz from 300 to 840 °C.

3. Results and discussion

Table 2 shows selected properties of A and B compositions. According to the bulk density and water absorption data, <0.5% as technically required, both compositions have similar values. Attending to the mechanical properties there was a clear increase of the rupture modulus, the Vickers hardness and the fracture toughness of B composition when compared to A one. The decreasing of both the surface roughness and the porosity size in both samples was a consequence of a higher amount of fluxes in the B composition.

The FE-SEM micrographs, Fig. 1(a), show the typical microstructure of a porcelain stoneware tiles constituted of a continuous vitrified matrix, irregular quartz crystals (5–25 μm of equivalent diameter), pores with the appearance of gas bubbles and small crystalline phases. High magnification micrograph for composition A, Fig. 1(b), illustrates the fibrous nature of the new crystalline phases that can be related to mullite crystals. Fig. 1(c) being a similar micrograph as the obtained for A shows a higher presence of quartz grains related to a high proportion of the quartz raw material used in the preparation of the composition. In some part of the microstructure as in the interior of the pore it is possible to identify smaller plate-like crystalline phases that have a similar morphology to the kaolin particles. The presence of mullite type crystallization was scarce and only incipient second phase crystallization was observed on selected areas as can be observed in Fig. 1(d).

XRD patterns of samples A and B fired at 1220 °C for 0.1 h and 1220 °C for 1 h were performed in order to investigate

Table 2
Technological and mechanical properties of the stoneware tile compositions of standard porcelain stoneware prepared fired at 1220 °C for 0.1 h

Properties	A	B
Bulk density (g/cm^3)	2.41 ± 0.05	2.42 ± 0.04
Water absorption (%)	0.06 ± 0.04	0.08 ± 0.03
Roughness R_a (μm)	2.2 ± 0.1	0.9 ± 0.1
Porosity (%)	5.5 ± 0.5	4.6 ± 0.4
Average size porosity (μm)	13.2 ± 0.2	9.2 ± 0.2
Modulus of rupture (MPa)	53 ± 7	61 ± 6
Vickers hardness H_V (MPa)	4.8 ± 0.8	7.3 ± 0.9
Toughness K_{IC} (MPa m$^{1/2}$)	1.6 ± 0.1	2.0 ± 0.2

Table 1
Chemical analysis of the compositions (wt%) used in the preparation of porcelain stoneware tiles

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O	CaO	MgO	P_2O_5	ZnO	BaO	I.L.
A	65.60	18.14	0.387	0.428	5.010	1.000	0.472	0.158	0.078	–	–	8.727
B	67.61	16.27	0.130	0.112	4.970	0.502	0.990	0.158	0.099	1.02	0.545	7.572

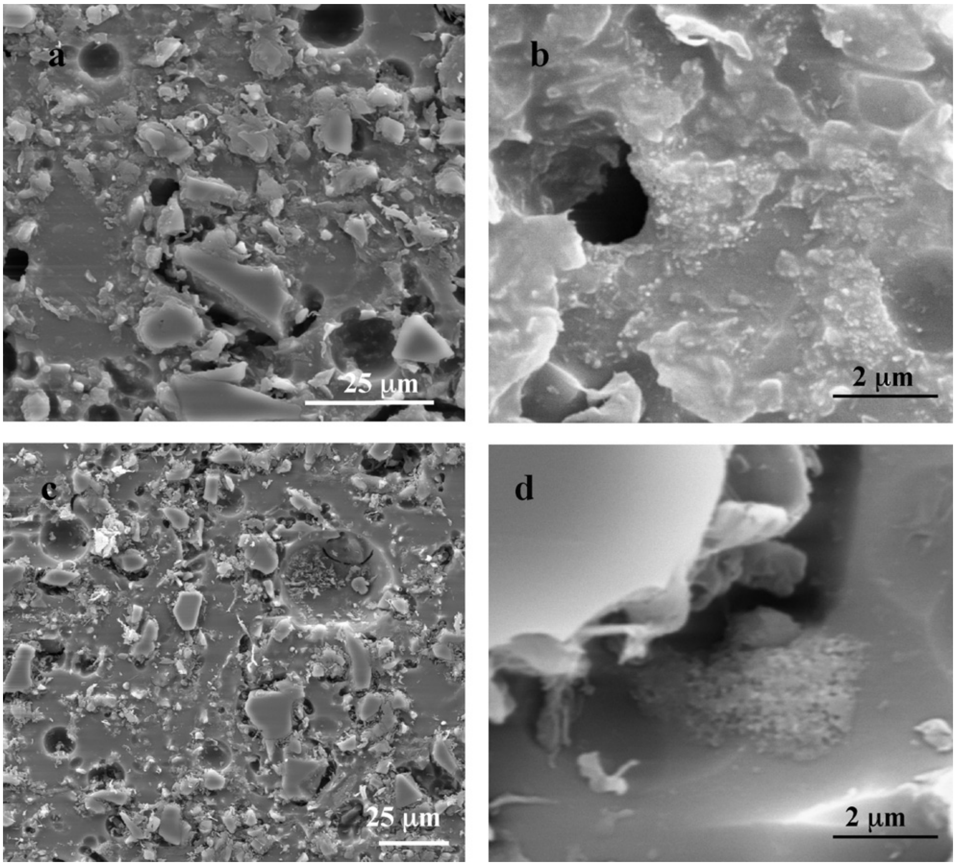

Fig. 1. FESEM micrographs of studied porcelain stoneware fired at 1220 °C, 0.1 h: (a) low and (b) high magnification of A composition; (c) low and (d) high magnification of B composition.

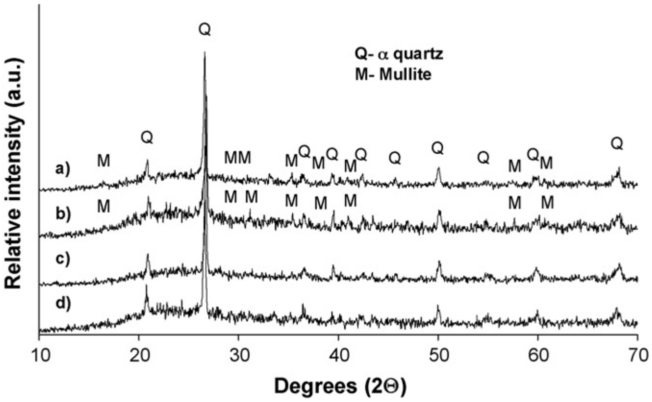

Fig. 2. XRD patterns of 1220 °C sintered compositions (a) A 0.1 h; (b) A 1 h; (c) B 0.1 h; and (d) B 1 h.

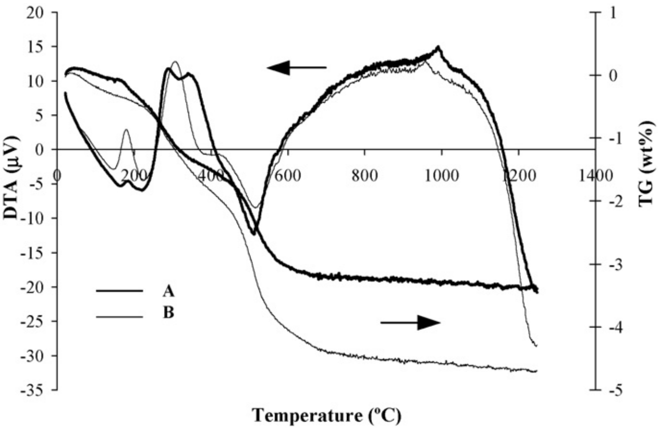

Fig. 3. DTA/TG curves of A and B compositions heated at 10 °C/min.

the crystalline phase composition of the samples, Fig. 2. XRD pattern for composition A fired at 1220 °C 0.1 h display that α-quartz was the mayor crystalline phase and proportion of mullite phase was quite low. Firing the same composition at 1220 °C for 1 h, to try to favour the growth of mullite crystals, produce an increasing of mullite peaks intensity. The same study for B composition shows that the mullite was not present for both sintering times.

Fig. 3 shows the DTA/TG curves recorded for both compositions. First weight loss observed was related to the exothermic removal of adsorbed water up to 250 °C, the second weight loss up to 425 °C was attributed to the exothermic combustion of the pressing organic additives and the third weight loss was correlated with an endothermic reaction at 520 °C, due to the dehydroxylation of the kaolinitic clay. The next endothermic reaction at 573 °C, for the two compositions, correspond to the $\alpha \rightarrow \beta$ quartz inversion, which takes place without weight loss. As most of the authors point out,[9,10] the last exothermic peak at 980 °C for composition A and at 950 °C for composition B, which occurs also without weight losses, was attributed to a

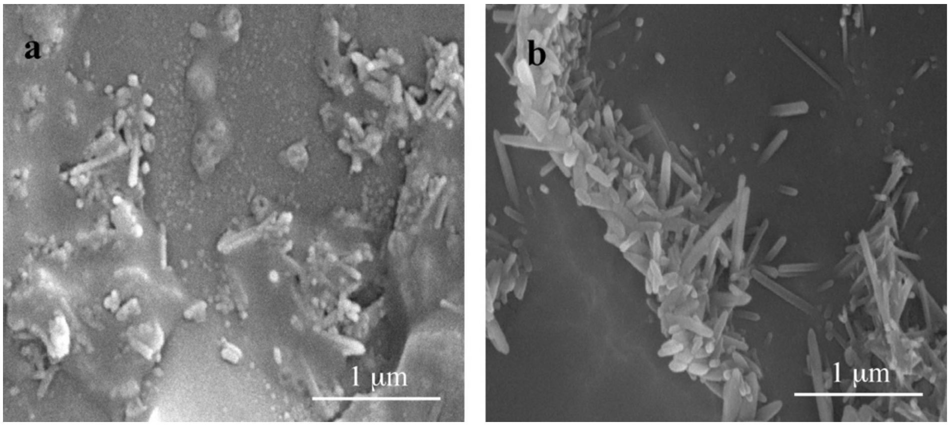

Fig. 4. FESEM micrographs of porcelain stoneware A fired at (a) 1220 °C, 0.1 h and (b) 1220 °C, 1 h.

transformation in which the SiO_4 groups combine with the AlO_6 groups to form the Al–Si spinel phase, precursor of the mullite phase. The presence of additional fluxes for B composition activates this transformation and produces a decreasing of the transformation temperature.

In a recent study Rambaldi et al.[11] determined the alumina solubility in the glassy phase as the ratio Al_2O_3:(R_2O + RO), that is a ratio between alumina and flux components. R_2O were Na_2O and K_2O, and RO were CaO and MgO. This ratio was established to be constant over the range of sintering temperatures and applicable to commercial porcelain stoneware compositions, and it was measured as 1.19 ± 0.1. The authors[11] considered that the alumina exceeding this solubility crystallizes from the glass as secondary mullite.

The A composition possesses an excess of 1.5 wt% Al_2O_3 that would produce 0.5 wt% of mullite whereas in the B composition the alumina excess was 0.41 wt% that would produce 0.1 wt% mullite. So the mullite proportion is low according to the material composition in both samples. In addition the microstructural study shown that the secondary mullite was formed in isolated zones and was kinetically limited as denoted by their increasing with the sintering time. Fig. 4 shows detailed microstructure of the secondary mullite needle-shaped crystals that grew with the sintering time. The nanometric size of the mullite crystals, <50 nm in thickness produced a large glass–crystal interface. However, the degree of agglomeration of mullite crystals reduces drastically this effect.

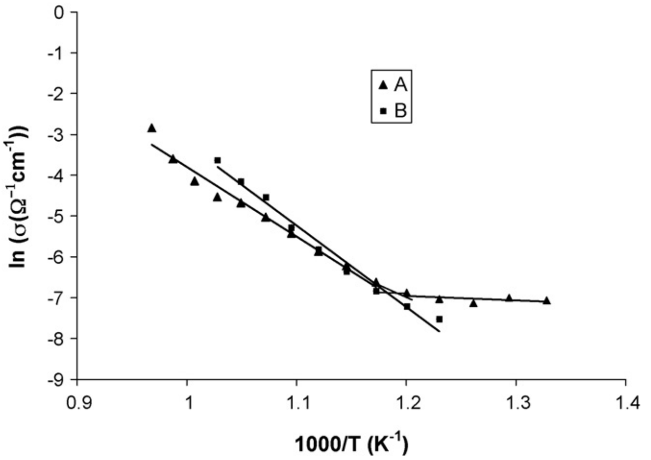

Fig. 5. Electrical conductivity vs. temperature of 1 h sintered A and B compositions.

Fig. 5 compares the electrical conductivity of sintered A and B compositions sintered for 1 h. As occurs in clay-based ceramics,[12] there was only one semicircle in the impedance spectra (not shown) which was attributed to continuous glassy phase. The charge carriers can transport along the network experiencing no significant blocking effect. For the A composition, at low temperature the conduction process may be described as extrinsic or impurity controlled and characterized by a higher conductivity and lower activation energy of conduction where the number of charge carriers taking part in the conduction process is essentially constant with temperature. In contrast for the B composition the activation energy is higher and it is related with a more homogenous glassy phase due to their higher glass forming ions content.

The higher homogeneity of the B glass matrix was a consequence of fluxes that reduce the viscosity of the liquid phase and thus the densification and the lower surface roughness was favoured. The improvement of the mechanical properties in B composition may have their origin in both the lower porosity size and the higher amount of quartz particles that stresses the glass matrix. Recently Tucci et al.,[13] reported that high mechanical properties in stoneware tiles can be attributed to both the increasing of elongated needle like mullite in low viscosity liquid phase assisted by spodumene addition and the presence of the high strength particles that embedded in the glassy matrix and behaved as hard inclusions, causing the deflecting of the crack path along the low fracture interfaces particle–matrix. In that sense the presence of higher amount of quartz particles account for the higher strength of the B composition.

4. Conclusions

The findings of this paper revealed that the glass matrix stress effect contributes to the material as the main reinforcement mechanism. The mullite reinforcement acted in a similar way as high strength particles but their nanometric contribution was quite limited by the usual mullite agglomeration appearance.

Mullite reinforcement mechanism would be more effective if the secondary mullite phase appeared as dispersed crystals in the glassy matrix.

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