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Journal of the European Ceramic Society 27 (2007) 1875–1881

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New body mixes for porcelain stoneware tiles with improved mechanical characteristics

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Abstract

Starting from an industrial body mix for porcelain stoneware tiles, part of its fluxing agent, a sodium feldspar, was replaced by the stronger fluxing agent spodumene. In addition, two alumina powders as reinforcing agents were considered: (i) a high purity alumina and, (ii) a calcined bauxite. The high purity alumina was added at 15 wt.% to the body mix, whereas the calcined bauxite (a mixture of alumina, mullite and quartz) was added at 20.5 wt.%. The resulting composite materials showed a significant microstructural improvement, with a decrease of both bulk porosity and average pores size and an increase of hardness and fracture toughness. The higher microstructural homogeneity of the systems decreased the likelihood of mechanical failure. In addition, the temperature over which sintering of the material occurs was extended and the dimensional stability of the material improved. Several of the results obtained can be attributed to the presence of spodumene which, during sintering, allows the development of a low viscosity liquid phase and favours strong links being formed between the added oxides (alumina and mullite) and the glassy phase.

Keywords: Porcelain stoneware tiles; Microstructure-final; Al_2O_3; Fracture; Mechanical properties

1. Introduction

Among ceramic tiles, porcelain stoneware is by far, the best product. Its very high density, due to selected raw materials used and the industrial fast firing cycles, confers to this class of products particular characteristics of mechanical strength and wear resistance.[1,2] This material is prevalently constituted by a glassy matrix in which bubbles of gas, developed during firing, are trapped and several crystalline phases, both residual crystals, such as quartz and feldspar, and new formed crystals, as mullite, are embedded.[3] These microstructural singularities inside a glassy matrix can lead to different toughening mechanisms. As regards, the quartz crystals can be responsible for different microcraking toughening mechanisms: (i) deflection of the crack trajectory, (ii) crack branching and sometimes, (iii) stopping of the crack.[4,5] In the toughening of the glassy matrix of porcelain stoneware material, the role both of the mullite content and the pores has been also considered.[2] On the basis of these observations, porcelain stoneware tiles, if compared with others typologies of products,[6] present a relatively high value of fracture toughness, very close in any case to the value of glass, in agreement to the glassy nature of its matrix. However, even if it has to take into account for this significant difference, the high sensitivity of the material to the stresses coming from the environment, keeps on representing a serious drawback. Scratches, cuts and large areas, from which the material has been removed, still visible on the working surface of the tiles after the polishing operation, can be attributed both to a not correct machining procedure and parameters[7,8] and to the rather low fracture toughness, not sufficient to react to crack propagation. Although many efforts have been addressed to improve the mechanical strength of these materials, crack resistance has received, until now, little consideration.

The reinforcing mechanisms, expressly investigated to obtain highly reliable structural ceramics, are based on different concepts: (i) control of flaws and, (ii) toughening. While the first approach concerns the control of the critical flaws, by analysing the process and identifying their source, the second one, acting in the microstructural feature, is addressed to achieve materials characterised by a high reliability and enhanced fracture resistance. The control of critical flaws does not seem to be a viable method, in these materials. Regarding the second approach, several ways to modify the microstructure and toughening a ceramic matrix exist: (i) toughening transforma-

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doi:10.1016/j.jeurceramsoc.2006.05.007

Table 1
Mineralogical composition of standard body mix ST

Crystalline phase	wt.%
Quartz	32
K-feldspar	11
Na-feldspar	25
Na–Ca-feldspar	3
Mica/Illite	11
Kaolinite	18

tion, (ii) in situ crystallisation of elongated second phases, (iii) addition of high strength ceramic particles, metal particles and short and long fibres and, (iv) direct metal oxidation. From this point of view, a reinforcing effect can be expected by the addition of high strength particles, such as alumina and zirconia powders.[9]

The heterogeneous microstructure characterising traditional ceramics, due both to the nature of the raw materials mixes, that have a wide range in composition, and the relatively high firing temperature, favours the conditioning of different materials and/or phases inside the matrix.[3,10] In spite to this peculiarity, attempts to reinforce this class of ceramic materials by the addition of alumina fibres, were not crowned with success. The most important drawbacks essentially consisted to obtain a not uniform dispersion of the fibres in the body mix and a too strong interface, due to the reaction fibres-matrix.[11] Recently, the addition of wollastonite fibres allowed to improve strength, toughness and reliability, even if the water absorption increased, passing from 6 to 12 wt.%, and the elastic modulus and the weight of the tiles decreased.[12] Nevertheless, these last aspects, very interesting for conventional products, cannot be proposed for porcelain stoneware tiles, the excellence of which is based on unequalled characteristics.

In the present investigation it was considered the possibility to reinforce a standard body mix for porcelain stoneware tiles, by the addition of two alumina powders: (i) a high purity alumina and, (ii) a calcined bauxite. This choice, overcoming the previously cited problems, allowed to prepare homogeneous particle-dispersed traditional ceramic composites. To decrease the refractoriness, due to alumina, a stronger fluxing agent was used, by replacing part of the fluxing agent, sodium feldspar, with the same amount of spodumene.

2. Experimental procedure

2.1. Raw materials

A standard industrial body mix for porcelain stoneware tiles, denoted ST, was used as reference material, the chemical and mineralogical compositions of which are reported in Tables 1 and 2. The mineral of spodumene (Johnson Matthey, UK), labelled S, was used to partially replace the sodium feldspar in the standard body mix, it contains 97% of α-spodumene and 3% of α-quartz. Its chemical composition is reported in Table 2.

As reinforcing materials, two alumina powders were considered, a high purity alumina (JRS 10013, Alcan Chemicals Europe, UK) and a calcined bauxite (Tarmac Central Ltd, UK), labelled in the following A and B, respectively. Their main physical-mineralogical characteristics are reported in Table 3. The single particles of A alumina are strongly grouped in round and porous aggregates, rather difficult to destroy. That is testified by the rather high value of the grain size distribution, measured by a grain size analyser (Malvers, Hydro 2000MU, UK) after an ultrasonically treatment. Alumina B is a rather fine powder, characterised by micronic and sharp particles.

2.2. Samples preparation

Four different mixes were prepared: (i) ST the reference material, (ii) $S_{10}ST$ by replacing, in the reference material, 10 wt.% of the sodium feldspar with spodumene and, (iii) $AS_{10}ST$ and $BS_{10}ST$ by adding to $S_{10}ST$, 15 wt.% of A and 20.5 wt.% of B, respectively.

The raw materials were wet milled in a laboratory milling jar for 18h, by using slips with 33 wt.% of water content. For the mixes $AS_{10}ST$ and $BS_{10}ST$, the powders A and B were added 1h before the end of the milling.

The slips were oven dried at 105 °C for 24 h and the dried cakes were crushed and then sieved through a 125 μm screen to obtain suitable powders for pressing. The test specimens, in the form of discs, for the firing tests, and bars, for the mechanical tests, were prepared by adding 6 wt.% of water to the sieved powders and pressed at 52 MPa by an uniaxial laboratory press.

The sintering behaviour was evaluated by firing, in a laboratory gradient furnace, the dried discs at 1180, 1200, 1220, 1240, 1260 and 1280 °C for 40 min (soaking time). The heating rate from room temperature to 600 °C was 60 $°C\,min^{-1}$, and from 600 °C to the different firing temperatures was $\sim 20\,°C\,min^{-1}$, holding at 600 °C for 30 min. After heating, the samples were left inside the furnace until naturally cooled to room temperature.

2.3. Experimentals

Density of green and dried specimens was geometrically determined, while for the sintered specimens Archimede's immersion technique was used. The sintering behaviour of the

Table 2
Chemical compositions, wt.%, of standard body mix ST, and spodumene S

	P.F.	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Li_2O	P_2O_5	K_2O	Na_2O
ST	3.22	72.27	17.32	0.53	0.49	0.48	0.13	–	–	2.45	2.94
S	0.20	64.00	26.00	–	0.07	0.05	–	7.60	0.17	0.08	0.15

Table 3
Properties of powders A and B

	Crystalline phases	Surface area (m^2/g)	Chemical analysis (wt.%)					
			SiO_2	Al_2O_3	Fe_2O_3	TiO_2	ZrO_2	Alkaline oxides
A	α-Al_2O_3 (99%)	0.7	0.03	99.3	0.02	–	–	0.42
B	α-Al_2O_3 (73%), α-quartz (7%), mullite (10%)	2.2	10.54	80.3	2.74	3.71	2.74	0.81

Table 4
Physical and mechanical characteristics of green and dried samples

	Density (g/cm^3)		σ (MPa)		E (GPa)		m	
	Green	Dry	Green	Dry	Green	Dry	Green	Dry
ST	2.03	1.93	1.2	3.2	0.6	3.6	5.1	6.8
S_{10}ST	2.03	1.93	1.2	2.6	0.6	3.4	8.8	5.8
AS_{10}ST	2.15	2.05	1.2	2.5	0.5	3.3	8.2	7.3
BS_{10}ST	2.10	2.02	1.2	2.3	0.6	3.2	8.4	7.1

fired test pieces was evaluated on the basis of the linear shrinkage and water absorption, the last one was carried out following the test method recommended in the Standard ISO 10545-3 for ceramic tile.

For the green, dried and fired specimens of all the prepared compositions, flexural strength was determined by using bars, 70 mm × 10 mm × 6 mm. At least twenty specimens for batch were tested using a universal testing machine (MTS, 10/M, USA), equipped with a 3-point bending fixture, 60 mm rollers span and with a crosshead speed of 5 mm min^{-1}. The modulus of elasticity was also evaluated measuring the deflection of the bars in correspondence to the middle of the surface subjected to tensile stress, by an extensometer integral with the bending fixture. The average flexural strength, σ, was calculated and Weibull's modulus, m, was evaluated via the least squares method and linear regression analysis, adopting $P_n = (i-0.5)/N$,[13] as the probability estimator.

The hardness of the materials was determined by Vickers indentation technique on a mirror finish surface by a semi-automatic hardness tester (Zwick, 3212, D), applying an indentation load of 4.91N. The fracture toughness K_{IC}, was determined by SENB technique.[14] Notches of 2mm in depth were introduced into bars 45 mm × 8 mm × 4 mm, with a diamond saw of 0.15 mm in thickness. The bars were then subjected, by the same apparatus and procedure previously described, to flexural bending test to evaluate the residual stress.

The mineralogical compositions of the fired samples were determined by X-ray diffraction analysis (PW3830, Philips, NL), for all the samples, the powder diluted with 10 wt.% corundum NIST 676 as internal standard, was side loaded to minimise preferred orientation of powdered samples. Data were collected in the angular range 10°–80° 2ϑ with steps of 0.02° and 5 s/step, the Rietveld refinements were performed using GSAS.[15]

The microstructure of the fired samples was analysed with a scanning electron microscope, SEM, (Jeol, T330, J) equipped with an energy dispersion X-ray attachment, EDS, (Noran, USA), the specimens were ground, polished and etched when appropriate, following standard ceramographic techniques.

3. Results

In Table 4 are reported the physical-mechanical characteristics of the green and dried samples. The modified formulations generally present, in dried condition, a slight decrease in flexural strength, essentially due to the introduction of non plastic component, that could have affected the brittleness of the specimens. Unlike, the values of Young's modulus do not seem to be influenced by that. The Weibull's modulus is always rather low and the variations between the green and dried specimens are not meaningful.

The firing behaviour has been evaluated by the determination of shrinkage and water absorption, WA, as a function of temperature, Fig. 1(a) and (b). The WA parameter, according to the standard ISO-1045–3, allows to define the class of the tiles. For porcelain stoneware tiles, WA has to be rather low, <0.5%. In the present study the modified mixes show at the same temperature, WA values lower than ST. All samples reach 0.00 wt.% of WA already at 1220 °C, while, at the same temperature, ST shows

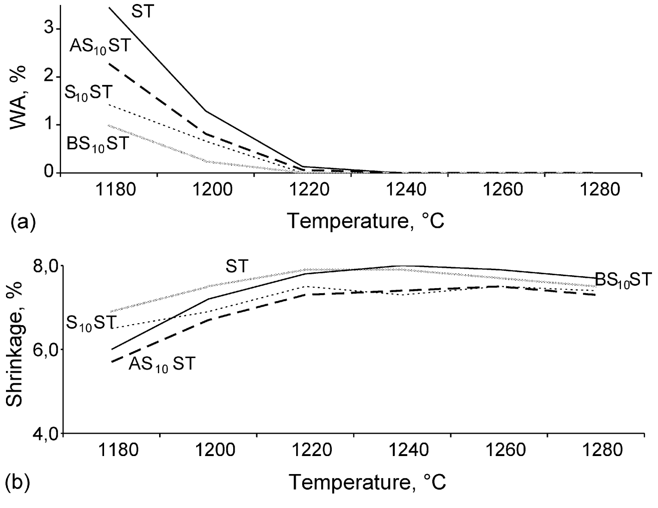

Fig. 1. Water absorption (a) and linear shrinkage (b) as a function of the firing temperatures for the tested samples.

Table 5
Physical and mechanical characteristics of fired samples

	Density (g/cm^3)	σ (MPa)	E (GPa)	m	HV$_{4.91}$ (GPa)	K$_{IC}$ (MPam$^{0.5}$)
ST[a]	2.42	78.6	58.8	8.1	5.8	1.6
S$_{10}$ST[b]	2.43	81.6	58.2	30.5	6.0	1.8
AS$_{10}$ST[b]	2.49	115.3	80.6	28.6	6.3	2.5
BS$_{10}$ST[b]	2.52	113.1	82.8	28.1	6.4	2.8

[a] 1240 °C.

[b] 1220 °C.

Table 6
Quantitative phase composition of fired samples

	Firing temperature (°C)	Quartz (wt.%)	Mullite (wt.%)	α-Allumina (wt.%)	Glass (wt.%)
ST	1240	26.1 ± 0.1	5.8 ± 0.4	–	68.1 ± 1.0
S$_{10}$ST°	1220	27.7 ± 0.1	6.8 ± 0.5	–	65.4 ± 1.0
	1240	25.9 ± 0.1	6.0 ± 0.4	–	68.1 ± 1.0
AS$_{10}$ST°	1220	20.7 ± 0.1	4.8 ± 0.3	15.0 ± 0.2	59.6 ± 0.7
	1240	17.9 ± 0.2	4.8 ± 0.3	15.0 ± 0.2	62.3 ± 0.8
BS$_{10}$ST°	1220	19.9 ± 0.2	7.2 ± 0.4	15.0 ± 0.2	57.9 ± 0.9
	1240	20.7 ± 0.2	6.0 ± 0.4	15.0 ± 0.2	58.3 ± 0.9

a WA of 0.13%. The presence of spodumene always allows to increase the sintering rate, so to obtain lower water absorption, also in the presence of refractory materials, as A and B.

The linear shrinkage of the modified compositions results to be lower and more stable with the temperature compared with ST, only BS$_{10}$ST shrinks slightly more.

In Table 5 the physical-mechanical characteristics of the fired samples are reported. The replacement of 10% of the fluxing agent, sodium feldspar with spodumene, allows to obtain a material that, even if fired at 1220 °C, 20 °C less than the firing temperature of the ST material, presents similar flexural strength and Young's modulus values, but higher fracture toughness and a significantly enhanced reliability.

The differences in phase composition between ST and S$_{10}$ST fired, respectively at 1240 °C and 1220 °C, Table 6, are not particularly remarkable, only a less amount of glassy phase and a slight increase of quartz and mullite is observed in the latter. It is interesting to note that when S$_{10}$ST is fired at 1240 °C, its phase composition is very similar to the one of ST.

Since, the differences found in the mechanical characteristics cannot be explained only on the basis of the phase composition, a careful microstructural analysis was carried out. The fracture surface of ST fired at 1240 °C, is characterised by the presence of large smooth areas, in which isolated round pores are embedded. The pore size distribution is rather wide, pores of about 50 μm in size are also present, Fig. 2a. The microstructure of S$_{10}$ST, slightly more compact in comparison with ST, is characterised by round, isolated and very narrow pores, Fig. 2b. The analysis of the etched surface revealed the presence of primary mullite derived from pure clay and secondary mullite derived from flux penetrated clay. In particular, large areas, filled of elongated secondary mullite crystals, have been observed, Fig. 3a. Furthermore, by the comparison of the etched surfaces of ST and S$_{10}$ST samples, it is evident as, in this latter, the elongated mullite crystals are rather long, of several microns

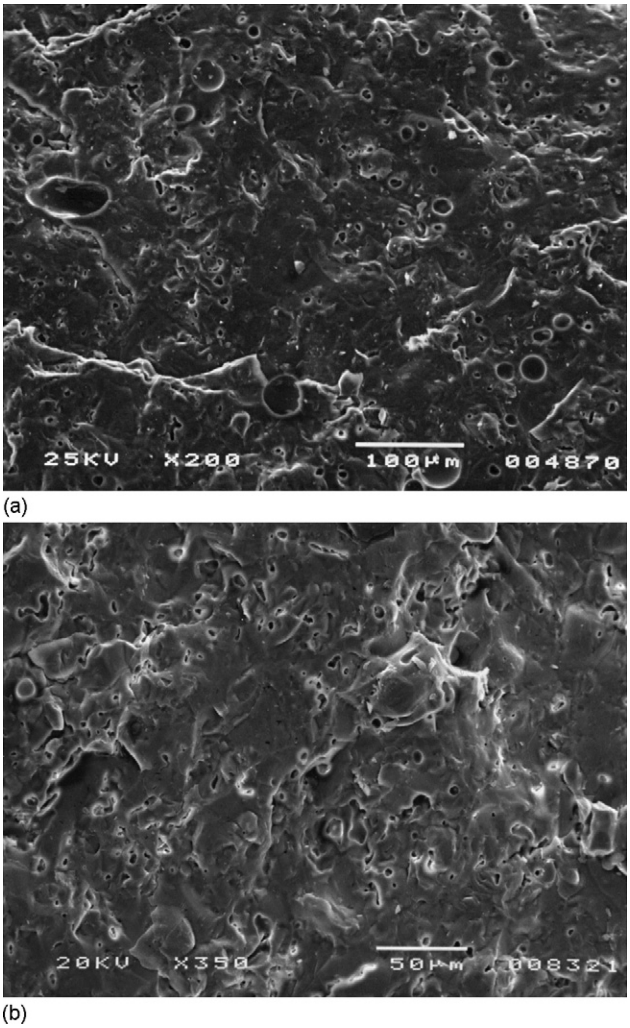

Fig. 2. SEM micrographs of the fracture surfaces of (a) ST fired at 1240 °C and (b) S$_{10}$ST fired at 1220 °C.

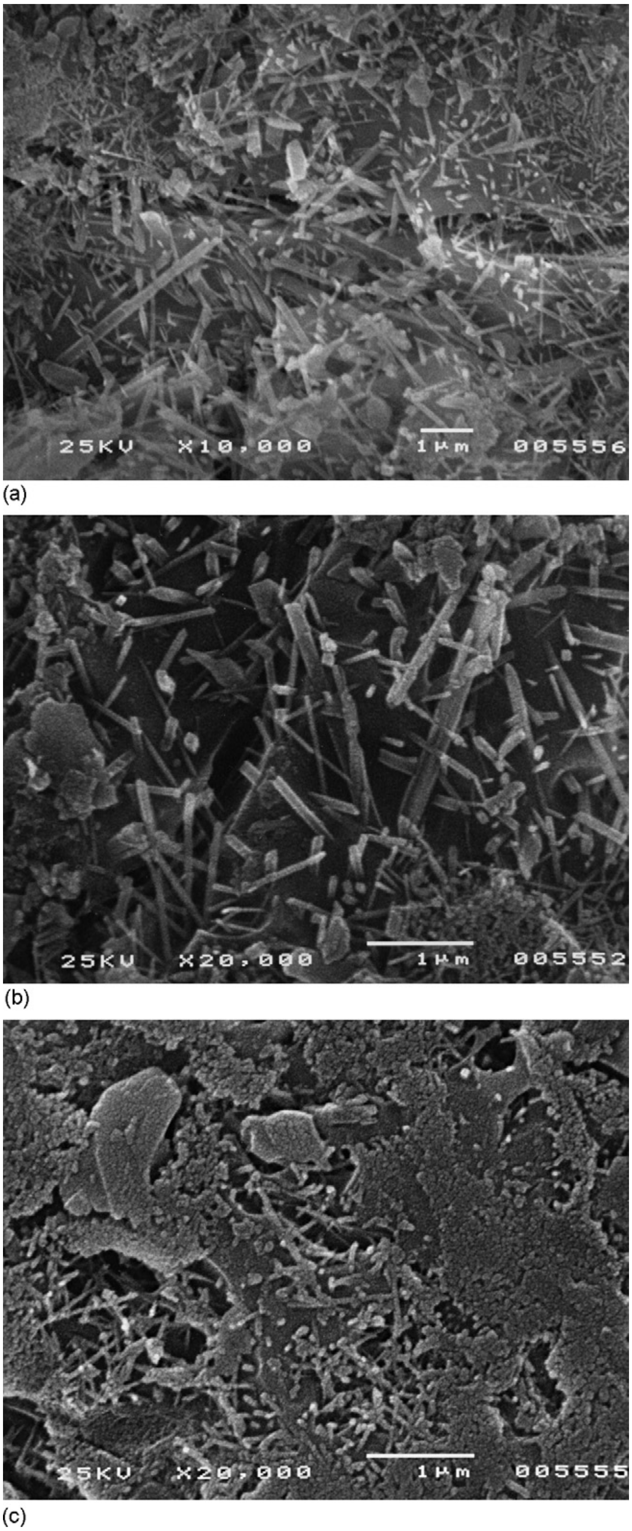

Fig. 3. SEM micrographs of the etched surfaces of (a) and (b) $S_{10}ST$ fired at 1220 °C, and (c) ST fired at 1220 °C.

Fig. 3b, while in the ST, Fig. 3c, the elongated crystals are always <1 μm.

The main difference in phase composition between ST and the alumina modified mixes, $AS_{10}ST$ and $BS_{10}ST$, fired at 1240 and 1220 °C, Table 6, is essentially due to a larger amount of crystalline phase, and the increase of the firing temperature, from 1220 to 1240 °C, does not meaningfully change the mineralogy of the modified bodies.

The presence of spodumene as fluxing agent allows to obtain a very dense material even when refractory materials, such as

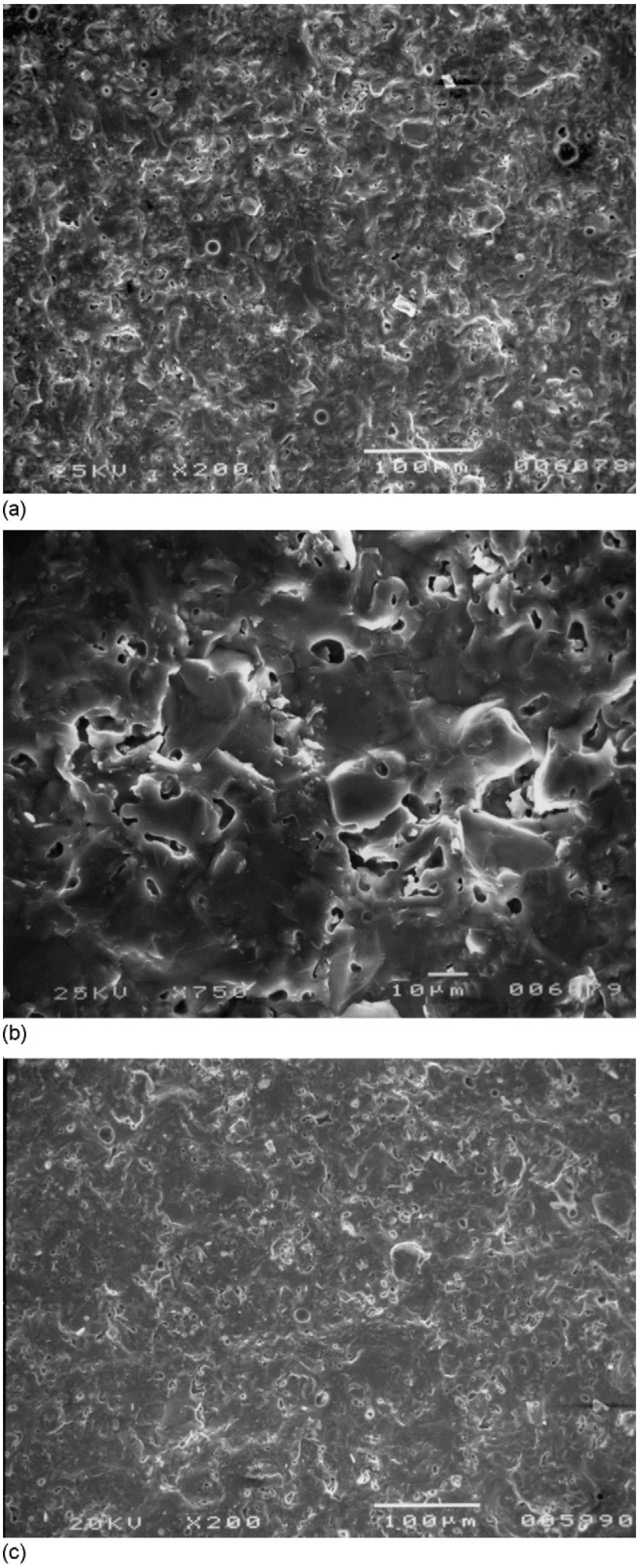

Fig. 4. SEM micrographs of the fracture surfaces of (a) and (b) $AS_{10}ST$ and (c) $BS_{10}ST$, all fired at 1220 °C.

alumina, quartz and mullite are added, as in $AS_{10}ST$ and $BS_{10}ST$ body mixes. The SEM analysis of fracture surfaces reveals the presence of very narrow pores, most of which in round form, Fig. 4a and c. For $AS_{10}ST$ also micro-areas, characterised by the presence of micropores, Fig. 4b, as relapse of the original agglomerates of alumina particles are present. In these samples rather long crystals of secondary mullite are also formed. In general, the good adhesion between alumina particle and glassy phase can be considered responsible of the increase in hardness, flexural strength and fracture toughness. The presence of a rather consistent amount of alumina also explains the drastic increase of the Young's modulus.

4. Discussion

The presence in a silicates body mix of a fluxing agent rich in lithium, as spodumene, promotes the development of a liquid phase, during its firing. That is due to: (i) low melting points of the lithium compounds, (ii) possibility to easily form eutectics and, (iii) high mobility of lithium ion. In the present study, part of the fluxing agent of the standard body mix has been replaced with the same amount of spodumene. This resulted in a higher densification at all the tested temperatures in comparison with the standard composition, without spodumene, ST, even when high refractory materials were added, such as A and B. While samples $S_{10}ST$ and $BS_{10}ST$ reached 0.0%WA and $AS_{10}ST$ 0.06%WA already at 1220 °C, STD reached 0.0%WA only at 1240 °C, having 0.16%WA at 1220 °C, a still high value for this class of material. In addition, to the development of a low viscosity liquid phase, the presence of spodumene produces a reduction of shrinkage. These phenomena, observed also by other authors,[16] can be due to the irreversible phase transformation α-spdumene–β-spodumene, that happen at about 1000 °C and it is accompanied by a large increase of volume, the density of spodumene changes from $3.2\,g\,cm^{-3}$ of the α phase, to $2.4\,g\,cm^{-3}$ of the β phase. As a consequence, the reduced shrinkage favours the dimension stability of fired products, that is particularly important for the industrial production of very large pieces. The different behaviour presented by $BS_{10}ST$, characterised by shrinkage higher than ST, is essentially due to the higher amount of alkali and iron oxides introduced in the mix with the addition of B.

Furthermore, the liquid phase, developed in presence of spodumene, results to have a lower viscosity, in comparison with ST, that is essentially due the low dimension of the lithium ion, in respect to the other alkaline ions, such as sodium and potassium.[17,18] A liquid phase having low viscosity is able to better fill the voids among particles and to form pores with smaller sizes, because the gases developed during firing can better come out of the bulk, as clearly shown in the SEM micrographs, Fig. 2b. In addition, the lower viscosity of the liquid phase allows the crystallisation of needle-shaped secondary mullite, having a rather aspect ratio. Even if, the sequence of the mullite formation in a porcelain body mix has been largely studied,[19,20] the same has not been performed for porcelain stoneware tiles body mix, that is a similar, but not identical material, and characterised by very different thermal firing cycle. It is reported,[20–22] as the secondary mullite forms by the reaction of clays with feldspar relicts. In particular, it originates from the surface of the clay relict, growing into the less viscous feldspar relicts, the more the matrix viscosity decreases, the more size of secondary mullite increases. That is in agreement with the results reported for the tested materials, the development of a low viscosity melt, due to the presence of spodumene, favours the growth of the longer mullite crystals, as reported in Fig. 3a.

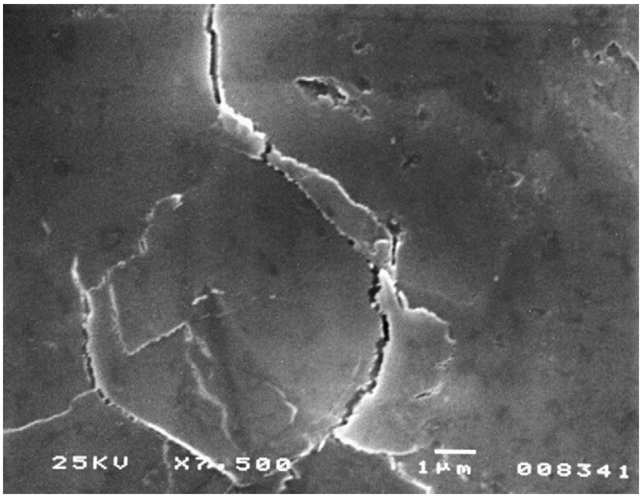

Fig. 5. SEM micrograph of the polished surface of $BS_{10}ST$. The lighter particle is alumina.

The general improvement of the mechanical behaviour of the materials modified with alumina, $AS_{10}ST$ and $BS_{10}ST$, has to be attributed to a microstructural texture, significantly different from the standard material. The modified body mixes are more compact, the presence of the spodumene, conferring to the material an enhanced stability, allows to obtain a decreasing of the average pores size. These concomitant effects allow to explain the general improvement of the mechanical strength and reliability. The higher Weibull's modulus can be attributed to the presence of a porosity homogeneously distributed in the bulk material and represents a noteworthy aspect for modular components, as porcelain stoneware tiles, especially addressed to rather severe applications.

The increase of fracture toughness found in these materials can be attributed to the presence of the high strength particles of high purity alumina and calcined bauxite. These particles well embedded in the glassy matrix behaved as hard inclusions, causing the deflection of the crack path along the low fracture energy interfaces particles-matrix, see the deflection in correspondence of an alumina grain of a radial crack emerging from the corner of a Vickers impression, Fig. 5.

5. Conclusions

The possibility to increase the mechanical characteristics of a standard body mix for porcelain stoneware tiles by the addition of alumina particles together a stronger fluxing agent, spodumene, was investigated.

The results obtained point out as the increase of crack resistance, registered for the modified body mixes, was attributed to the presence of the alumina particles. Since, the fracture toughness of these particles is higher than that of the glassy matrix, it is justified to believe that different toughening mechanisms, deflection of the crack path and crack stopping, influenced crack propagation.

Besides, the presence of spodumene, due to its capability to develop a low viscosity liquid phase, improves the sintering performances of the modified products, reduces porosity and favours the crystallisation of rather elongated needle like mullite. This last phenomena could have contributed to further increase the mechanical characteristics.

Finally it is to be underlined as the presence of spodumene is able to strongly reduce the firing temperature and shrinkage, with positive aspects both from an energetical point of view and for a possible reduce of scraps products.

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