Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 6267–6272

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Utilization of granodiorite in the production of porcelain stoneware tiles

S.M. Naga[a,*], F. Bondioli[b], M.M.S. Wahsh[a], M. El-Omla[c]

[a] *Ceramics Department, National Research Centre, 12311 Cairo, Egypt*
[b] *Department of Materials and Environmental Engineering, Faculty of Engineering University of Modena and Reggio Emilia, Modena, Italy*
[c] *Department of Geology, Suez Canal University, Ismailia, Egypt*

Received 13 March 2012; received in revised form 27 April 2012; accepted 27 April 2012
Available online 9 May 2012

Abstract

In the present study, the use of granodiorite, as fluxing agent in a body mix for stoneware ceramic tiles production, was assessed. Four batches were formulated using clay from Khaboba, and natural granodiorite from Saint Katherine, Sinai, Egypt. The batches were tailored to completely replace both feldspatic and inert components of stoneware ceramic tiles. Densification was studied according to ISO rules, while sinterability was estimated by optical dilatometry. The dependence of microstructure and mechanical properties of stoneware ceramic tiles on granodiorite content was discussed. Strength measurements showed that increasing granodiorite content the bending strength of the bodies increased. In particular the studied batches can be used for the production of industrial fast firing tiles. The obtained ceramic tiles possess properties similar to commercial ceramic floor and/or wall tiles.

Keywords: A. Sintering; B. Microstructure-final; C. Thermal properties; C. Mechanical properties

1. Introduction

The ceramic tile industry is being progressively moving its production towards new materials with excellent technical properties, i.e. porcelain stoneware tiles [1,2]. These products are manufactured using clay, quartz and large amounts of fluxes such as sodic and potassic feldspars. The high density of the porcelain stoneware tiles confers to this class of products particular characteristics of mechanical strength and wear resistance [3]. The densification of porcelain stoneware tiles proceeds throughout a viscous phase sintering, with developing of a liquid phase [4]. In the formed liquid phase several crystalline phases, both residual crystals, such as quartz and feldspar, and newly formed crystals, as mullite, are embedded [5]. The viscosity of the liquid phase is influenced by the kind of the fluxing agent used.

Feldspars, both sodic and potassic with high alkali content, are generally used as fluxing agent in the production of tiles [6,7]. Rocks of volcanic origin such as, nepheline synenite [8–10], gabbro [11,12], granite [13–16], basalt and basaltic tuffs [17–20] were used in the production of vitrified ceramic tiles fired at temperature range of 1100–1300 °C. However the high price of feldspar has a remarkable impact on the cost of the end-product. Therefore, many of the recent studies related to stoneware compositions concerned the substitution of the traditional fluxes with other low cost minerals and/or waste [16,21,22].

Based on the need to obtain less expansive materials and to improve the stoneware ceramic tiles properties together with the availability of granodiorite deposits, the present work has the formulation of industrial stoneware ceramic tile from Egyptian raw materials as its main objective. Granodiorite rock is a rock with large amount of feldspars and mica. Both feldspars and mica favor the formation of liquid phase and contribute to lower the porosity of the final product.

The study of the chemical and mineralogical composition of Egyptian granodiorite was carried out in order to

---

[*] Corresponding author. Tel.: +20 233337143; fax: +20 233370931.
E-mail address: salmanaga@yahoo.com (S.M. Naga).

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.04.081

assess its suitability for flux replacement. The densification and thermo-mechanical properties of the sintered tiles were studied in relation with their phase composition and microstructure.

2. Materials and methods

2.1. Materials

The starting materials used in the present study are clay from Khaboba, Sinia Egypt; granodiorite from Saint Katherine, Sinai Egypt, and calcined alumina (provided by Almatis Gmbh Ludwigshafen/ RH, Germany).

2.2. Processing

The raw materials were crushed, ground and finally powdered separately to pass $<90\,\mu m$ sieve. Four batches with different clay-granodiorite content were prepared (Table 1). Batch components were mixed and semi-dry pressed using a hydraulic laboratory press (Nannetti, Mignon S, 930777, Italy) under a specific force of 400 kg/cm^2. Disks of 4.0 cm diameter and 0.5 cm thickness as well as rectangles of $10.98\times5.5\times0.8\,cm^3$ were pressed to measure the physicomechanical properties. Samples were dried at 110 °C over night before firing at 1220 °C in an industrial furnace (Italy) with a firing rate of 42 °C/ min.

For the microstructure analysis by Environmental Scanning Electron Microscope (ESEM), granodiorite rock samples were crushed using a steel hammer into small grains. The obtained fresh grains were crushed in a vibrating pulverize disk grinder at a coarse setting, with oscillating disks (about 15 s); the crushed product was hand sieved using two small sieves (0.050 and 0.16 mm), and pass through a 60-mesh US Standard sieve and concentrated from the power by the panning method in a 1000 mL beaker. A strong horse shoe magnet was used to remove the magnetic minerals. Bromoform and methylene iodide, followed by setting with Cleric solution, were used to separate the investigated samples. Hot concentrated HCl, magnetic and electromagnetically separations of the heavy minerals fraction were used to separate zircon from apatite.

Table 1
Chemical analysis of the starting raw materials, mass%.

Oxide	Clay	Granodiorite	Calcined alumina
SiO_2	59.50	69.10	0.74
Al_2O_3	27.29	14.70	98.20
TiO_2	1.96	0.51	0.23
Fe_2O_3	1.00	2.54	0.41
CaO	0.22	2.74	0.27
MgO	0.20	1.67	0.07
MnO	0.03	0.04	–
K_2O	1.28	3.56	0.05
Na_2O	0.16	4.10	0.10
P_2O_5	–	0.16	–
LOI	8.20	0.78	–
Total	99.94	99.90	100.07

2.3. Characterization

Chemical analysis of the raw materials was determined using X-ray fluorescence spectrometer (AXIOS, WD-XRF Sequential Spectrometer P Analytical, Netherlands). The Environmental Scanning Electron Microscope (ESEM) was used to analyze the different minerals in granodiorite samples. The thermal behavior of the green mixtures were investigated by DTA/TG apparatus (Netzsch STA 429, Germany), at a heating rate of 10 °C/min up to 1250 °C. The dilatometric behavior of the green mixtures was determined using a vertical optical non-contact dilatometer (model Misura, Expert System Solution, HSM/ ODHT 1600/80). For this measurement, pressed samples of $15\times4\times4\,mm^3$ were heated from 20 °C to 1400 °C with heating rate of 50 °C/min.

Microstructure of the sintered samples was observed using scanning electron microscope (Jeol JSM-T20), while the phases developed during firing were followed up using XRD technique, (Philips 1730 diffractometer with a Ni-filtered Cu-Kα radiation). The densification parameters, such as water absorption, bulk density and apparent porosity, were measured according to EN ISO 10545-3 and ASTM C373-88 respectively. The coefficient of reversible linear thermal expansion was determined using a horizontal dilatometer (NETZSCH, DIL 402 EP) with a heating rate of 5°/min up to 700 °C. Three point bending strength was measured according to EN ISO 10545-4 standards using three point bending test, Gabrielli Srl 50019 Model CRAB 424, Sesto Florentino, Italy.

3. Results and discussion

3.1. Raw materials characterization

The chemical analysis of the raw materials is presented in Table 2. The main constituents of the clay are SiO_2 and Al_2O_3 in addition to minor amounts of Fe_2O_3 and alkalis (K_2O+Na_2O). Granodiorite rock consists of 69.10 wt% of SiO_2, 14.70 wt% of Al_2O_3 with some impurities, such as Fe_2O_3, CaO, MgO and TiO_2. Its total alkali content is 7.66 wt%. However, aluminum oxide represents the major constituent of the calcined alumina with trace amount of impurities such as SiO_2, CaO, Fe_2O_3 and TiO_2.

The ESEM examination showed that granodiorite is a medium to coarse grained material with hypidiomorphic granular texture. It is essentially composed of plagioclase, microperthite orthoclase, and quartz with subordinate

Table 2
Batch compositions of the ceramic tile samples, mass%.

Sample symbol	Clay	Granodiorite	Al_2O_3
A	75	20	5
B	70	25	5
C	65	30	5
D	60	35	5

amounts of biotite and hornblende. Sericite and kaolinite occur as secondary minerals with accessory minerals such as apatite, zircon and iron oxides. Plagioclase crystals occur as euhedral to subhedral prismatic crystals. It is commonly altered to kaolinized and sericite. Plagioclase crystals are twinned according to the albite (lamellar) and combined (albite-carlsbad) twinning (Fig. 1a). Secondary zonation in the plagioclase crystals is recorded by sericitized and kaolinized cores (Fig. 1b). Quartz crystals are the second most abundant mineral and occur as subhedral to anhedral crystals. They corroded both of plagioclase and orthoclase and sometimes cracked due to deformation. Quartz grains form consertal and subgrain texture display mosaic extinction (Fig. 1c). Orthoglase crystals are less abundant than plagioclase and occur as subhedral to anhedral crystals. The microperthite crystals are almost kaolinized and sericitized. Biotite, iron oxide, and zircon are found as inclusions within plagioclase. Zircon occurs as large prismatic crystals and sometimes shows zoning (Fig. 1d).

3.2. Thermal analysis (TG and DSC) of the ceramic tile batches

Fig. 2 shows the TG and DSC curves of the ceramic tile batches. Two endothermic peaks at 130 °C and 540 °C and one exothermic peak at 1000 °C were observed. The first broad endothermic peak is due to the evaporation of physically adsorbed water which corresponds entirely to the first gradually weight loss of ~1 wt%. The second endothermic peak at 450–600 °C is due to both clay dehydroxylation reaction and $\alpha \rightarrow \beta$ quartz transformation [23]. The weight loss associated to the clay endothermic dehydroxylation is ≈6.5 wt%. The dehydroxylation process is an endothermic process accompanied by a reorganization of the metakaolin octahedrally coordinated aluminum to a mostly tetrahedrally coordinated aluminum [24]. The exothermic peak at 1000 °C is due to mullite formation [25].

3.3. Sintering behavior of the ceramic tile batches

The sinterability of the green mixtures was defined by an optical non-contact dilatometer. The obtained curves allowed estimating the initial sintering temperature and the temperature of maximum sintering rate (Fig. 3). Independently from the granodiorite content, the samples initially present a thermal expansion until ≈550 °C and successively, after two decomposition steps, start to sinter at ≈1150 °C. In particular the slow and steady shrinkage behavior in the range 980–1000 °C was attributed to a transformation reaction in which SiO_4 groups combine with the AlO_6 groups to form the Al–Si spinel phase. A rapid shrinkage is then observed at a temperature higher than 1000 °C. It is due to glassy phase formation and re-crystallization of mullite phase. The increase of granodiorite content of the bodies led to the presence of additional fluxing ions, which activates this transformation and produces a decreasing of the transformation temperature. The temperature of maximum sintering rate, identified by the negative peak on the first derivate curve of shrinkage (Fig. 3), decreases (from 1220 °C for 20 wt% to 1160 °C for 35 wt%) as the granodiorite content increases. This behavior is due to the low viscosity of glassy phase which favors the enhancement of sintering kinetics. These results evidence the fluxing nature of granodiorite and suggest the possibility to perform the bodies consolidation in an

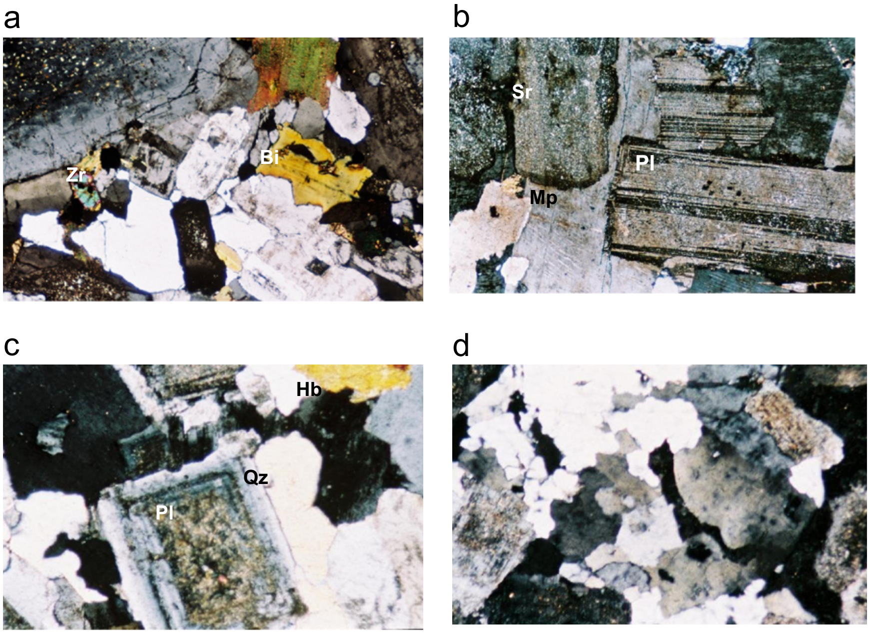

Fig. 1. ESEM micrograph of granodiorite feldspar. (a) Photomicrograph showing Biotite (Bi), Zircon (Zr), and iron oxides. Quartz monzonite, Gebel Nakhla area; magnification ×5, XPL. (b) Photomicrograph showing plagioclase (Pl), sericite (Sr), orthoclase microperthite (Mp). Granodiorite, Gebel Nakhla; magnification ×5, XPL. (c) Photomicrograph showing zoning of plagioclase (Pl), hornblende (Hb) and.quartz (Qz). Granodiorite; magnification ×5, XPL. (d) Photomicrograph showing consertal and sub-grain textures. granodiorite; magnification ×5, XPL.

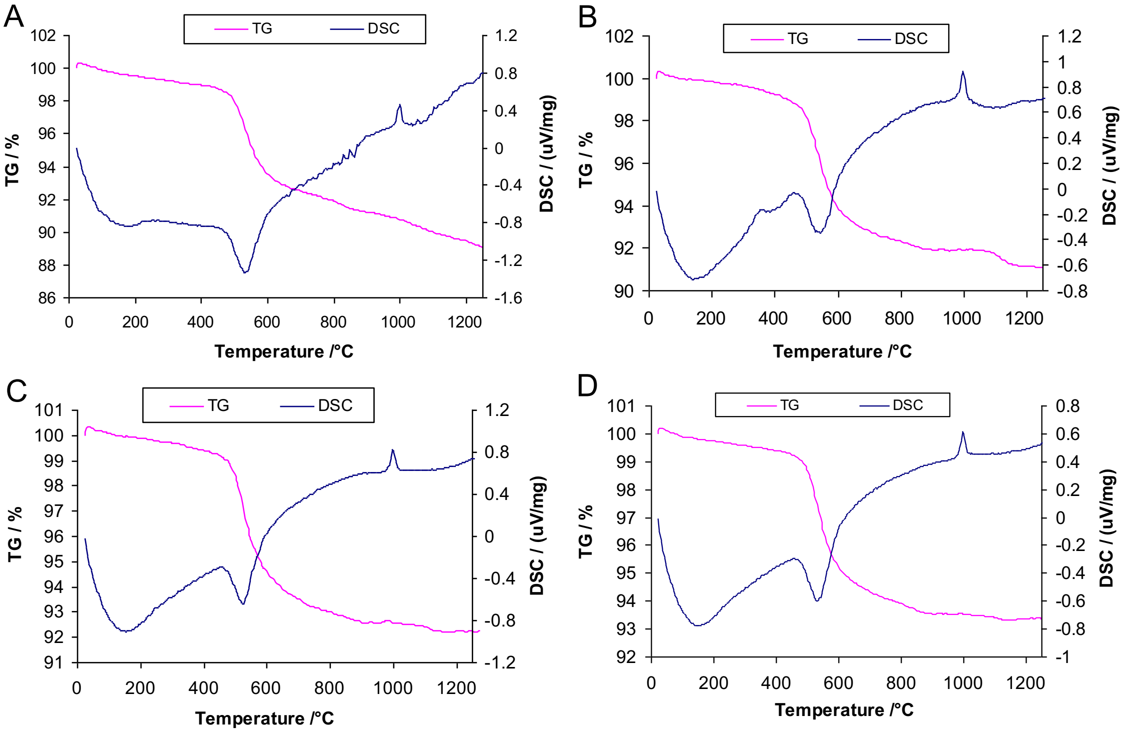

Fig. 2. DSC and TG analysis of the ceramic tile batches (A–D).

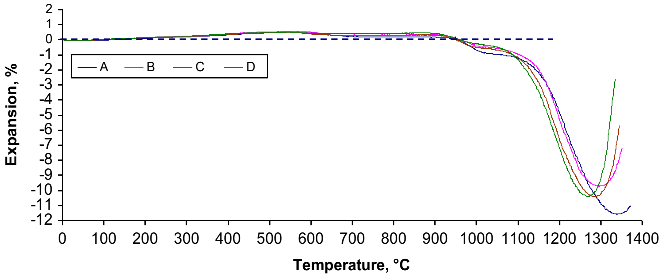

Fig. 3. Optical dilatometer curves of the ceramic tile batches (A–D).

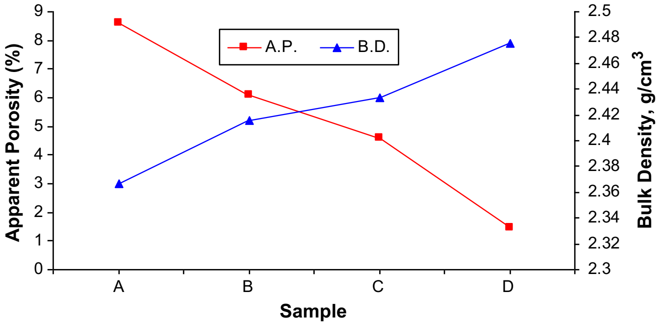

Fig. 4. Apparent porosity and bulk density of the ceramic tile samples (A–D) fired at 1220 °C.

industrial fast firing kiln for stoneware ceramic tiles (T_{max} 1220 °C, 40 min of thermal cycle).

3.4. Densification parameters

Fig. 4 illustrates the bulk density and apparent porosity of the ceramic tile samples fired at 1220 °C. It shows a decrease in the apparent porosity and an increase in the bulk density with increasing the granodiorite content of the samples. We believe that the increase in the granodiorite content led to an increase in the liquid phase content and decrease in its viscosity. The formed liquid phase fills the open pores, improves the bulk density and decreases the apparent porosity of the fired samples.

Table 3 indicates that water absorption decreases with the decrease in the apparent porosity of the bodies and the increase of the granodiorite content (from sample A to D). According to the ISO 13006 standard, ceramic tile samples B, C and D can be classified as group I (water absorption $<3\%$) and also sub-classified as group BIb (vitrified ceramic tiles, $0.5\% < $ water absorption $<3\%$). In particular sample D is very close to the water absorption limit of BIa group (fully vitrified ceramic tiles, water absorption $<0.5\%$).

3.5. X-ray diffraction

XRD patterns of the samples fired at 1220 °C (Fig. 5) indicate the presence of mullite and quartz as major phases. In addition, weak diffraction peaks of albite phase ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) were observed. The intensity of the albite peaks increases with increasing of granodiorite content.

3.6. Thermal expansion

The overall thermal expansion coefficient of the sintered samples measured between (20 °C and 500 °C) is ranging between 7.6×10^{-6} and $7.7\times10^{-6}\,°C^{-1}$ (Table 3).

Table 3
Physical, thermal and mechanical properties of the ceramic tile samples fired at 1220 °C.

Sample	WA (%)	α ($°C^{-1}$)	BS (MPa)
A	3.64	7.66×10^{-6}	26.4
B	2.51	7.62×10^{-6}	32.2
C	1.87	7.72×10^{-6}	38.9
D	0.58	7.74×10^{-6}	41.1

WA: water absorption; α: thermal expansion; BS: bending strength.

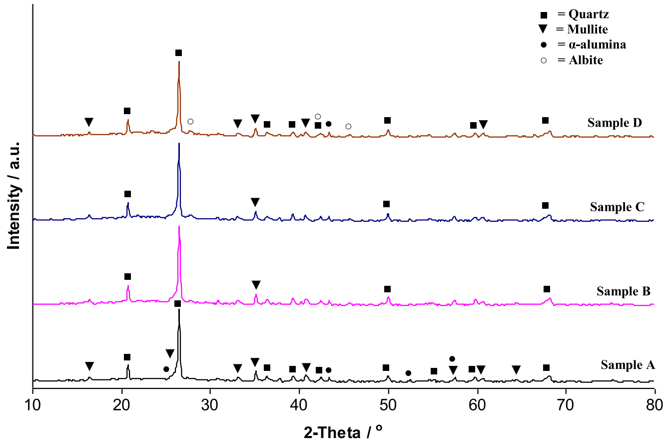

Fig. 5. X-ray diffraction of the ceramic tile samples (A–D) fired at 1220 °C.

3.7. Bending strength

The relationship between the granodiorite content and the sintered bodies bending strength was determined. The strength increased with increasing granodiorite addition from 26.4 to 41.1 MPa for the bodies containing 20 and 35 wt% granodiorite respectively. It is readily apparent from Table 3 that the strength increases with the decrease in the apparent porosity. The results confirm a typical strength–porosity exponential dependency. The bending strength of polycrystalline ceramics decreases with the grain size and pore fraction. The pores decrease the cross-sectional area at which the load is applied. They also act as stress concentrators. The increase in the granodiorite content increases the quartz content of the body. The mismatch in the thermal expansion coefficient, between quartz particles [$\alpha\approx15–26\times10^{-6}\ °C^{-1}$] and the silicate glass matrix [$\alpha\approx5–8\times10^{-6}\ °C^{-1}$] generate a compressive stress on the matrix, which leads to additional strength reinforcement in the bodies [16,21,22,25].

3.8. Microstructures

Both 20 and 35 mass% granodiorite bodies show a microstructure comprise of primary and secondary mullite, partially dissolved quartz with solution rim, glassy phase and pores especially around quartz particles, which is in agreement with the results reported by Lee et al. [26]. SEM micrograph of 20 wt% granodiorite containing bodies has revealed the presence of submicrometer mullite particles, Fig. 6(a). Secondary mullite formed from molten glassy phase is detected as elongated particles, while primary mullite formed from clay–rich relics is distinguished as large batches of fine particles. 35 wt% granodiorite containing bodies show more developed and longer needle like mullite particles, Fig. 6(b). The micrograph showed clusters or pocks of

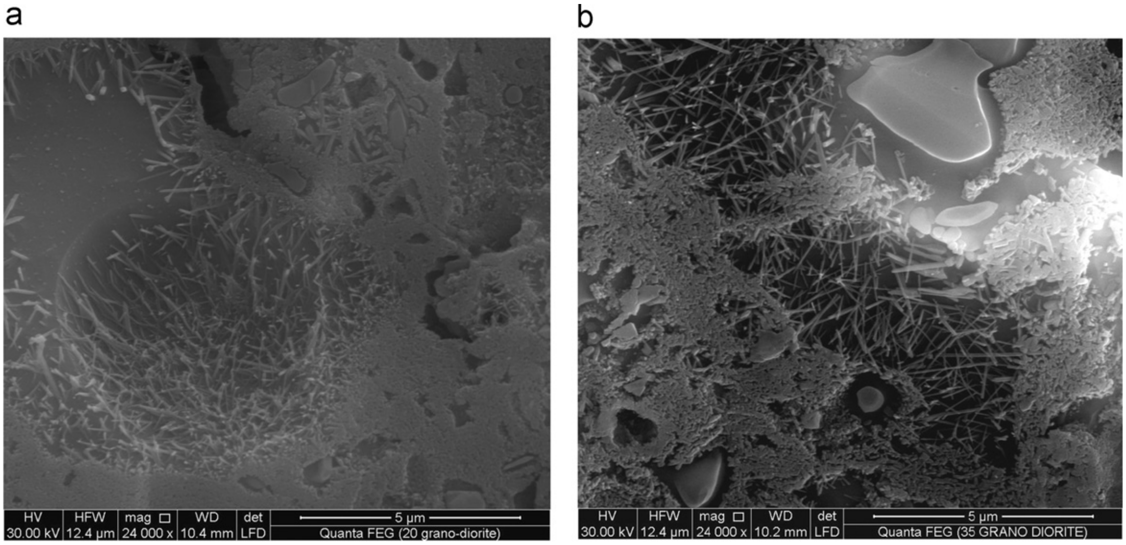

Fig. 6. SEM micrograph of 20 mass% (a) and 35 mass% (b) granodiorite bodies showing different types of mullite.

secondary mullite. Iqbal and Lee [27] suggested that such clusters are composed of several mullite needles joined together.

4. Conclusion

(1) The high content of total fluxing oxides of granodiorite favoured the maturation of the produced bodies. It is a good substitute for feldspar in porcelain stoneware tiles products that satisfy the most demanding requirements of the group BIIa (batch A) and close to group BIb (batches B and C) and group BIa (batch D) of the ISO 13006 standard.

(2) The findings of this study revealed that the strength increases with increasing granodiorite content. It confirmed a typical strength–porosity exponential dependency.

Acknowledgments

This work has been carried out within the project “Transfer of innovative technology of dry milling for high value ceramic product with low environmental impact”, Italian-Egypt executive program for scientific and technological co-operation (2008–2010), MAE. Thanks go also to Dr. Salah Abo-Bakr, department of geology, Suez Canal University, Ismailia, Egypt for Khaboba clay providing.

References

[1] T. Manfredini, G.C. Pellacani, M. Romagnoli, Porcelainized stoneware tiles, American Ceramic Society Bulletin 74 (1995) 76–79.
[2] L. Esposito., A. Tucci, D. Naldi, The reliability of polished porcelain stoneware tiles, Journal of the European Ceramic Society 25 (9) (2005) 1487–1498.
[3] E. Sánchez, Technical considerations on porcelain tile products and their manufacturing process, Part I, International Ceramic Reviews. 52 (1) (2003) 6–16.
[4] W.M. Carty, U. Senapati, Porcelain—raw materials, processing, phase evolution, and mechanical behavior, Journal of the American Ceramic Society 81 (1) (1998) 3–20.
[5] G.P. Souza, E. Rambaldi, A. Tucci, L. Esposito, W.E. Lee, Microstructural variation in porcelain stoneware as a function of flux system, Journal of the American Ceramic Society 87 (10) (2004) 1959–1966.
[6] H. Mörtel, St.. Krebs, K. Pham-Gia, Examining reaction kinetics in the fast firing of porcelain in dependence from different raw materials, cfi/Ber DKG 77 (5) (2000) 26–32.
[7] G. Klein, Application of feldspar raw materials in the silicate ceramics industry, International Ceramic Reviews 50 (1–2) (2001) 8–11.
[8] D.M. Ibrahim, E.H. Sallam, A.A. Khalil, S.M.H. Naga, Nepheline syenite-talc low temperature vitrified bodies, Ceramics International 7 (2) (1981) 69–72.
[9] F. Burat, O. Kangal, G. Onal, An alternative mineral in the glass and ceramic industry: Nepheline syenite, Minerals Engineering 19 (4) (2006) 370–371.
[10] A. Salem, S.H. Jazayeri, E. Rastelli, G. Timellini, Dilatomeric study of shrinkage during sintering process for porcelain stoneware body in presence of nepheline syenite, Journal of Materials Processing Technology 209 (2009) 1240–1246.
[11] E.H. Sallam, S.D. Naga, D.M. Ibrahim, Clay–gabbro mixtures, Interbrick 3 (2) (1987) 13–14.
[12] S.M.H. Naga, H. Mörtel, A.A.O. El-Maghraby, Whiteware bodies on gabbro concentrate fraction basis, International Ceramic Reviews 54 (5) (2005) 316–319.
[13] D.M. Ibrahim, E.H. Sallam, S.M. Naga, Effect of the degree of crystallinity of flux on tile bodies, TBI 6 (1) (1990) 7–10.
[14] M.I. Ryshchenko, L.P. Shchukina, E.Yu. Fedorenko, K.N. Firsov, Possibility of obtaining ceramogranite using quartz-feldspar raw material from Ukraine, Glass and Ceramics 65 (1–2) (2008) 23–26.
[15] I.M. Tereshchenko, G.N. Pun’ko, L.V. Serikova, Optimization of ceramic granite compositions, Glass and Ceramics 57 (11–12) 435–437.
[16] H.F. El-Maghraby, Mohamed M. El-Omla, F. Bondioli, S.M. Naga, Granite as flux in stoneware tile manufacturing, Journal of the European Ceramic Society 31 (12) (2011) 2057–2063.
[17] E.H. Sallam, A.A. Khalil, S.M. Naga, D.M. Ibrahim, China clay–basalt mixtures, Transactions and Journal of the British Ceramic Society 81 (1982) 156–159.
[18] S.M. Naga, E.H. Sallam, D.A. Abdel Aziz, Assessment of some Egyptians basalt and low – grade clays for ceramic tiles manufacture, Industrial Ceramics 13 (3–4) (1993) 143–148.
[19] S. Ergul, M. Akyildiz, A. Karamanov, Ceramic material from basaltic tuffs, Industrial Ceramics 27 (2) (2007) 89–94.
[20] S. Ergul, F. Ferrante, P. Pisciella, A. Karamanov, M. Pelino, Characterization of basaltic tuffs and their applications for the production of ceramic and glass–ceramic materials, Ceramics International 35 (7) (2009) 2789–2795.
[21] A. Tucci, L. Esposito, E. Rastelli, C. Palmonari, E. Rambaldi, Use of soda – lime Scrap – glass as a fluxing agent in a porcelain stoneware tile mix, Journal of the European Ceramic Society 24 (2004) 83–92.
[22] F. Andreola, L. Barbieri, F. Bondioli, I. Lancellotti, P. Miselli, A.M. Ferrari, Recycling of screen glass into new traditional ceramics materials, International Journal of Applied Ceramic Technology 7 (6) (2010) 909–917.
[23] J. Martín-Márquez, J.Ma. Rincón, M. Romero, Ceramics International, Effect of firing temperature on sintering of porcelain stoneware tiles 34 (2008) 1867–1873.
[24] W.M. Cam, U. Senapati, Porcelain-raw materials, processing, phase evolution, and mechanical behavior, Journal of the American Ceramic Society 81 (1) (1998) 3–20.
[25] P. Torres, H.R. Fernandes, S. Agathopoulos, D.U. Tulyaganov, J.M.F. Ferreira, Incorporation of granite cutting sludge in industrial porcelain tile formulations, Journal of the European Ceramic Society 24 (2004) 3177–3185.
[26] W.E. Lee, G.P. Souza, C.J. McConville, T. Tarvornpanich, Y. Iqbal, Muliite formation in clays and clay—derived vitreous ceramics, Journal of the European Ceramic Society 28 (2) (2008) 465–471.
[27] Y. Iqbal, W.E. Lee, Fired porcelain microstructures revisited, Journal of the American Ceramic Society 82 (1999) 3584–3590.