Sintering and mechanical properties of porcelains prepared from algerian raw materials

(Sinterização e propriedades mecânicas de porcelanas preparadas com matéria-prima argelina)

S. Kitouni, A. Harabi

Constantine Ceramics Laboratory, Mentouri University Constantine 25000, Algeria
souad0714@yahoo.fr

Abstract

Porcelain is a type of ceramics highly valued for its beauty and strength. The overall goal of this work is to utilize local raw materials within the following fractions: 37 wt.% kaolin, 35 wt.% feldspar and 28 wt.% quartz. This composition has been selected on the basis of the ternary phase diagrams (kaolin-feldspar-quartz). The densification behaviour indicated that specimens sintered at 1200 °C for 2 h with a heating rate of 5 °C/min, have a bulk density of about 2.50 g/cm^3. This value is slightly higher than that reported for the conventional porcelain products (2.45 g/cm^3). Porcelain specimens with and without calcination sintered at 1200 °C for 2 h have tensile strength values of about 45 and 73 MPa, respectively (equivalent flexural strength values of about 122 and 197 MPa, respectively). The flexural strength values of both specimens are much higher than those reported for conventional porcelains (ranged between 60 and 80 MPa). Furthermore, the value of micro-hardness of the fired samples without calcination at 1200 °C is 9.3 ± 0.2 GPa which is higher than the commercial porcelain products (5.5 GPa).
Keywords: porcelain, kaolin, feldspar, quartz, density, strength.

Resumo

A porcelana é um tipo de cerâmica altamente valorizada pela sua beleza e resistência mecânica. O objetivo geral deste trabalho é utilizar matérias-primas locais nas seguintes frações: 37% em peso de caulim, feldspato 35% em peso e 28% em peso de quartzo. Esta composição foi escolhida com base em diagramas de fase ternários (caulim, feldspato-quartzo). O comportamento de densificação indicou que amostras sinterizadas a 1200 °C por 2 h com taxa de aquecimento de 5 °C/min, tem uma densidade de cerca de 2,50 g/cm^3. Este valor é ligeiramente superior ao relatado para os produtos de porcelana convencional (2,45 g/cm^3). Espécimes de porcelana, com e sem calcinação sinterizadas a 1200 °C por 2 h têm valores de resistência à tração de cerca de 45 e 73 MPa, respectivamente (valores equivalentes de resistência à flexão de aproximadamente 122 e 197 MPa, respectivamente). Os valores de resistência à flexão de ambos os espécimes são muito superiores aos relatados para porcelanas convencionais (variou entre 60 e 80 MPa). Mais ainda, o valor da micro-dureza das amostras sem calcinação a 1200 °C é de 9,3 ± 0,2 GPa que é maior do que os produtos comerciais de porcelana (5,5 GPa).
Palavras-chave: porcelana, caulim, feldspato, quartzo, densidade, resistência.

INTRODUCTION

The most significant development in the history of ceramics many centuries ago was the production of a vitrified, translucent porcelain body in China [1]. Today, porcelain is produced in many countries and its technology is well known and described in different textbooks and papers. Although the term porcelain is sometimes applied to a variety of vitreous and near vitreous ware, it is more properly restricted to translucent vitreous ware. A wide range of triaxial ceramic compositions that are used in white ware industries basically contain clay, quartz and feldspar. The triaxial porcelain is one of the most widely studied ceramic systems. It has got diverse applications like whiteware, stoneware and insulators. Extensive research on porcelain for a long time [2-4] confirmed its complexities, so they

remain significant challenges in understanding porcelain in relation to raw materials, processing science, phase and micro structural evolution. In view of that, the raw materials used for the body compositions of porcelain can be divided into three groups of minerals, each having its own function: the clay raw materials give plasticity to the body, while the complementary non-plastic ones include melting minerals and structural ones. The clay minerals of illitic-kaolinitic or montmorillonitic origin belong to the first group and show more or less remarkable plastic characteristics with regard to their mineralogical structure and to their particle-size distributions. The melting minerals are feldspars and feldspathoids, talc, pegmatites. The feldspar is the most abundant mineral group in the world, forming around 60% of earth's crust, and is found in igneous, metamorphic and sedimentary deposits in most countries [5]. They are used

in the production of glass, ceramics and in polymer, paper and paint industries as fillers and extenders. Silica is often associated with the feldspars, as quartz in pegmatic deposits and silica in feldspathic sand deposits. Additionally, Quartz and generally quartzites are the most refractory ones of those having a structural function.

In porcelain composition, clay serves as a dual purpose of providing fine particle size and good plasticity for forming. Feldspar acts as a flux, forming a viscous liquid at firing temperature and aids in vitrification. The quartz is mainly an inexpensive filler material which remains unreactive at low temperatures of firing and forms a highly viscous liquid at higher temperatures.

In order to select the suitable raw materials, the properties of the final product had to be taken into consideration. A sufficient amount of feldspar is necessary to obtain the desired glassy phase. As in all traditional ceramics, the presence of quartz is necessary in order to decrease shrinkage. It also reduces the body tendency to warp or distort during firing, whereas, kaolin is characterized by low plasticity. Hence, the raw materials used to prepare porcelain bodies play a vital role in the ultimate product quality.

The major raw materials used in this study were derived from different Algerian deposits (kaolin was derived from Debbagh deposit, quartz derived from El Oued and feldspar was derived from Ain Barbar deposit). In Algeria, there are several factories that produce porcelain wall and floor tiles. They mainly use raw materials coming from abroad and only very limited proportions of Algerian raw materials are being used. So, the main aim of this work is an attempt to replace most of them by Algerian raw materials in order to produce porcelain which satisfies the same level required by the standards. In this way, many studies have been carried out on this Algerian kaolin as a starting material, because of its interesting characteristics and a wide range of applications. For example, this kaolin type was successfully used as a raw material for the preparation of porous ceramic supports for membranes (using kaolin and doloma mixtures) [6]. It has also been used for the preparation of mullite and zircon based ceramics (using kaolin and ZrO_2) [7]. Consequently, this kaolin is used in this study as a raw material for porcelain production.

EXPERIMENTAL PROCEDURE

The basic raw materials used for porcelain preparation are local quartz, Potassic Feldspar (PF) and kaolin. All these raw materials were derived from different deposits in Algeria. More precisely, kaolin was derived from Debagh deposit (Guelma region), Quartz was derived from El Oued region and PF was derived from Ain Barbar deposit (Annaba region).

Chemical composition is an important factor because of its effect on ceramic properties. Various techniques are employed for samples characterization. In this study, the chemical compositions of the three used raw materials were determined by fluorescence X (see Table I).

Table I - Chemical compositions of the used raw materials (wt.%).
[*Tabela I - Composição química das matérias-primas utilizada (% em peso).*]

Oxides content	kaolin	feldspar	quartz
SiO_2	37.77	60.68	86.68
Al_2O_3	35.50	10.68	0.91
Fe_2O_3	0.34	0.66	4.57
CaO	0.80	0.17	6.48
SO_3	0.95		
K_2O	0.28	>10.0	0.78
Cl	0.01		
MnO	0.89		0.09
TiO_2	0.06	0.11	0.12
Na_2O			0.48

On the basis of mineralogical, physical and chemical properties of the all raw materials, the selected composition of the porcelain body was determined without any additives. The composition of the produced porcelain was 35 wt.% kaolin, 28 wt.% quartz, and 37 wt.% feldspar. The raw material mixtures were wet milled and homogenised in a laboratory milling jar for 5 h to obtain the typical size distribution. Afterwards, the powder mixtures were oven dried at 200 °C for 2 h in an electrically operated laboratory furnace using an on/off control system. A part of the powdered batches was calcined separately at 1000 °C for 6 h to remove all types of water from the mixture so that during firing excessive shrinkage may be avoided. After drying and humidification, the mixtures were uniaxially compacted into discs shape, at 75 MPa. The dried discs or samples were subsequently sintered at 1125, 1150, 1200, 1225 and 1250 °C for 2 h. A constant heating rate of 5 °C/min was maintained in each firing. After heating, the samples were left inside the furnace until naturally cooled to room temperature. Finally, the fired samples were subjected to physical analysis.

Density of green and dried specimens was geometrically determined from their weight and dimensional measurements, which were accurate to ±0.001 g and ±0.001 mm, respectively.

The composite mechanical properties were investigated in terms of tensile strength and flexural strength. The Tensile strength testing of sintered samples at room temperatures was carried out using the diametral compression test. Generally, three samples of each composition sintered under the same conditions were tested and an average value was taken. Following previous strength testing procedures, packing strips (Manila office file) of 0.30 mm thickness were used [8]. Vickers microhardness was measured using micro-indenter. Indentations were carried out in air with loads varying from 500 to 900 g. The time period of the indentation was 15 s immediately after the indentation, the diameters of the formed indents were measured. Only well-defined indents, without chipping or cracks were taken into account.

X-ray diffraction (XRD) data were obtained from dried samples without calcination. Preferred orientation was not detected. The sample diffraction patterns were recorded at room temperature using a PW 1130/90 X-ray diffractometer (Philips) with Ni filter (Cu-kα radiation, λ = 1541.78 nm) in the range of 2θ values 10-70°.

Morphology was furthermore investigated by scanning electron microscopy (SEM). The microscopic examination was performed on fracture surfaces of fired samples, using SEM. All the samples were gold coated before their examination by SEM.

RESULTS AND DISCUSSION

All the raw materials used in the experimental bodies were chemically analysed, and the results are given in Table I. These results indicate that kaolin, quartz and PF were of the common type generally used in porcelain body with small amounts of impurities. Table I reveals that El Oued quartz had a higher Fe_2O_3 content. A small amount of colouring oxides such as Fe_2O_3 and TiO_2 is required to all components, so as to avoid the colouring pollution of the body natural colour. The amount of TiO_2 in kaolin is acceptable but may cause a yellowish colour which was not adequate for white wares. The kaolin has in addition an amount of K_2O, which conveniently forms a liquid phase that contributes to densification at higher temperatures. The quantities of the components depend on the mineralogical nature of the clays, on the clay particle size distribution and finally on their reactivity to the melting minerals. These oxides may play a significant role towards vitrification, phase transformation and mullite grain growth in the porcelain body as reported by other workers [9, 10] in their studies, where the presence of such oxides in a porcelain body and kaolin-alumina silica mixture enhances their properties.

Sintering is a process of consolidation of particles under the temperatures below the melting point (1125-1200 ºC) and caused, therefore, mostly by solid-state reactions. Sintering during firing forms solid bonds between particles. Such bonding reduces the surface energy by reducing the free surface. In this process, the grain boundaries are partially eliminated through grain growth and the pore volume is reduced, leading to a condensed mass. The temperature necessary to induce such bonding depends upon the characteristics of both starting materials and the particle size distribution. Many theories describing various stages and transport phenomena have been proposed to describe the sintering phenomenon. Solid-state sintering takes place between particles of single or multiple phases, where homogenization takes place during the sintering of mixed phases that form a single-phase product. However, in many cases, sintering takes place in the presence of a liquid phase, especially when many phases are present, and is known as liquid-phase sintering. The sintering behaviour of the fired samples was evaluated by using the vitrification curves, which present the variation in properties of a ceramic as a function of firing temperature for otherwise

identical firing schedules in terms of heating rates, cooling rates and holding times at peak temperatures. Vitrification curves allow establishing the optimum firing temperature and the firing range at which the open porosity reaches a minimum, which usually corresponds to higher values of mechanical strength [11].

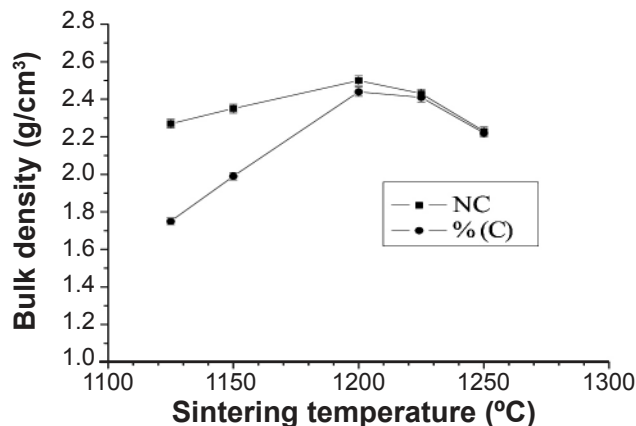The relationship between bulk density and firing temperature is shown in Fig. 1.

Figure 1: Bulk density versus the sintering temperature. NC: Samples without calcination, C: calcined samples.
[Figure 1: Densidade versus temperatura de sinterização. NC: amostras sem calcinação, C: amostras calcinadas.]

The bulk density of specimens was plotted against the sintering temperature. Fig. 1 clearly displays differential changes in bulk density through the firing temperature. The results show that the composition exhibited an increase in bulk density up to 1200 °C after which it started to decrease. In fact, this behaviour is analogous to those of all porcelain types, at higher firing temperature; the higher bulk density of porcelain bodies should be obtained. The increase in density is due to increased consolidation with temperature. Densification takes place above 1200 °C, since the thermal reaction between decomposed kaolin and feldspar starts. At 1200 °C, the maximum reached density was 2.50 g/cm³ for samples without calcination and about 2.44 g/cm³ for the calcined ones. Therefore, it can be said that the sintering of calcined samples is slightly inhibited. This may be due to the freeze of large quartz particles size or/and pores left after issue gas contain feldspar during calcination [12]. However, at temperature above 1200 °C the bulk densities are decreased and upon further heating, more porosity developments begin (Fig. 1). The significant decrease in bulk density of samples, at 1250 °C, may be most likely attributed to anisotropic grain growth or the effect of liquid phase sintering [13]. Another possibility of the decrease in bulk density after reaching a maximum can be regarded as a result of the increase in the number and/or size of closed pores in the porcelain body due to bloating. The origin of "bloating" could be O_2 released from the reaction of Fe_2O_3 to Fe_3O_4, the expansion of the air enclosed in the pores and dehydration of OH from the crystal structure of kaolonite

started at 500 °C, but was trapped in the closed pores [14]. All standard porcelains have no open porosity after regular firing, but they always contain a considerable numbers of closed pores (6-10 vol.%) [15]. According to other authors [15, 16], in the final stage of sintering, densification proceeds by the removal of closed pores by grain growth, but mainly in the presence of a small amount of liquid phase. In that case, a contact between the solid grains and liquid phase depends on surface tension forces and the wetting degree. The wetting degree is defined as the contact angle (dihedral angle) between the liquid phase and solid grains. During vitrification in ceramic bodies, with the contact angle lower, the liquid will make contact with solid grains more readily, enhancing their growth. In porcelain densification, this mechanism might be partly related to the crystallization of secondary mullite from the glassy melt but its crystal growth must be from the glassy melt, but its crystal growth must be limited to the optimum size. This mechanism could not be accepted as the predominant one in the densification of porcelain due to the creation of a large amount of liquid phase at maximum firing temperature which surrounds the grains completely.

XRD of samples sintered at 1200 °C are shown in Fig. 2. The crystalline phases (quartz and mullite) dispersed in the vitreous phase are identified by XRD in samples without calcination fired above 1200 °C. According to this, both quartz and mullite were found to be the major crystalline phases. Quartz is a residual phase derived from the as received raw materials, and mullite, formed during firing. Mullite is an important material widely used, specifically, in the refractories industry because of its low thermal expansion coefficient, excellent chemical stability and resistance to thermal shock. Mullite crystal forms from the clay matrix increases the volume about 10% [17]. The increase in volume helps to disappear any cavity or porosity or any cracks formed due to shrinkage and other thermal expansion. The primary mullite formation from the clay matrix in a porcelain body mix has been largely studied. The same has not been performed for the secondary mullite forms by the reaction of clays with feldspar relict which it originates, in particular, from the surface of the clay relict, growing into the less viscous feldspar relicts, more the
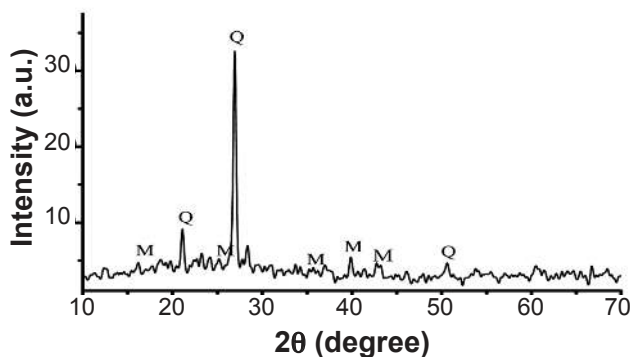

Figure 2: XRD pattern of batches without calcination (Q, quartz; M, mullite).
[Figura 2: DRX da amostra sem calcinação (Q, quartzo; M, mulita).]

matrix viscosity decreases, more size of secondary mullite increases [18, 19]. In fired samples, amorphous phase was furthermore detected in the samples studied in this work. In the main, the amount of amorphous phase in porcelains depends on the exact conditions of production, especially the firing temperature.

Densification is generally achieved by particles rearrangement and viscous flow. Many sintering mechanisms are contemporarily active (melting, pore coalescence and coarsening) due to wide range of pore and particle size in the green compacts. However, the densification appears to be rate-controlled by the solubility of solids in the liquid phase and the strong dependence of melt viscosity on temperature. As a result, at 1200 °C, densification is basically driven by progressive melting of feldspar and quartz (Fig. 1). Above 1200 °C, the decrease in densification is emphasised by coarsening phenomena, the phase composition seems to reach an equilibrium and the unique transformation are solution / nucleation of mullite and some dissolution of quartz in the liquid phase.

Figs. 3 and 4 show SEM observations on typical fracture surfaces of porcelain bodies without calcination fired at 1200 and 1250 °C. For samples fired at 1200 °C, a small amount of pores was observed as shown in Fig. 3a and pores were uniformly distributed. But it led to formation of large interconnected pores, owing to the coalescence of pores during sintering in the compact. Although, some spherical pores were observed in the specimens (Fig. 3b), most of the pores were round, but not spherical. In contrast, a higher sintering temperature led to a lower porosity due to the enhanced densification at higher temperatures. Sintering reduces the porosity because the sintering process inevitably involves the exclusion of pores [20]. SEM examinations revealed that the number of pores diminished and the size of pores increased at elevated temperatures (Fig. 4a). The shape of pores changed from irregular elongated shape to more spherical and ellipsoidal shapes at 1200 °C. Kobayashi et al. [21] also noticed changes in shape and size of pores with elevated temperature, and between the core and rim of porcelain. At high temperatures, feldspar grains are completely melted and spherical shape closed porosity increased clearly because of bloating pores (Fig. 4a). It is therefore still valid to state that the results of image analysis indicate that the porosity and pore morphology (Figs. 3a, 3b), i.e. the shape (roundness or sphericity) and the size of pore, are all positive points for better sintering (Fig. 3b). The roundness of the pores improved with temperature since the viscosity of the bodies was low enough for near spherical gas bubbles to form and retain their shapes. The technical characteristics and, in particular, mechanical strength of porcelain are closely related to the material porosity [22, 23].

In many porcelain applications, the requisites for the finished product (nearly zero water absorption, very high values of flexural strength and resistance to deep abrasion) are affected by both the choice of the raw materials and the processing conditions during the basic phases of batching, grinding, pressing, drying and firing.
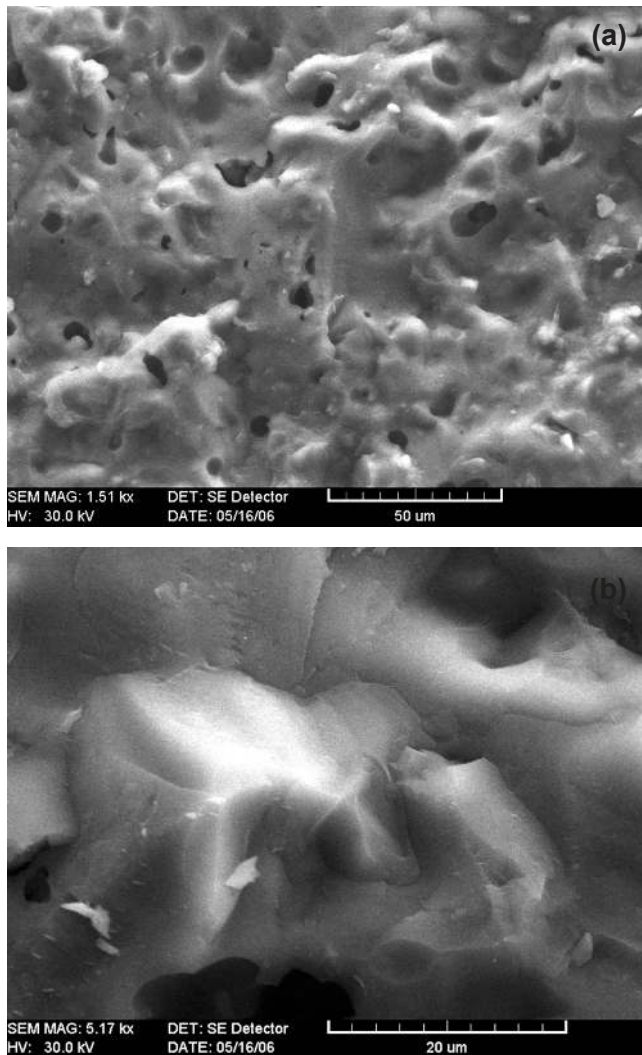
Figure 3: SEM micrographs of fracture surfaces of specimens sintered at 1200 °C (a) and details at higher magnification (b).
[Figura 3: Micrografias MEV das superfícies de fratura das amostras sinterizadas a 1200 ° C (a) e detalhes com maior ampliação (b).]

Figure 4: SEM micrographs of fracture surfaces of specimens sintered at 1250 °C (a) and details at higher magnification (b).
[Figura 4: Micrografias MEV das superfícies de fratura das amostras sinterizadas a 1250 ° C (a) e detalhes com maior ampliação (b).]

The influence of starting material composition on flexural strength of porcelain bodies have been experimentally studied by many researchers, because of its economic importance in ceramic industry. It is known that quartz grains in different sizes have significant effects on mechanical strength of porcelain bodies. Especially, it is proposed that flexural strength of the porcelains increases with an increase in inter planar spacing of quartz crystals, so the quartz is under the tensile stress, and consequently, the glassy matrix surrounding the quartz grains is a compressive stress which acts as pre-stress, improving mechanical strengthening. The pre-stressing effect due to the residual compressive stress at the glassy phase around the grain is large, which is related to the quartz grain size and the firing temperature [14]. Internal stresses arise, first, because of the difference in thermal linear expansion coefficients of α-quartz and the glassy phase and, second, because of polymorphic transformation in silica. These stresses can be
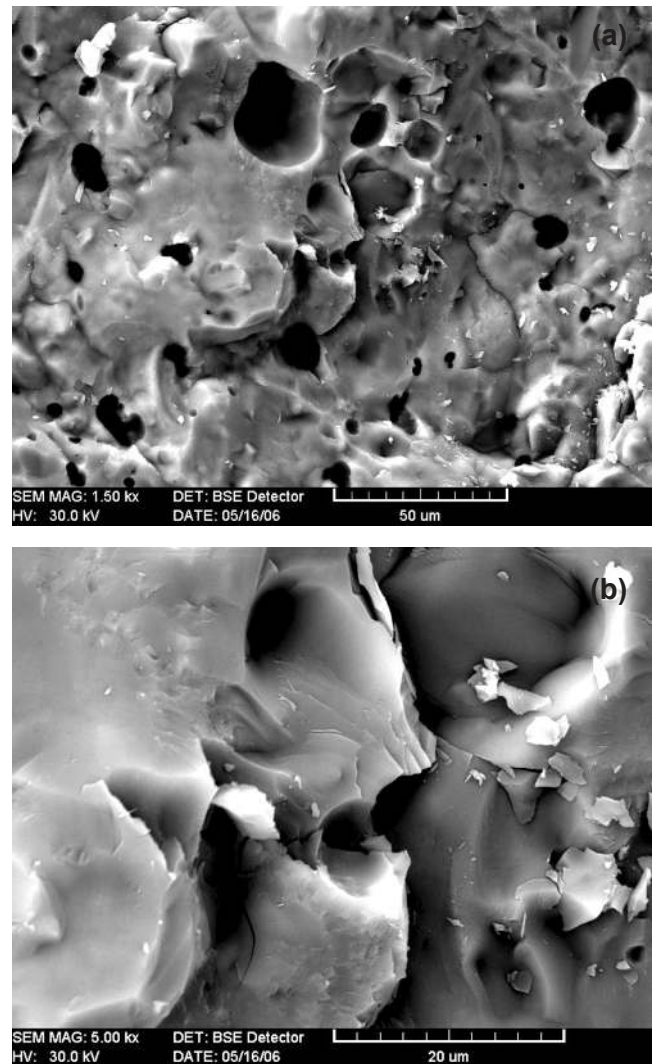
reduced substantially by decreasing dispersity of the initial and residual quartz. On the other hand, quartz makes up part of the crystalline phases of porcelain that develop the needed mechanical strength to engineering components. A considerable part of quartz passes into molten feldspar, which increases the strength of the glassy phase. A similar conclusion had been also reached that the mechanical strength of porcelain is influenced mainly by stresses set up in the glassy matrix rather than by the amount or size of mullite crystals formed [24]. The flexural strength of porcelain bodies were measured as function of temperature (T) (Figs. 5, 6). The flexural strength behaviours of calcined porcelain bodies and those without calcination are not different. Even though, the flexural strength bodies without calcination are higher than the others. It is obvious that these changes in flexural strength are related to total porosity developments in bodies. The modified formulations generally present, in

calcination, a slight decrease in flexural strength that could have affected the brittleness of the calcined specimens. The flexural strength of porcelain bodies increased with an increase in firing temperature and reached maximum values of about 122 MPa for calcined samples (Fig. 6) and about 197 MPa for samples without calcination (Fig. 5), sintered at 1200 °C. It can be noticed that the strength of fired samples increased with the increase in sintering temperature due to a more pronounced sintering process.
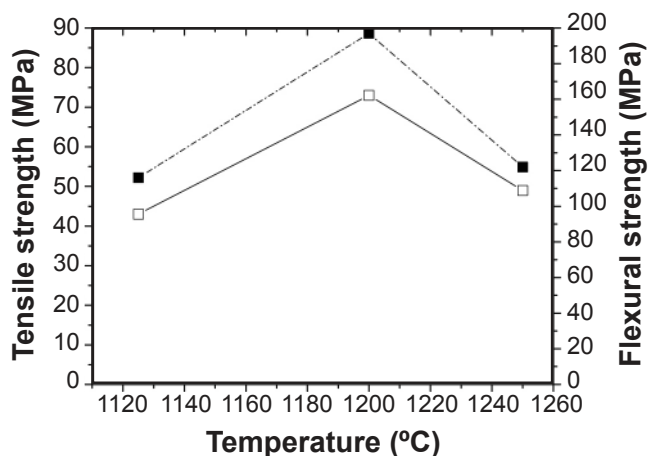

Figure 5: Tensile and flexural strength versus sintering temperature for Porcelain samples without calcination.
[Figura 5: Resistências à tração e à flexão em função da temperatura de sinterização para as amostras de porcelana sem calcinação.]
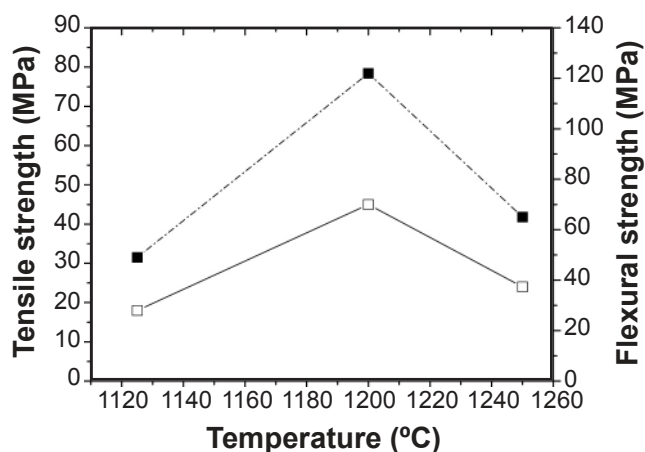

Figure 6: Tensile and flexural strength versus sintering temperature for calcined porcelain samples.
[Figura 6: Resistências à tração e à flexão em função da temperatura de sinterização para as amostras de porcelana calcinada.]

Theoretically, a maximum flexural strength may be obtained when the apparent porosity decreased to zero. After continuing the heating, the flexural strength values decreased with corresponding micro structural changes, mainly caused by porosity coalescence and liquid phase. Generally, at the higher firing temperature, the higher

flexural strength should be attained. However, after reaching the maximum temperature, the flexural strength begins to decrease due to closed porosity development (Fig. 4). The correlation between mean flexural strength and bulk density of the fired materials is well established. The mechanical strength is strongly dependent on the microstructure, especially on defects such as pores and cracks. The flexural resistance of porcelain is strictly correlated with the material porosity. The prepared porcelain with a high flexural resistance presents a very compact texture, a smooth surface with low porosity ratio and almost some coarse pores (Fig. 3b). On the contrary, surface with a wide range of pore sizes, in particular coarse and spherical, show lower mechanical performances. Generally, porosity may affect the mechanical properties of ceramic materials in two ways. Firstly, it reduces the effective cross-sectional (load-bearing) area such that the mechanical property will be dependent on the minimum contact-solid area. The minimum solid (load-bearing) area is the actual sintered or the bond area between particles in the case of stacked particles, and it is the minimum web cross-sectional area between pores in the case of stacked bubbles. Secondly, porosity leads to stress in-homogeneities (stress concentrations) near the pores such that under mechanical loading, the true stress in the material is higher near the pores than at a far distance from them [24]. The surface of porcelain presents diverse micro structural elements, either intrinsic features of the ceramic body (e.g. residual pores) or superficial defects created during the grinding process. In particular, different kinds of residual pores are usually found [22]: (a) small-sized (commonly <10 μm), spherical pores, that were probably gas-filled, so resulting insinterable during the industrial firing (Fig. 3 (a)); (b) coarse-sized (often >20 μm), irregularly shaped pores, presumably originated from coalescence of smaller pores during sintering or inherited by large defects of the green compact; (c) Discontinuities around bigger particles, partly deriving from residual stresses (e.g. polymorph transition of quartz).

The fracture surfaces morphologies of fired specimens without calcination were carefully examined using SEM techniques (Figs. 3 and 4). At 1200 °C, porous structure was observed (Fig. 3a). The first possible reason for the formation of structure might be due to entrapment of vapour derived from the volatilization. The second possible reason might be due to the decomposition of any thermally unstable material and / or the water vapour present in raw materials. The derived vapour partially trapped by viscous body may cause the formation of pores. Above this temperature, flexural strength decreased sharply (Figs. 5 and 6). This sharp decrease may be due to the increase in pore sizes and porosity ratio coupled with the bloating effect (Fig. 4a). The shape, size and linkage trend of pores with each other played an important role in the flexural strength. These irregular elongated pores decrease the flexural strength. By contrast, spherical pores formed after melting of quartz, show relatively higher strength.

The measurement of local mechanical properties is

another important technique to understand the macroscopic behaviour of prepared materials. The micro-hardness of a material is measured by pressing a rod tip into a material and finding the amount of deformation from the dimensions of the formed indenter. The indentation hardness test is probably one of the simplest methods of measuring mechanical properties. Microhardness measurements are easy to make but hard to interpret. The stress distribution under the indenter is complex, and cracking, elastic and inelastic deformation, faulting, and plastic deformation are all possible around the indentation.

In micro-hardness measurements, the discussion of errors [25] is chiefly directed toward the use of hardness measurements as a screening test to predict compressive strengths. Under ambient conditions, moisture can decrease measured hardness to about 15% below that obtained with carefully dried surfaces. Machining, grinding, and mechanical polishing work harden surfaces, and result in hardness values that are higher than one-third the bulk compressive strength. Surface preparation by cleavage and chemical polishing can alleviate this problem. To avoid cracking of ceramics, hardness tests are usually carried out with low loads (-100 g); however, this results in hardness values that are higher by 20 to 40% owing to greater proportional amounts of elastic recovery and difficulties in determining smaller indent dimensions. SEM gives deeper indent values than optical measurements. Since hardness is not an isotropic property and variations of 40 to 50% are common between different crystal planes in anisotropic materials, texture and orientation specimens must also be taken into account in some cases. Grain size affects hardness; therefore, hardness values should be expected to correlate with compressive strength only for specimens of similar grain size. However, porosity will usually not affect the hardness as much as it does the compressive strength; therefore, hardness measurements may seriously
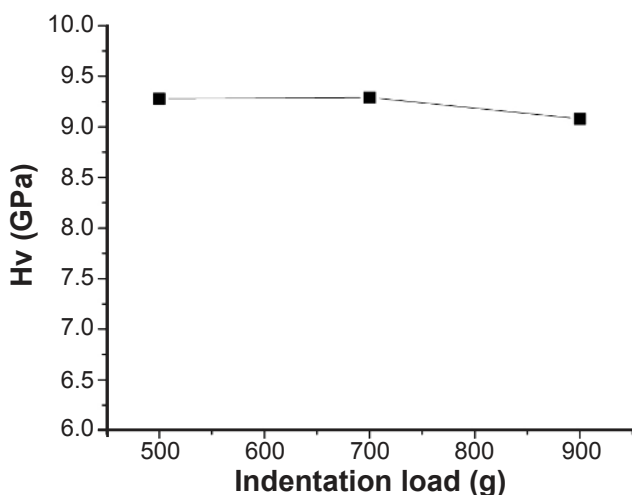
overestimate the compressive strength especially if the porosity is located primarily at the grain boundaries. As the indent becomes larger or the porosity distribution becomes finer, porosity effects on the hardness are more observable and the results may be a more accurate reflection of compressive strength.

The indentation procedure allowed determining the Vickers hardness (Hv). It is known from the literature [26] that the produced impression dimension is related to the applied load according to the hardness of the material. The evolution of the hardness as a function of the indentation load (P) is reported in Fig. 7. The micro-hardness of samples sintered at 1200 °C was 9.3 GPa for indentation load equal to 700 g. According to Moh's scale theses samples shows value near quartz which is 7 on the nonlinear Mohs scale and no far from Alumina which is 9 on the nonlinear Mohs scale. The variation of Vickers micro hardness in specimen appears to be relatively insensitive to indentation load, because the variation is less significant. Fig. 7 shows the Vickers micro-hardness (in GPa) as function of indentation load in the samples without calcination sintered at 1200 °C which include mullite and quartz. The existence of mullite increased the micro hardness of porcelain (mullite hardness $\approx$15 GPa) [27, 28]. The hardness or micro-hardness depends generally on the mechanical strength of the microstructure and if there are weak points such as defects or micro-cracks, the hardness will be lower as a result of the cracks.

CONCLUSION

Based on the results and observations presented in this work, it was possible to prepare porcelain bodies from a formula containing local Algerian raw materials. The optimum firing conditions were 1200 °C as a firing temperature and 2 h as a holding time. These conditions gave a relatively higher density (2.50 g/cm^3). The difference in densification behaviour and mechanical properties of batches of fired samples calcined and those without calcinations were studied. It has been found that both densification and mechanical properties of porcelains without calcination were significantly better than those of calcined ones. XRD revealed the formation of quartz, mullite and amorphous phases. It was also demonstrated that the porcelain body may be produced without using any addition of other kaolin types. Actually, the porcelain product present the best technical characteristics, as it is a product basically composed of crystallized phases (having higher microhardness values). A relatively higher flexural strength (about 197 MPa) was achieved. This value was in fact much higher than that obtained for conventional porcelains (ranged between 60 and 80 MPa). Moreover, Vickers micro-hardness values ranging from 9.1 to 9.3 GPa were reached.

REFERENCES

[1] W. E. Cox, "The book of pottery and porcelain", Crown

Figure 7: Vickers micro-hardness versus Indentation load for porcelain samples without calcinations sintered at 1200 °C for 2 h. *[Figura 7: Micro-dureza Vickers versus carga de indentação para as amostras de porcelana sem calcinação sinterizadas a 1200 ° C por 2 h.]*

Publ., 2nd vol., New York, USA (1944) 603.

[2] P. Rado, "The strange case of hard porcelain", Trans. Brit. Ceram. Soc. **70**, 6 (1971) 131-139.

[3] S. B. Vasquez, J. C. Valequez, M. J. R. Gausa, "Alumina addition affects elastic properties of electric porcelains", Am. Ceram. Soc. Bull. **77**, 4 (1988) 81-85.

[4] W. M. Carty, U. Senapati, "Porcelain raw materials processing, phase evolution and mechanical behaviour", J. Am. Ceram. Soc. **81**, 3 (1998) 3-20.

[5] A. Vidyadhar, K. Hanumantha Rao, "Adsorption mechanism of mixed cationic-anionic collectors in feldspar-quartz flotation system", J. Colloid Interface Sci. **306**, 2 (2007) 195-204.

[6] F. Bouzerara, A. Harabi, S. Achour, A. Larbot, "Porous ceramic supports prepared from kaolin and doloma mixtures", J. Eur. Ceram. Soc. **26**, 9 (2006) 1663-1671.

[7] A. Mecif, J. Soro, A. Harabi, J. P. Bonnet, "Preparation of mullite-and zircon-based ceramics using kaolinite and zirconnium oxide: a sintering study", J. Am. Ceram. Soc. **93**, 5 (2010) 1306-1312.

[8] A. Harabi, PhD thesis, Manchester Materials Science Centre, UMIST, Manchester, UK (1990).

[9] S. P. Chaudhuri, "Influence of mineralizers on the constitution of hard porcelains: minerological compositions", Am. Ceram. Soc. Bull. **53**, 2 (1974) 809-812.

[10] Kr. D. Swapan Das, D. Kausik, "Differences in densification behavior of K- and Na feldspar containing porcelain bodies", Thermochim. Acta **406**, 1-2 (2003) 199-206.

[11] J. Martın-Marquez, J. M. Rincon, M. Romero, "Effect of firing temperature on sintering of porcelain stonware tiles", Ceram. Int. **34**, 8 (2008) 1867-1873.

[12] C. A. Jouenne, "Traité de céramiques et matériaux céramiques minéraux (Ceramics treaty and mineral ceramic materials)", Ed. Septima, Paris, France (1990) 58-250.

[13] M. D. Snel, G. De With, F. Snijkers, J. Luyten, A. Kodentsov, «Aqueous tape casting of reaction bonded aluminium oxide (RBAO)", J. Eur. Ceram. Soc. **27**, 1 (2007) 27-33.

[14] O. Isik Ece, Nakagawa Zenbe-e, "Bending strength of porcelains", Ceram. Int. **28**, 2 (2002) 131-140.

[15] Z. D. Tasic, "Improving the micro structural and physical properties of alumina electrical porcelains with Cr_2O_3 MnO_2 and ZnO additives", J. Mater. Sci. **28**, 21 (1993) 5693-5701.

[16] R. W. Grimshaw, "The Chemistry and Physics of Clays and Allied Ceramic Materials", Ernest Benn Ltd., London, UK (1971) 685.

[17] A. I. Rashed, Y. C. Chana, M. I. Fakhrul, "Structure-property relationship in high-tension ceramic insulator fired at high temperature", Mater. Sci. Eng. B **106**, 2 (2004) 132-140.

[18] H. Y. Lu, W. L. Wang, W. H. Tuan, M. H. Lin, "Acicular mullite crystals in vitrified kaolin", J. Am. Ceram. Soc. **87**, 10 (2004) 1843-1847.

[19] Y. Iqbal, P. F. Messer, W. E. Lee, "Microstructural evolution of porcelain", J. Am. Ceram. Soc. **83**, 12 (2000) 3121-3127.

[20] N. Tsutomu, Y. Fumiaki, O. Kaneto, U. Teruo, N. Nobuyoshi, "Moisture absorption characteristics of porous calcium oxide powders produced by calcination of pulverized limestone with inorganic salts using a powder-particle fluidized bed", J. Ceram. Soc. Jpn. **115**, 7 (2007) 443-446.

[21] Y. Kobayashi, O. Ohira, Y. Ohashi, E. Kato, "Effect of firing temperature on bending strength of porcelains for tableware", J. Am. Ceram. Soc. **75**, 7 (1992) 1801-1806.

[22] M. Dondi, "The role of surface microstructure on the resistance to stains of porcelain stoneware tiles", J. Eur. Ceram. Soc. **25**, 4 (2005) 357-365.

[23] E. Sànchez , M. J. Ibáñez, J. García-Ten, M. F. Quereda, I. M. Hutchings, Y. M. Xu, "Porcelain tile microstructure: Implications for polished tile properties", J. Eur. Ceram. Soc. **26**, 13 (2006) 2533-2540.

[24] N. A. Andreeva, S. S.Ordan'yan, "Effect of quartz particle size on the strength of triaxial porcelain", Refrac. Ind. Ceram. **43**, 11-12 (2002) 3761-3768.

[25] R. W. Rice, "The compressive strength of ceramics", in Ceramics in Severe Environments, W.W. Kriegel and H. Palmour, Plenum Press, New York, USA (1971) 195-229.

[26] G. D. Soraru', P. Tassone, "Mechanical durability of a polymer concrete: a Vickers indentation study of the strength degradation process", Const. Build. Mater. **18**, 8 (2004) 561-566 .

[27] L. Sidjanin, D. Rajnovica, J. Ranogajec, E. Molnar, "Measurement of Vickers hardness on ceramic floor tiles", J. Eur. Ceram. Soc. **27**, 2-3 (2007) 1767-1773.

[28] P. Ramaswamy, S. Vynatheya, S. Seetharamu, "Significance of structure-property relationship in alumina based porcelain insulators to achieve quality", Bull. Mater. Sci. **28**, 7 (2005) 681-688.