

Effect of wollastonite addition on sintering of hard porcelain

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Abstract

Hard porcelain body with wollastonite additive was produced by the slip casting method using quartz, potassium feldspar and kaolin raw materials. Wollastonite powders were added to the porcelain formulation by replacing the potassium feldspar up to 5 wt% to explore its effect on the sintering behaviour and also technological properties of sintered end products. By means of rheological behaviour optimization of ceramic suspensions using several dispersants and sintering enhancement by wollastonite addition, hard porcelain of higher strength at lower firing temperature was obtained. By studying the effect of the additive concentration, on the firing temperatures of the hard porcelain, it is found that reducing firing temperature 25 °C without compromising its quality and thereby producing energy saving was achieved by 1 wt% wollastonite addition.

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1. Introduction

Porcelain is highly vitrified ceramic material produced from a body formulated by mixtures of clay, quartz and feldspar [1–4]. Porcelains typically have a triaxial formulation comprising about 50% clay, 25% flux and 25% filler. The clay acts as a binder for the other constituents in the green state, confers plasticity on the body for shaping and is usually kaolinite. The flux is a low melting phase that reacts with the other constituents and lowers the temperature of liquid formation in the system. This liquid permeates the microstructure leading to densification. Fluxes used commercially are alkali feldspars. The filler is reasonably stable at commercial firing temperatures and reduces distortion and shrinkage. Vitrification indicates a high degree of melting on firing which confers low (often < 0.5%) porosity and high (> 40%) glass contents on fired porcelains [4–6]. Porcelain microstructures are grain and bond type with large particles of filler (usually quartz) held together by a finer matrix, which is almost fully dense, composed by mullite crystals and a glassy phase [1–4].

Firing process is a heat treatment that gives sufficient strength to formed ceramic green body in-service condition. Activation energy is required for sintering process and it is transferred into heat energy; thereby, body temperature increased. Most of the reaction enthalpies required for sintering silicate ceramic products is between 25 and 550 kJ/kg [7]. Hard porcelain tableware ceramics have often fired in 1380–1450 °C [8]. This means that relatively high specific energy consumption and approximately 10–15 MJ is around for 1 kg porcelain in the fast firing conditions [7,9,10]. However, in practice, these values are the values 3–8 times as much as being more in industrial firing processes. In fact, only a fraction of the energy consumed in formation reactions for body the rest is devoted to the significant loss. Total cost share of energy in the production of ceramic products is enormous [7].

For keeping up competitive capability and high quality the porcelain industry needs new innovations which also require a change in firing process, sintering time, and energy cost. First improvements were achieved with introduction of the fast firing process in the past years. Here for example time for glost firing was reduced from 20 to 25 h (1965) to approximately 5 h (2000). Second improvements can be the change to the single firing technology which is rarely used at the moment for the

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Table 1
Chemical composition of raw materials.

Compositions (wt%)	Kaolin	K-feldspar	Quartz	Wollastonite
SiO ₂	47.00	66.33	99.04	52.37
Al ₂ O ₃	37.00	17.80	0.52	0.36
Fe ₂ O ₃	0.45	0.11	0.03	0.21
TiO ₂	0.50	0.03	0.02	0.01
CaO	0.30	0.18	0.02	45.80
MgO	0.20	0.28	0.02	0.36
Na ₂ O	0.20	2.83	0.10	0.24
K ₂ O	0.80	11.90	0.02	0.06
LOI*	13.55	0.54	0.21	0.59

LOI*: loss on ignition.

production of tableware. Another promising idea to decrease energy demand is the reduction of temperature during glaze firing. A reduction of energy consumption implies a decline of energy cost and a lower environmental pollution because of less CO₂ emission. An innovative way of reduction of firing temperature can be reached by addition fluxing agents for higher reactivity [11].

Optimizing the use of flux has been increasingly intensified in the ceramic industry, due to the large reduction in energy costs provided. However, instability in non-crystalline phases formed by the flux, developed during the firing process of the ceramic material will directly influence the final properties of different ceramic materials produced industrially [12]. Glassy phase determines the temperature and the firing range of ceramics formulated with silicate raw materials. Glassy phase control is a key factor to reduce firing temperature, which means a direct reduction in cost associated with the fuel. Realizing this aspect, whenever possible, industry chooses to use strong fluxes [13]. A great quantity of a glassy ingredient in the raw materials promotes liquid phase formation at a lower temperature. This resultant glassy phase has a higher reactivity in body sintering, glaze firing and frit melting, which allows a reduction of the processing temperature. Fully crystallized alkali containing raw materials (feldspars and pegmatites) have a lower fusibility due to the higher energy threshold for crystal network destruction. In respect of reactivity on heating, the fine fibred microcrystal quartz varieties are preferred because of their specific surface [14].

Wollastonite (CaSiO₃) is an important material in fine ceramics, and the tile and cement industries. A host of favourable properties such as low shrinkage, good strength, lack of volatile constituents, body permeability, fluxing characteristics, whiteness, and acicular shape render wollastonite useful in several ceramic and other applications [15]. Use of wollastonite is desired for rapid heating and cooling without cracking or warping. Other sources of CaO, such as limestone, enhance loss on ignition. Besides, wollastonite is interesting to use in white porcelain due to its very low level of colorants oxides, such as Fe₂O₃, FeO, and TiO₂ [13]. Wollastonite can be used in the production of porcelains as a CaO source. The high content of CaO decreases the liquid phase viscosity of the porcelain at high temperatures, which makes it particularly easy to generate shape distortion of the porcelain bodies [16]. Some studies

have been devoted to the creation of low firing porcelain and to reduce energy consumption [17,18]. In these studies, it was observed that addition of additives such as wollastonite to porcelain can reduce the firing temperature of the triaxial body to a great extent and also increase bending strength which was attributed to relatively advantageous microstructure [16,18].

This study presents the initial results on the use of wollastonite, in partial substitution of feldspar, for hard porcelain production. Thus, different ceramic compositions were formulated based on a wollastonite, quartz, potassium feldspar and kaolin raw materials. Samples were fired at temperatures of 1250, 1275 and 1300 °C to determine the influence of wollastonite additions on sintering temperature and post-firing properties of hard porcelain.

2. Experimental procedure

The raw materials used in the present investigation were kaolin ($d_{50}=9.822\ \mu\text{m}$ and specific surface area $11.804\ \text{m}^2/\text{g}$), quartz ($d_{50}=25.690\ \mu\text{m}$ and specific surface area $0.588\ \text{m}^2/\text{g}$), potassium feldspar ($d_{50}=18.434\ \mu\text{m}$ and specific surface area $0.961\ \text{m}^2/\text{g}$) and wollastonite ($d_{50}=14.992\ \mu\text{m}$ and specific surface area $1\ \text{m}^2/\text{g}$) provided by Ceramic Companies in Turkey. The chemical composition of raw materials, as determined by X-ray fluorescence (XRF) is shown in Table 1.

A standard composition for hard porcelain production was prepared by mixing 50 wt% kaolin, 25 wt% potassium feldspar and, 25 wt% quartz. Typically, potassium feldspar is used as fluxing agent in the industrial manufacture of hard porcelain stoneware. However, in the present study, wollastonite was chosen as another fluxing agent partially replacing potassium feldspar since fully crystallized alkali containing raw materials such as feldspars have a lower fusibility due to the higher energy threshold for crystal network destruction. Five additional body mixes were formulated on the basis of a standard composition. The major additive to the mixtures was wollastonite powder where the added amounts were 0, 1, 2, 3, 4 and 5 wt%. The prepared powder mixtures are encoded as W_0 , W_1 , W_2 , W_3 , W_4 and W_5 where, W stands for wollastonite while '0, 1, 2, 3, 4 and 5' stand for wt% wollastonite. The batch compositions of bodies with additives are given in Table 2. The suspensions of W_0 , W_1 , W_2 , W_3 , W_4 and W_5 were prepared so that each solution had solid loading levels given in Table 2, and favourable dispersant, determined as a result of rheological studies on the standard composition, was added to achieve a good dispersion of ceramic particles in aqueous solution.

The homogenisation and the rheological behaviour of the suspensions has been shown to play a significant role on the slip casting processing, and in turn, on the microstructure and

Table 2
Compositions of powder mixtures.

Compositions (wt%)	W_0	W_1	W_2	W_3	W_4	W_5
Kaolin	50	50	50	50	50	50
Quartz	25	25	25	25	25	25
Potassium feldspar	25	24	23	22	21	20
Wollastonite	0	1	2	3	4	5

properties of the final products. A well dispersed slurry can be obtained by choosing a suitable dispersant, a critical concentration of this dispersant and a proper pH value [19]. Therefore, a rheological study on the standard composition was carried out in order to optimise the processing of the slip casting by using a rotational viscometer (Brookfield DV-II model). The stability of the suspensions with different dispersants such as sodium tripolyphosphate (STPP), sodium silicates (Water glass), ammonium polyacrylate (Darvan 821A), synthetic polyelectrolyte (Dolapix FF7), carboxylic acid (Dolapix CE64) also was determined in order to select the suitable dispersant (type and wt% used) combined with ageing time correctly. The measurements were performed at room temperature.

Batches (250 g each) were prepared by milling the constituents with distilled water (1.5:1) for 10 min in a planetary ball mill and using alumina balls as grinding media. The resulting aqueous slurries were sieved to pass through a 100 μm and then poured into a plaster of Paris mould with dimensions of approximately 12.4 cm \times 2.1 cm \times 1 cm. The shaped green bodies were first air-dried at room temperature for 24 h and then oven-dried at 105 $^{\circ}\text{C}$ for 2 h. After drying, the samples were placed into an electric furnace and fired at 1250, 1275 and 1300 $^{\circ}\text{C}$ in air atmosphere. In all cases, the samples were heated from room temperature to the required firing temperature at 10 $^{\circ}\text{C}/\text{min}$, and after being soaked for 60 min at the maximum temperature, the samples were cooled in the furnace at 50 $^{\circ}\text{C}/\text{min}$ to room temperature. Indeed, hard porcelain stoneware is typically fired at high temperatures (1380–1450 $^{\circ}\text{C}$) in the industrial practice, the chosen firing temperature range under study (1250–1300 $^{\circ}\text{C}$) is lower due to fluxing characteristics of wollastonite and here its effect on sintering, microstructure and technological properties of the porcelain stoneware body composition is further investigated.

The sintering behaviour of the fired samples was evaluated by using the vitrification curves, which in this case present the variation in properties of a ceramic as a function of firing temperature. 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. Linear shrinkage and water absorption, which are directly related with open porosity, are properties easy to measure and hence, are usually used to represent the vitrification curves [2]. Since strength and porosity are two important parameters for the application of hard porcelains, they were evaluated as a function of wollastonite addition and firing temperature.

The fired samples were then subjected to various tests including linear shrinkage, water absorption, bulk density, apparent porosity and bending strength.

The linear shrinkage, LS (%), of fired samples was determined using the following equation below:

$$\text{Linear shrinkage}(\%) = \frac{l_g - l_p}{l_g} \times 100$$

where l_g and l_p is the height (mm) of green and fired product, respectively. The height was measured by sliding gage. The

linear shrinkage values obtained of five specimens were averaged for each firing temperature.

The water absorption, bulk density and apparent porosity were measured using the conventional liquid displacement method according to Archimedes's principle (ASTM C373-88), which involves drying the test specimens to constant mass (D), boiling in distilled water for 5 h and soak for an additional 24 h at ambient temperature. After impregnation, the mass (S) of each specimen while suspended in water and their saturated mass (M) is determined. The test was carried out on five representative specimens. Water absorption, WA (%), expresses the relationship of the mass of water absorbed to the mass of the dry specimen as follows:

$$\text{WA}(\%) = \left(\frac{M-D}{D} \right) \times 100$$

The bulk density, B (g/cm^3), is calculated as follows: $B = D/V$ where V (cm^3) is the exterior volume ($V = M - S$).

The open porosity, ϵ_{oo} (%), expresses the relationship of the volume of open pores to the exterior volume of the specimen and is calculated as follows:

$$\epsilon_{oo}(\%) = \left(\frac{M-D}{V} \right) \times 100$$

Phase identification was carried out by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) using Cu $K\alpha$ radiation and operating at 40 kV and 40 mA. For XRD, bulk sample (crushed < 1 cm) were scanned in the 0–90 $^{\circ}$ (2θ) interval at a scanning speed of 3 $^{\circ}/\text{min}$. The powder diffraction files belong to Mullite (00-006-0258), Quartz (00-005-0490) and Anorthite (00-018-1202) were selected from the International Centre for Diffraction Data (PDF) and used to identify the present crystalline phases.

The microstructure of fired samples was examined by scanning electron microscopy (SEM, Leo 1430 VP) using an accelerate voltage of 20 kV. For analysis of phase assemblages and morphology, the fracture surfaces of fired samples were polished with diamond pastes after initial grinding with SiC powder and water. The polished surfaces of samples were etched for 4 min in 15% HF solution, washed ultrasonically with distilled water and ethylic alcohol, dried and subsequently carbon coated. Secondary electron images (SEI) were used for microstructural examination.

Finally, bending strength (σ_f) of the fired samples having dimensions of approximately 110 mm \times 20 mm \times 10 mm was measured using Schimadzu AG-IS 100 kN in an electronic universal tester on five test pieces of by a three-point loading test with a span of 61.1 mm and at a cross-head speed of 0.05 mm/min.

3. Results and discussions

Fig. 1 shows the rheological flow curves of ceramic suspensions based on the standard hard porcelain composition (with 60 wt% solid) with different dispersant concentrations. It is seen that the flow behaviour greatly depends on the amount and type of dispersant used. Among the five different dispersants under study,

0.4 wt% of Dolapix CE 64 which provided the lowest viscosity was the most effective dispersant amount and type on viscosity of the suspensions, respectively.

It is important that the rheological behaviour of ceramic suspensions based on the standard hard porcelain composition alter with time as a function of dispersant types. The effect of aging time (0, 15 and 30 min) on the flow curves of the suspensions with various dispersant (at optimum concentration) is demonstrated in Fig. 2, where it is seen that the rheological behaviour is more dependent on aging time. The results show that the addition of some dispersants to ceramic suspensions greatly increases thixotropy and decreases stability. On the other hand, some of dispersant used under study have not more negative effect on the stability of suspensions than the others. Among these dispersants, Dolapix CE 64 is the most effective dispersant type on stability of the suspensions due to slightly increases thixotropy with ageing time.

Pyroplastic deformation and bloating occurred in the samples with wollastonite additives more than 1 wt% and 2 wt% fired at 1300 and 1275 °C, respectively, which might be because surface tension or viscosity of glassy phase is too low to resist pressure within pore, and coarsening and solubility of gases filling the closed pores due to the excessive sintering. Therefore, those samples fired in the temperature at 1275 and 1300 °C were not used for characterization as seen in Tables 3–5. However, the deformation on firing did not occurred in the samples fired at

1250 °C as the surface tension of glassy phase was high enough to avoid distortion of the pieces.

The values of linear shrinkage (LS) and water absorption (WA), after firing at the 1250–1300 °C temperature range, are presented in Tables 3 and 4, together with the corresponding open porosity and bulk density as a function of the temperature. The experimental error was estimated as 0.01% for all physical properties. Upon firing, these properties show the typical trend of a ceramic body sintered by a viscous liquid phase mechanism. It is seen in Table 3 that linear shrinkage in the samples subjected to characterisation was increased depending on both firing temperature and addition of wollastonite. As one would expect, firing shrinkage increases depending on the degree of sintering up to firing temperature reaching the optimum sintering temperature. On the other hand, the increase in shrinkage by addition wollastonite could be explained with the closing of pores in body by wollastonite for developing a greater amount of liquid phase. Porosity values decreased by addition of the wollastonite support this situation as seen in Table 4 in which the physical properties of the fired samples are summarized. With the addition of wollastonite up to 5 wt% the water absorption decreased gradually. Especially, the values of water absorption decreased gradually to 0.11% and porosity values decreased below 0.5% by the addition of wollastonite more than 2 wt% at 1250 °C firing temperature. The mean bulk density of the samples was approximately 2.41 g/cm³. Due to the lower amount of wollastonite additive, there was not a remarkable difference between bulk densities of the samples fired at 1275 and 1300 °C. However, bulk density changes were not proportional to the wollastonite addition in the samples at fired 1250 °C. The difference in the bulk density values of samples through addition of different amount of wollastonite fired at 1250 °C was caused by porosity. A solid that has a well-developed structure will become less dense as porosity increases; as a result the bulk density of the solid will decrease. As the sintering degrees increases, the size of internal pores decreases, and the packing degree increases, which results in higher values of bulk density as seen in Table 4.

It is to be noted that water absorption, open porosity and bulk density values of the samples without wollastonite fired at 1300 °C were quite similar to those of the samples with 1 wt% wollastonite added fired at 1275 °C, and the values of the samples without wollastonite fired at 1275 °C was also quite similar to those of the samples with 1 wt% wollastonite added fired at 1250 °C. The results indicated that firing temperature decreased about 25 °C by addition of 1 wt% wollastonite. To

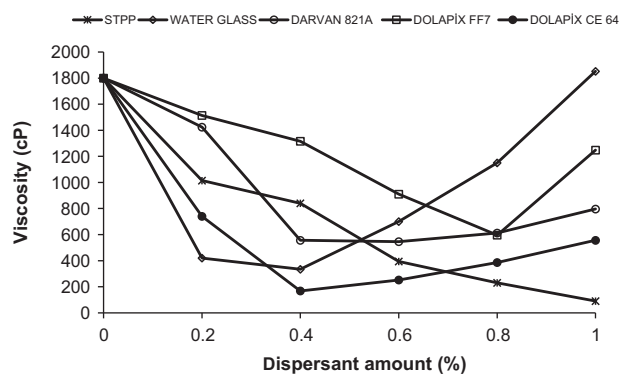


Fig. 1. The effect of dispersant type and amount on the rheological behaviour of suspensions (with 60 wt% solid).

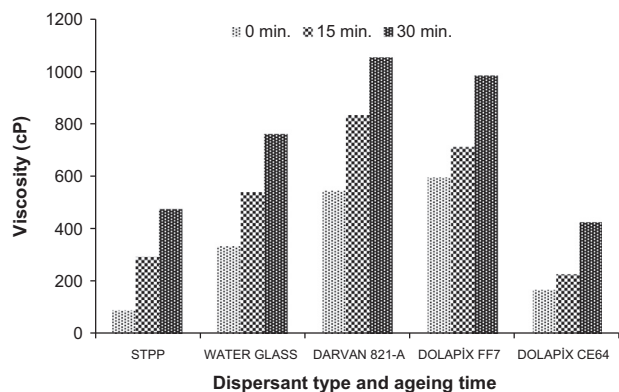


Fig. 2. Viscosity of suspensions as a function of ageing time (0, 15 and 30 min).

Table 3
The linear shrinkage of fired samples at different temperatures.

Firing temperature (°C)	W ₀	W ₁	W ₂	W ₃	W ₄	W ₅
1300	10.97	11.23	a	a	a	a
1275	10.50	11.08	10.46	a	a	a
1250	10.40	10.46	10.35	11.50	11.20	11.58

a Could not be measured owing to the deformation and bloating effect occurred.

Table 4
Some physical properties of fired samples at different temperatures.

Samples	Water absorption (%)			Porosity (%)			Bulk density (g/cm ³)		
	1250 °C	1275 °C	1300 °C	1250 °C	1275 °C	1300 °C	1250 °C	1275 °C	1300 °C
W ₀	2.03	0.78	0.54	4.79	1.88	1.29	2.36	2.42	2.41
W ₁	0.77	0.54	0.27	1.90	1.30	0.65	2.42	2.41	2.41
W ₂	1.34	0.52	a	3.18	1.26	a	2.37	2.42	a
W ₃	0.18	a	a	0.43	a	a	2.41	a	a
W ₄	0.16	a	a	0.38	a	a	2.40	a	a
W ₅	0.11	a	a	0.27	a	a	2.40	a	a

^aCould not be measured owing to the deformation and bloating effect occurred.

Table 5
Bending strength values of fired samples at different temperatures.

Firing temperature (°C)	W ₀	W ₁	W ₂	W ₃	W ₄	W ₅
1300	14.24	19.35	a	a	a	a
1275	16.46	17.45	12.30	a	a	a
1250	13.15	16.67	15.24	18.09	24.39	30.56

^aCould not be measured owing to the deformation and bloating effect occurred.

explain the lower firing temperatures it is proposed that wollastonite, providing higher amounts of SiO₂ and CaO in glassy phase, facilitates sintering by viscous flow, without significantly changing the viscosity of the glassy phase. In fact, a higher amount of CaO in glassy phase increases the surface tension of glassy phase. Therefore, wollastonite can provide a lower temperature of vitrification, without compromising the resistance of pyroplastic deformation.

As indicated in Table 5, the bending strength of the samples without wollastonite was in the range of 12.24 to 16.46 MPa and the highest bending strength value obtained was 16.46 MPa in the samples fired at 1275 °C. When the changes in the strength values of samples by addition of wollastonite analysed, bending strength values increased at all temperatures for 1 wt% wollastonite addition and the samples having 2 wt% wollastonite addition for the temperature range studied showed slightly lower strengths than those containing 1 wt% wollastonite. Furthermore, with the addition of wollastonite more than 2 wt% in the samples fired at 1250 °C, the bending strength increased gradually and the maximum value of bending strength was obtained as 30.56 MPa at 5 wt% wollastonite addition. Consequently, the differences between the strength values of the samples shown in Table 5 are caused by the reasons such as difference in porosity values and the greater amount of glassy phase induced by the wollastonite.

The usual methods, used for the evaluation of the degree of sintering, are the linear shrinkage, LS, and the water absorption, WA, of samples. These methods, however, give incomplete information about densification. Fig. 3 shows the variation of LS and WA of samples without and with 1 wt% wollastonite addition as a function of firing temperature at the 1250–1300 °C range. The water absorption, directly related to open porosity, depicts a similar trend to linear shrinkage, which increases, decreases depending on open porosity reduction with the increasing temperature. These

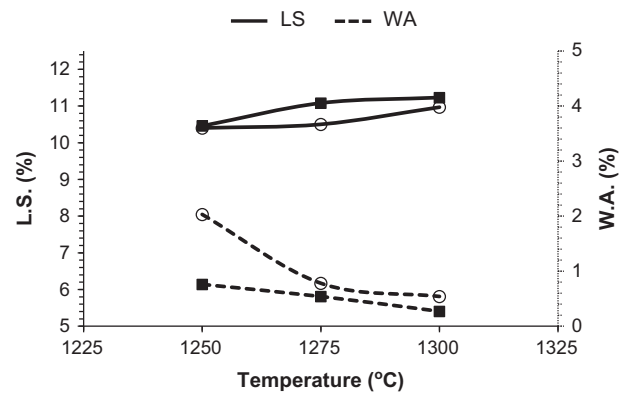


Fig. 3. Linear shrinkage (LS) and water absorption (WA) in the samples as function of firing temperature (○: W₀; ■: W₁).

observations are comparable with those of Martin-Marquez et al. [2]. Ceramic pieces must have water absorption lower than 0.5% to be classified as porcelains [13]. Thus, the firing curve showed the firing ranges between 1275 and 1300 °C for fired samples (except 1275 W₀), which were formed by values of water absorption about 0.5%. On the other hand, considering the water absorption values in Table 4, they are seen below 0.5% in the samples with wollastonite additives above 2 wt% and fired at 1250 °C. The optimum vitrification range is also achieved when open porosity reaches a minimum value, which usually corresponds to higher values of mechanical strength. Firing above vitrification range results in a drastic fall of the mechanical properties due to forced expulsion of the entrapped gases, resulting in blisters and bloating. The open porosity decreases gradually with the increasing temperature; however, the mechanical strength does not differ similarly (Fig. 4). The lowest porosity and the highest mechanical strength values are observed with samples above 2 wt% wollastonite addition that fired at 1250 °C (Table 4). Considering all results presented above, incorporation above 2 wt% wollastonite into porcelain bodies for a corresponding amount of potassium feldspar at the 1250 °C, improves the mechanical properties and decrease water absorption and open porosity gradually. Thereby, firing temperature of 1250 °C is defined as the optimum.

Considering the samples that have similar physical properties, microstructure and phase analysis were carried out only without wollastonite additives and with 1 wt% for the

temperature range studied, and 5 wt% wollastonite additive samples fired at 1250 °C, which gives the best results.

The XRD patterns of fired samples for the temperature range studied are given in Fig. 5. All the peaks due to a given phase have been labelled. The phase composition of the sample without wollastonite and that fired at 1250 °C (1250W₀) consisted of quartz, mullite and glassy phase. With 1 wt% wollastonite addition (1250W₁), no change in phase composition was observed. On the other hand, it was observed that peak intensities, belonging to quartz phase, decreased by the addition of wollastonite, which may be illustrated as crystalline SiO₂ turns into liquid phase by dissolution of silica in the feldspatic glass. With the addition of 5 wt% wollastonite (1250W₅), anorthite as another crystalline phase besides mullite and quartz, and also raised glassy phase was observed while intensity of crystalline peaks decreased. The results revealed that added wollastonite was responsible for the appearance of anorthite, an extra crystalline phase besides mullite and quartz, and appearing

by the reaction of alumina silicates with CaO released from decomposition of wollastonite. When the firing temperature was increased to 1275 °C from 1250 °C, it was observed that intensity of mullite peaks increased slightly; however, there was not a remarkable difference in the peak intensities belonging to quartz phase. Amorphous phase existence decreased by the addition of 1 wt% wollastonite in the samples fired at 1275 °C; however, there was not a remarkable difference in intensity of crystalline phase peaks. When the firing temperature was increased to 1300 °C from 1275 °C, a high resemblance between XRD pattern of the sample without wollastonite fired at 1300 °C and that of the sample with 1 wt% wollastonite additive fired at 1275 °C was determined. This situation supports “firing temperature decrease of about 25 °C by addition of 1 wt% wollastonite” just as stated before as a result of the physical tests. On the other hand, there is an increase in the intensity of diffraction peaks of mullite and decrease in the intensity of the diffraction peaks of quartz by the addition of 1 wt% wollastonite in the samples fired at 1300 °C. Moreover, partial dissolution of quartz due to wollastonite addition at this temperature also contributes to an increase of glassy phase. Furthermore, from all samples listed in Table 5 the 1300 W₁ sample is the one showing the highest value of bending strength. Concerning mechanical properties of porcelain bodies, several theories have evolved, which assume that strength can be attributed to factors such as mullite content and morphology. Thus, in a recent paper Martin-Marquez et al. [20] have pointed out that bending strength increases with increasing mullite content. Consequently, the addition of 1 wt% wollastonite at this temperature had a positive effect on the increase of mullite content.

Figs. 6 and 7 show SEM observations on the fracture surfaces of the porcelain samples fired for the temperature range 1250–1300 °C. It was observed that the typical grain and bond microstructure of porcelain consisting of quartz grains was held together by a bond that is compact and dense, composed by mullite

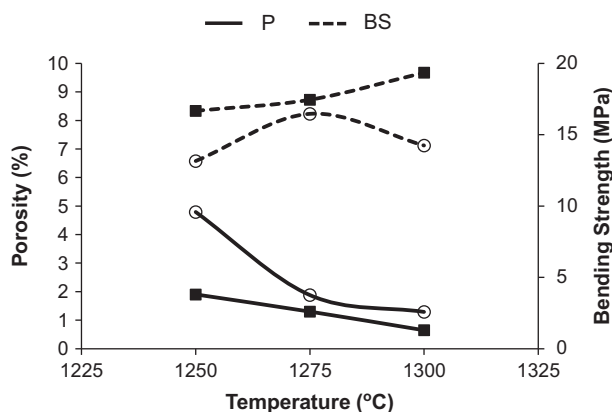


Fig. 4. Porosity (P) and bending strength (BS) in the samples as function of firing temperature (○: W₀; ■: W₁).

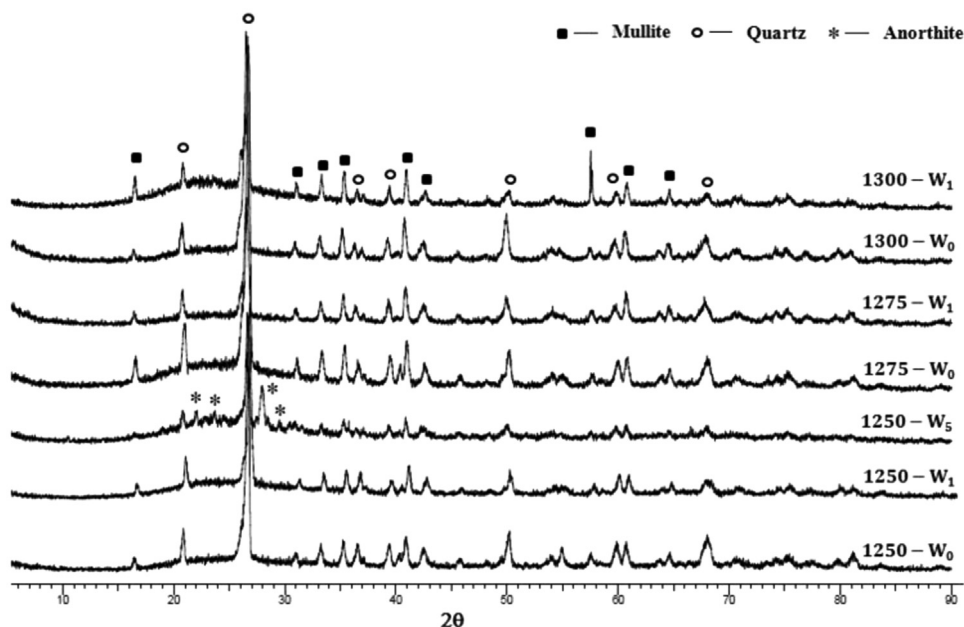


Fig. 5. The XRD patterns of fired samples at the different temperatures.

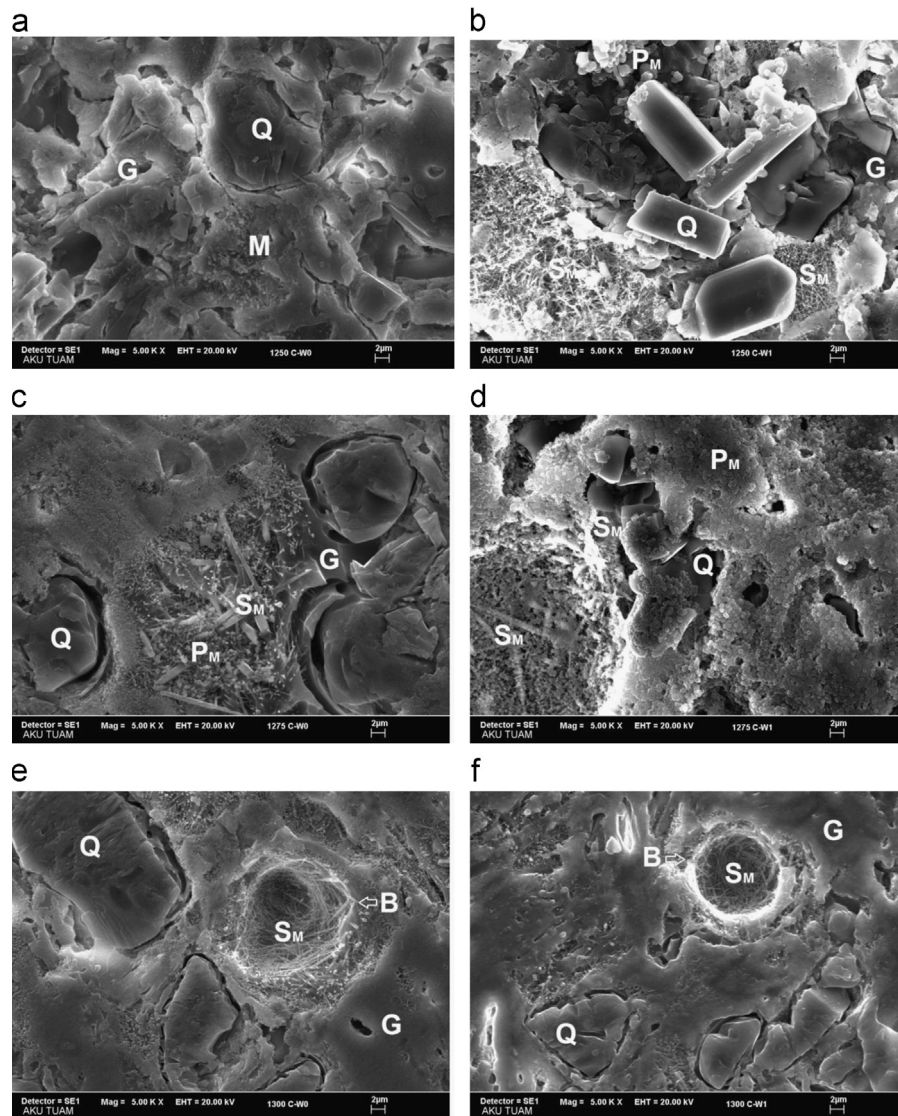


Fig. 6. SEM observations on the fracture surfaces of the samples fired in the different temperature; (a) 1250W₀, (b) 1250W₁, (c) 1275W₀, (d) 1275W₁, (e) 1300W₀, (f) 1300W₁ (G: glassy phase, Q: quartz, M: mullite, P_M: primary mullite, S_M: secondary mullite, B: bloating).

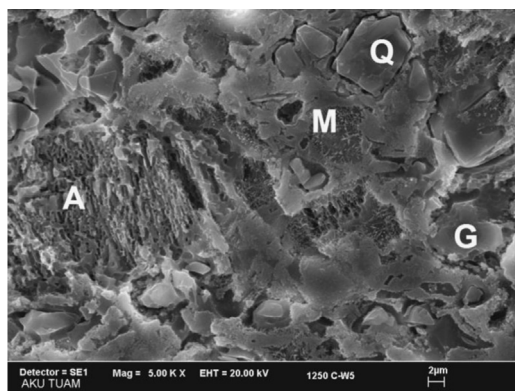


Fig. 7. SEM observations on the fracture surfaces of the samples fired in the 1250 °C with addition of 5 wt% wollastonite. (G: glassy phase, Q: quartz, M: mullite, A: anorthite).

crystals and a glassy phase in the samples with and without wollastonite fired at 1250 and 1275 °C (Fig. 6a–d). The microstructure of the sample fired at 1300 °C (Fig. 6e and f) was more

compact and dense than that observed at lower temperatures because of the liquid phase formed from the fluxing agents and also large rounded pores within microstructure due to onset of bloating were clearly identified by SEM micrographs. However, needle-like mullite crystals showing an aspect ratio in the 10:1 interval ($\sim 2 \mu\text{m}$ long and $\sim 200 \text{ nm}$ wide) were also observed in all the samples exposed to microstructure examination. On the other hand, anorthite as another crystalline phase was introduced to this traditional porcelain microstructure by addition of 5 wt% wollastonite as shown in Fig. 7 and also found in the XRD results before.

4. Conclusions

The use of wollastonite (partially replacing potassium feldspar) in this work reached a lower firing temperature, without occurring pyroplastic deformation of parts at lower temperatures. The reduction of the firing temperature obtained for wollastonite bodies was explained by a higher amount of glass phase, compared to feldspar body. The wollastonite flux improved the viscosity of the

glass phase by increasing the amount of calcium oxide in it, which allowed a larger firing range. This is a consequence of a higher level of CaO (and a higher distribution of CaO in the microstructure) which increases the surface tension of glass phase. The results indicated that firing temperature giving rise to porcelain with similar technological properties decreased of about 25 °C by addition 1 wt% of wollastonite.

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