

Effect of spodumene addition on pyroplastic deformation of porcelain stoneware

Tuna AYDIN^{a,*} and Alpagut KARA^{b,c}

^aKirikkale University, Engineering Faculty, Metallurgy and Material Engineering Department, 71451, Kirikkale, Turkey

^bAnadolu University, İki Eylül Campus, Department of Material Science and Engineering, 26555, Eskisehir, Turkey

^cCeramic Research Center, 26555, Eskisehir, Turkey

Lithium aluminosilicates, such as spodumene, have been used as raw materials in the production of thermal shock resistant whiteware and sanitaryware. The presence of spodumene causes enhancement of mullitization and imparts better physical and mechanical properties to ceramics. In this study, the influence of Li_2O -content on the properties of a standard porcelain stoneware body was investigated. Sodium feldspar was replaced by the spodumene in varying amounts (up to 4 wt. %). The results showed a significant microstructural improvement, the presence of spodumene which, during firing, allows the development of a low viscosity liquid phase with a decrease of closed porosity, also with increasing bulk density and bending strength.

Key words: Porcelain stoneware, Spodumene, Pyroplastic deformation, Sintering.

Introduction

A glass-bonded porcelain stoneware material has excellent technical performances for ceramic tiles such as mechanical, wear, frost and chemical resistance. In the last years, the development of porcelain stoneware tile production has increased more than other ceramic materials; in fact, the technical properties of porcelain stoneware, has coupled with even more improved aesthetic appearance, a prominent role on the tile market [1]. Porcelain stoneware bodies consist of a mixture of clays (30-40%), alkaline feldspars (40-50%), and quartz sands (10-15%) [2]. Their chemical composition may depend on the kind of fluxes (sodium or potassium feldspars) and their ratio, the possible use of sintering aids (i.e. alkaline-earth compounds, such as talc, spodumene or wollastonite) or glass-ceramic frits [3]. Porcelain tiles are sintered by fast single firing up to 60 minutes cold-to-cold, 1200-1250 °C of peak firing temperature and 5-10 minutes of soaking time [4]. As a result of sintering process phase final composition consist of crystalline phases, both new formed (mullite) and residual ones (quartz and feldspars) embedded in an abundant glassy matrix [5].

The main standard requirement for porcelain stoneware is a very low water absorption (0.5% according to TS EN 13006) that is largely fulfilled, being < 0.1% in the products. In industrial firing process, a residual closed porosity cannot be completely removed-ranging usually from 2 to 8%- consisting of both small <10 μm

and spherical, gas-filled pores and irregularly shaped, coarser pores probably due to coalescence of smaller ones [5].

The densification is achieved by particle rearrangement and viscous flow, occurring over 1100 °C. Many sintering mechanisms are contemporarily active (melting, pore coalescence and coarsening, etc.) due to a wide range of pore and particle size in the green compacts, making difficult any effective design of the microstructure of porcelain stoneware. However, the densification appears to be rate-controlled by the strong dependence of melt viscosity on temperature and by the solubility of solids in the liquid phase. Nevertheless, in the final stage, coarsening and solubility of gases filling the closed pores become the most important phenomena affecting the microstructure [6].

Lithium aluminosilicates, such as spodumene, have also been used as raw materials in the production of thermal shock resistant whiteware and sanitaryware. It has been reported that the presence of spodumene causes development of mullitization degree and imparts better physical and mechanical properties to ceramics. In general, the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems are well known for their low or even negative thermal expansion coefficients. As a result, much more effort has been directed at producing ceramics which contain eucryptite (LiAlSiO_4) and spodumene ($\text{LiAlSi}_2\text{O}_6$) with relatively high content of Li_2O . Tulyagonav *et al* have investigated influence of Li_2O doping on non-isothermal evolution of phases in K-Na-containing aluminosilicate matrix and influence of lithium oxide as auxiliary flux on the properties of triaxial porcelain bodies [5, 7]. The phase transformations in Li_2O -doped model formulations (using 1-7 wt. % Li_2CO_3), which comprised 50% kaolin,

*Corresponding author:
Tel : +90-318-357-42-42/1287
Fax: +90-318-357-24-59
E-mail: tunaaydin1978@yahoo.com

25% feldspar, and 25% quartz (in wt. %), was studied. Experimental and theoretical approaches agree fairly well with another and indicated that the presence of Li_2O and other alkalis, such as K_2O , in aluminosilicate matrices plays an important role in the phase transformations that occur at different temperatures during firing. Discrepancies in experimental results from thermodynamics was attributed to slow kinetics, also likely because of the nature of the raw materials used [7]. The latter, the influence of Li_2O -content on the properties of standard triaxial porcelains was investigated. Two series of porcelain formulations were produced. The first one comprised seven model formulations with increasing amount of Li_2CO_3 (1-7 wt. %), with respect to the standard triaxial porcelain formulation. The experimental results showed that desirable properties for tableware porcelains can be attained if the Li_2O -content does not exceed 1.5 wt. %. In the light of this conclusion, the second series of formulations aimed at producing new porcelains using Li-bearing natural rocks. Under an industrial perspective, the most important finding was that these compositions matured at temperatures 100°-120 °C lower than the standard triaxial porcelain formulation and exhibited remarkable resistance at over-firing conditions. The role of increasing Li_2O -content at the different stages of firing was interpreted in the light of its influence on densification, the evolution of crystalline phases and microstructure [5]. Yamuna *et al.* have investigated the effect of the fluxes Li_2CO_3 and LiCl in kaolinite and other systems with the same Si/Al ratio during sintering. Mullite and spodumene were detected at elevated temperatures (1350 ° and 1450 °C). High spodumene concentration was developed at the surface of high (4 wt. %) Li_2O -containing sintered bodies [7].

The present work focused on crystalline phase and pyroplastic deformation evolution upon firing. Although triaxial porcelain systems have been long and extensively documented, systematic investigations on the influence of lithium oxide, as auxiliary flux, on the pyroplastic deformation and the properties of triaxial porcelain bodies are restricted.

The present work addresses itself to this aim. In particular, it was produced model formulations of Li_2O -doped standard porcelain stoneware bodies, whose batches contained 1-4 wt. % spodumene. The physical and the mechanical properties, together with the microstructure and the crystalline phase analyses of these porcelains were presented. The effect of spodumene addition on pyroplastic deformation was also studied.

Studying the viscosity of liquid phases formed during sintering of ceramic bodies is more complex because of changing of the compositions during heat treatment. However indirect information on the viscosity of bodies during firing can be obtained by measuring the rate of deformation suspended between two supports.

The trend of deformation for ceramic materials during heat treatment without loading is referred to as pyroplasticity. Viscosity may be determined using the formula defining the deflection of a beam supported at the ends and subjected to its own weight:

$$y_{\max} = \frac{5pgL^4}{32\delta_{\max}h^2}$$

Where: y: deflection

ρ : density (g/cm^3)

g: acceleration of gravity (cm.s^{-2})

L: distances between supports (cm)

$\delta_{\max}$: maximum deformation (cm/s)

h: thickness (cm)

The rate of deformation is therefore a function of viscosity and for small deflection values the elastic modulus (E) can be replaced by the viscosity (η) and the deflection (y) replaced with the deflection rate ($\dot{y}$) [8].

Considering the maximum value of deflection at the centre of the beam ($\dot{y}_{\max}$) obtained

$$\dot{y}_{\max} = \frac{5pgL^4}{32\delta_{\max}h^2}$$

Moving the viscosity (η) to the left obtained the result:

$$\eta = \frac{5pgL^4}{32\delta_{\max}h^2}$$

Pyroplastic deformation is bending of a ceramic specimen caused by gravity during heat treatment. It can be defined as the loss of shape of a product during its firing. Pyroplasticity is related to an excess of liquid phases formed during firing or to reduced viscosity of these phases. The pyroplastic deformation magnitude is determined by the pyroplastic index (PI), pointing out the tendency to deformation of a specimen with fixed dimensions submitted to gravity during its firing under specific conditions.

$PI = \frac{s\dot{b}}{l}$ where s is the maximum deformation (cm), b is the bar thickness (cm), l is the distance between supports (cm) PI: tendency of pyroplastic deformation [9].

Material and Method

Porcelain stoneware bodies having four different formulas were designed as D1, D2, D3, and D4 under industrial condition with different ratios of spodumene (up to 4 wt.%). Spodumene was substituted for albite in the standard body body designed as STD. All the compositions were formulated with clay, kaolin, quartz, and albite. The raw materials used in this study and their chemical compositions are given in Table 1. After grinding, the compositions were dried (100 °C, 1 h). Then, the dried powders consisting of about 5 wt. % humidity were uniaxially pressed under 147 kg/cm^2 to

Table 1. Chemical composition of the raw materials (wt. %, XRF).

Raw materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Li ₂ O	L.o.I
Kaolin 1	65	23.0	0.5	0.20	0.15	0.20	0.30	–	10.0
Kaolin 2	78.78	13.34	0.02	4.78	0.01	2.1	0.04	–	0.51
Clay 1	59	26.0	1.20	0.60	0.10	0.10	2.00	–	10.0
Clay 2	59	25.0	1.00	0.60	0.70	0.60	2.70	–	8.50
Clay 3	65	21.5	2.50			0.10	2.00	–	7.50
Quartz	97.6	0.730	0.18	0.10	0.01	0.01	0.47	–	0.43
Na Feldspar	71.1	17.40	0.05	0.60	0.10	9.36	0.34		0.50
Spodumene	65.2	25.12	0.15	0.21	0.1	0.34	0.57	7.5	0.36

*L.o.I: loss on ignition.

obtain 5 mm × 110 mm × 50 mm tiles. Finally tiles were sintered at 1210 °C, 60 min. in an industrial roller kiln.

Bulk density (*Db*) and open porosity (*Po*) was determined by water saturation and Archimedes' principle (ISO 10545-3). Also, total porosity (*Pt*) was calculated with the relation $Pt = 1 (Db/Ds)$, where *Ds* is the theoretical density of the ceramic material measured by Helium pycnometry (Quantachrome He pycnometry). X-ray fluorescence chemical analyses was conducted with a Rigaku ZSX Pirumus spectrometer. Mineralogical qualitative phase analysis of powder was performed using data collected with a Rigaku Rint 2200 diffractometer. Sintering behavior of the bodies were performed using a non contact optical dilatometer (Misura, ODHT Expert System). The trend of flexion of a 6-mm-wide and 85-mm-long sample suspended on supports with an interaxis of 70 mm of compositions was also analyzed with an optical fleximeter (Misura Flex) using a heating rate of 10 °C/min. for all the formulations.

Results and Discussion

Physical and microstructural characterization

The chemical compositions of the raw materials and the porcelain tile formulations are reported in Tables 1 and 2.

Fig. 1 gives the representative X-ray diffraction spectra of the fired bodies; residual quartz, albite, mullite and abundant amount of glassy phase were detected. As can be seen with the incorporation of spodumene, it appears that both amount of mullite and

glassy phase increased but albite and quartz decreased. As mentioned earlier, since spodumene is highly effective fluxing agent its addition reduces viscosity of liquid phase and in turn further dissolution of quartz and albite takes place. Furthermore liquid phase begins to flow easily to fill open pores as seen in Tables 3 and 4. However, as more spodumene is added, the bulk density of the samples decreased.

Thermal properties

The thermal expansion coefficients of the investigated bodies were determined using a dilatometer. The measured thermal expansion coefficients of spodumene containing formulations are comparable to that of standard formulation. In Fig 2, it is seen that in comparison with standard body by emerging of Na feldspar and by adding spodumene provide to decrease

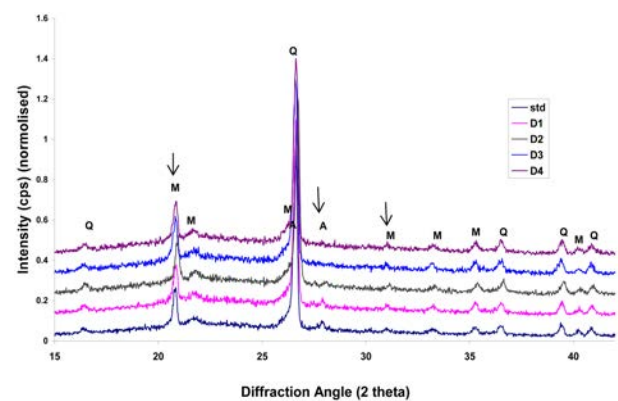


Fig. 1. XRD spectra of the investigated porcelain tile bodies (M: Mullite, Q: Quartz, A: Albite).

Table 2. The investigated formulations (wt. %).

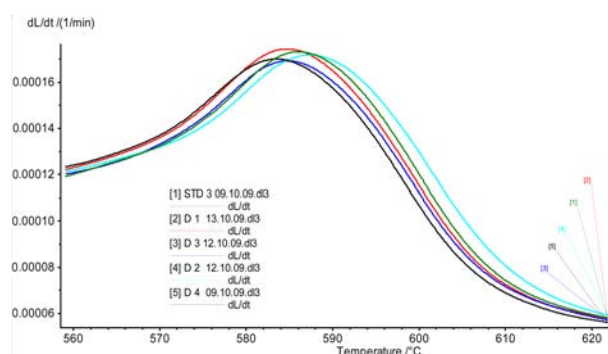
	Kaolin 1	Kaolin 2	Clay 1	Clay 2	Clay 3	Quartz	Na Feldspar	Spodumene
STD	5.5	9	6	18	6.5	8	47	–
D1	5.5	9	6	18	6.5	8	46	1
D2	5.5	9	6	18	6.5	8	45	2
D3	5.5	9	6	18	6.5	8	44	3
D4	5.5	9	6	18	6.5	8	43	4

Table 3. Technological properties of the investigated formulations.

	True Density (g/cm ³)	Bulk Density (g/cm ³)	Firing Shrinkage (%)	Porosity		
				Open por. (%) (P _O)	Closed por. (%) (P _C)	Total por. (%) (P _T)
STD	2.52	2.38	8.36 ± 0.151	0.43	5.50	5.94
D1	2.48	2.39	8.31 ± 0.045	0.00	3.61	3.61
D2	2.49	2.37	8.11 ± 0.069	0.00	4.48	4.48
D3	2.48	2.38	7.91 ± 0.013	0.39	3.65	4.04
D4	2.47	2.37	7.89 ± 0.097	0.42	4.0	4.42

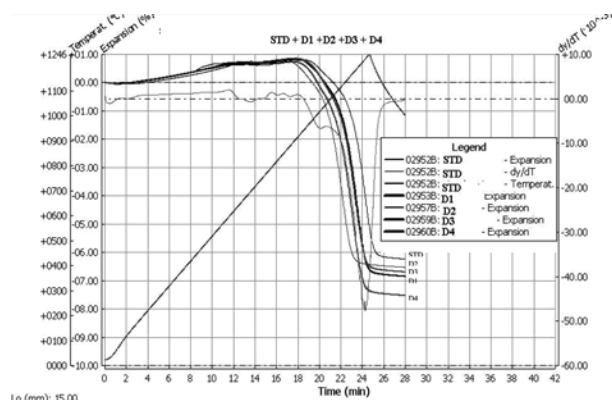
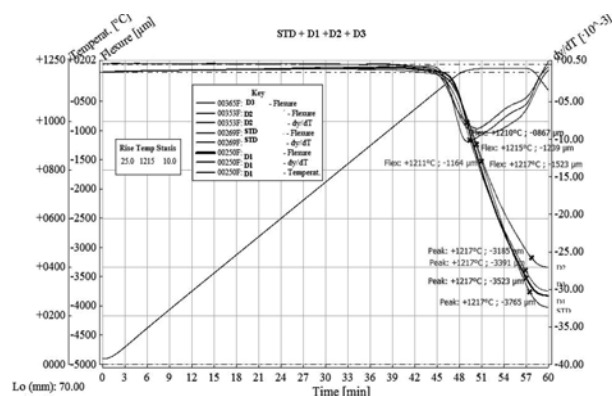
Table 4. Technological properties of the investigated formulations.

	Bending strength (N/mm ²)	Water Abs. (%)	Chromatic coordinates		
			L*	a*	b*
STD	51	0.13	76.4	1.56	10.4
D1	54	0.00	75.4	1.6	10.3
D2	66	0.00	75.2	1.61	10.2
D3	61	0.17	75.1	1.54	10.2
D4	58	0.19	75.1	1.56	10.0

**Fig. 2.** Thermal expansion coefficient curves of the investigated formulations.

the thermal expansion coefficient depending on quartz amount. Dissolution of quartz in the glassy phase resulted in decreasing of thermal expansion. Especially it was determined that as amount of spodumene in formulation increases thermal expansion coefficient decreases. At the quartz transformation temperature lowest thermal expansion coefficient belongs to D3 ($84.3 \cdot 10^{-7} / K$)

The fast firing of the bodies containing varying amounts of spodumene (from 1 to 4 wt. %) in partial replacement of Na-feldspar was given in Fig 3. The graphs were plotted with the firing percentage as the x-axis and the time as the x axis. The measurement was conducted using a continuous heating rate (50 °C/min.) up to 1250 °C so as to identify the sintering behavior of the compositions. The temperature interval where the sintering speed reaches maximum was identified by plotting the derivative of sintering curve. The flex temperatures corresponding to the maximum amount of shrinkage and maximum sintering speed can

**Fig. 3.** Sintering curves of the investigated formulations.**Fig. 4.** Pyroplastic deformation curves of the investigated formulations.

be seen on the graph for each composition. Incorporation of spodumene into the standard composition led to a considerable decrease in maximum peak firing temperatures. The maximum sintering speed for D1 was found to be at 1217 °C, which is nearly 8 °C lower than that of the standard body. It appears that the magnitude of this effect is dependent on amount of spodumene addition. The developed sintering behavior can be explained by both the reduced eutectic temperatures and liquid phase viscosity. Thus the formulations with increasing amount of spodumene exhibited lower values of peak firing temperature, 1217, 1213, 1206 and 1203 °C, respectively.

In Fig. 4, pyroplastic deformation curves of the bodies are given. Flex temperature of STD body is much higher than that of the formulations with

Table 5. Viscosity in flex and soaking temperature of the investigated formulations (η_{Flex} : viscosity at flex point, η_{Soaking} : viscosity at soaking temperature.).

	Flex Temp. (°C)	Soaking Temp. (°C)	Deformation at Flex Temp. (cm)	Soaking Def. (cm)	η_{Flex} (GPa.sn)	η_{Soaking} (GPa.sn)
STD	1217	1217	0.1708	0.3634	1.327	0.820
D1	1210	1217	0.0867	0.3609	2.182	0.824
D2	1215	1217	0.1169	0.3006	1.458	0.872
D3	1211	1217	0.1164	0.3391	1.161	0.688

Table 6. Pyroplastic deformation index of the investigated formulations (PI: pyroplastic deformation index, S_{max} : maximum deformation, PI_{flexion} : pyroplastic deformation index at flex temp., PI_{soaking} : pyroplastic deformation index at soaking temperature.

	PI (cm ⁻¹)	S_{max} (cm)	PI_{flexion} (cm ⁻¹)	PI_{soaking} (cm ⁻¹)
STD	7.4×10^{-5}	0.4068	3.14586×10^{-5}	6.69323×10^{-5}
D1	6.2×10^{-5}	0.3824	1.41055×10^{-5}	5.87158×10^{-5}
D2	5.6×10^{-5}	0.3365	1.94472×10^{-5}	5.0007×10^{-5}
D3	6.6×10^{-5}	0.3744	2.07356×10^{-5}	6.04075×10^{-5}

spodumene. This can be attributed to the fact that the addition of spodumene leads to further dissolution of quartz and thus increases the viscosity of glassy phase. This is supported by calculated viscosity values of bodies shown in Table 5.

The calculated pyroplastic index values of the spodumene containing bodies (Table 6) are comparable to that of the standard body. Viscosity increase provides a resistance against to pyroplastic deformation. As can be seen in Fig. 4, significant portion of pyroplastic deformation occurs before the dwell (soaking time) period at the peak temperature (1200-1210 °C). The onset of deformation occurs around 1150 °C and continues at a much higher rate than deformation observed during the dwell time. The prominent deformation mechanism is viscous creep. Viscous creep in the low-temperature region occurs at a high rate. But at the peak temperature creep occurs at a slow rate. The microstructure changes because of increasing temperature causing further formation of mullite and dissolution of quartz, and viscosity increases. Thus, body gains a resistivity against deformation. $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio has also a important role in viscosity. As increasing of Al_2O_3 and K_2O in formulations, they become more refractive. K_2O provides larger eutectic period but also eutectic temperature and viscosity is higher. As seen in Table 6, by adding spodumene pyroplastic deformation index was decreased but D3 formulation has slightly higher value than that of other formulations with spodumene. It is considered that since no more sufficient residual quartz to dissolve and also too high liquid phase, viscosity in D3 was somewhat lower than the others. As a result, D3 formulation likely to prone to pyroplastic deformation than the rest.

Conclusions

Sintering of porcelain stoneware body is an example of densification process proceeding through viscous flow. The surface tension/viscosity ratio controls total porosity during the sintering process. In this study, addition of up to 4 wt. % spodumene enhances the removal rate of total porosity. Spodumene was found to increase sintering rate which produces dense porcelain stoneware body compared to the standard body. In addition, mechanical properties of the porcelain tile bodies were improved by spodumene addition due to increasing density and decreasing total porosity. Thermal properties of the porcelain tile bodies with spodumene were improved. As seen on sintering curves, compared with, the standard body, peak firing temperature of the investigated formulations decreased because of because of spodumene being more active fluxing agent. Thermal expansion coefficient was decreased. Pyroplastic deformation index was also decreased with spodumene addition so that more resistance bodies against to pyroplastic deformation were obtained.

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