

Use of borosilicate glass waste as a fluxing agent in porcelain bodies

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Porcelain is a material produced from kaoline, quartz and potassium-feldspar. Recently, research of new materials, for example non-hazardous wastes, that are able to replace traditional fluxing agents without changing the process or quality of the final products has been realized. The aim of this investigation is to study the possibility of the use of borosilicate glass waste powder for manufacturing porcelain. The borosilicate glass waste was added partially and fully in replacement of potassium-feldspar. Samples were fired in an electric furnace with a heating rate of $10\text{ }^{\circ}\text{C minute}^{-1}$ at 1000, 1100, 1200 and $1300\text{ }^{\circ}\text{C}$ for periods of 1, 2, 3 and 5 hours. The sintered samples were characterised by XRD (X-ray diffraction) and SEM (scanning electron microscopy). Sintering activation energies were determined based on the bulk density results. With 0, 5, 10, 15 and 25 wt.% glass waste additions, the apparent activation energies were calculated to be 166, 110.73, 109.85, 65, 43 kJ/mol, respectively. It was found that the sintering activation energy decreased with an increase in the waste glass addition.

Key words: Porcelain, Borosilicate glass waste, Microstructural evolution, Sintering kinetics.

Introduction

Porcelain bodies have excellent technical characteristics that make possible their use in many different places with hard use it is necessary to have high mechanical resistance and surface hardness, and walls where impermeability is essential [1].

Porcelain bodies are typically fired mixtures of 50 wt.% clay (commonly kaolin), 25 wt.% flux (commonly feldspar), and 25 wt.% filler (commonly quartz). The clay provides plasticity, allowing easy shape formation and acts as a binder for the other body components when they are in the green state. Quartz are class of materials of high melting temperature that are chemically resistant at commercial firing temperatures ($< 1300\text{ }^{\circ}\text{C}$). They reduce the tendency of the body to warp, distort, or shrink when it is fired to temperatures resulting in substantial quantities of viscous glass. Feldspars are low-melting mineral alkali alumina silicates and serve to lower the temperature at which a viscous liquid forms. The liquid phase reacts with other body constituents and gradually permeates the microstructure, leading to its densification [2].

Boron minerals used extensively in the glass and ceramics industry as vitrification and flux agents [3]. Borates can benefit the heavy clay ceramics industry due to their glass-forming effects. Moreover, reduction of the firing temperature is anticipated. However, use of water-soluble borax and boric acid is disadvantageous as they are water soluble. Tests with the above products showed a large degree of migration of the borate to the

surface as water is expelled during the drying process [4]. Many researchers have investigated the use of boron minerals and waste as additives in ceramic tiles. When mineral and waste were mixed with the tile slurries improvements were observed in the physical properties of the tile [3]. Olgun et al. [5] reported that adding tincal waste and boron ash to a wall tile slurry increased the fired strength of the tiles. The strength of tiles including tincal waste is greater than that of standard tiles and that of tiles with bottom ash. With an increase in the amount of tincal waste additional water absorption of tiles was observed to decrease. Kurama et al. [6] found that borax waste increased the vitrification and thereby provided better technological features. Bayca et al. [7] observed that tincal can be used as a flux material in ceramic bodies due to its favorable effect on the water absorption and fired strength.

Summarizing the above findings, it is evident that: (a) boron waste (BW) functions as a flux promoting the liquid phase formation in the body and (b) an excess in the body mixture or a high sintering temperature may deteriorate the sintered bodies. Nonetheless, there is only one work focusing on BW in bricks and there is room for a contribution especially in the area of thermal behavior and microstructural development [4].

A basic porcelain composition consisting of 50 wt.% kaolin, 25 wt.% potassium-feldspar and 25 wt.% quartz were chosen by our group to study the effects of various waste materials on the sintering properties. The sintering properties of porcelain bodies made from waste glass and fly ash were studied and already published [8] and this present study is a continuation of the previous investigation. The aim of this study is to investigate the effects of borosilicate glass waste as a fluxing agent

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addition on the sintering properties of porcelain bodies.

An attempt was also made to study the densification behavior of samples with different compositions and different sintering temperatures and sintering times by using bulk density, SEM and XRD techniques.

Experimental Procedure

A basic porcelain composition consisting of 50% kaolin, 25% potassium-feldspar and 25% quartz was selected as the reference porcelain composition. Borosilicate glass waste was added to the mixture to form the glass phase instead of potassium-feldspar. The waste powder glass is a waste material obtained from borosilicate glass waste pieces. Kaolin and potassium-feldspar were supplied from the Çelvit Company, Turkey. The chemical compositions of the raw materials are given in Table 1. Five compositions, marked as B₀ (the reference porcelain composition), B₁, B₂, B₃ and B₄, were studied. The compositions of the raw materials and the marking system are shown in Table 2. Each composition was ball-milled in ashless rubber-lined ceramic jars for 2 h using zirconia balls and distilled water as the milling media. After drying, the mixtures were granulated in moist conditions and then semi-dry pressed at 100 MPa to prepare specimens 20 mm in diameter and 8 mm thick. The samples were fired in an electric furnace with a heating rate of 10 °C.minute⁻¹ at 1000, 1100, 1200 and 1300 °C for periods of 1, 2, 3 and 5 h. Then, the fired samples were cooled to room temperature in the furnace.

Characterisation of the phases in the sintered specimens was carried out by X-ray diffraction using CuK radiation. For microstructural observation, scanning electron microscopy (SEM) was used.

The sintering kinetics of all compositions were based on the bulk density measurements. The bulk densities of the sintered samples were measured using Archimedes' method. The empirical equation for the sintering kinetics is given as follows:

$$D = K \log t + C \quad (1)$$

where D is the density, C is a characteristic constant of the powders, K is the reaction rate constant and t is the sintering time. In order to calculate the sintering activation energy, the Arrhenius equation was used:

$$K = A \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

where Q is the activation energy, R is the gas constant, T is the absolute temperature and A is a constant [8, 9].

Results and Discussion

Microstructural characterization

The XRD analysis of B₀ and B₄ compositions sintered at 1000 and 1300 °C 1 h are given in fig. 1 (a, b). In the XRD analysis of the samples B₀ at 1000 °C and 1300 °C for 1 h, the main phases identified are quartz, microcline and mullite. The microcline phases disappeared with an increase of the sintering temperature, because these phases were melted at a low eutectic temperature [2]. Mullite peaks increased in intensity with the firing temperature, whereas quartz peaks decreased slightly, associated with its partial dissolution [10]. An increase of the amount of borosilicate glass waste in the mixture led to the formation of mullite at 1000 °C. In addition, the intensities of the quartz peaks decreased with an increase in the borosilicate glass waste (from B₀ to B₄). Also, in the B₄ composition the microcline phase was not seen. Quartz and mullite phases were formed with an increase in the temperature (at 1300 °C). The addition of borosilicate glass waste in the mixture had no significant change in the phase formation at 1300 °C. Only, the intensities of the mullite peaks were increased very little. Therefore, an increase of the temperature and borosilicate glass waste are thought to increase the formation of mullite. Mullite is the only stable phase in the Al₂O₃-SiO₂ system at atmospheric pressure. The mullite phase is believed to play a significant role in the development of traditional and advanced ceramics [11]. The quartz content decreases with an increase of the sintering temperature due to its gradual dissolution into the glassy phase [12]. Also, part of the quartz combined with Al₂O₃ to give mullite.

Table 1. Chemical composition of raw materials.

	Raw materials (wt.%)			
	Quartz	Kaolin	Potassium-feldspar	Borosilicate Glass
SiO ₂	100	48.00	65.10	77,32
Al ₂ O ₃	-	37.00	19.50	4,34
B ₂ O ₃	-	-	-	12,34
Fe ₂ O ₃	-	0.75	0.12	0.22
CaO	-	-	0.37	0,20
K ₂ O	-	1.85	11.00	0.33
Na ₂ O	-	-	3.00	4.83
MgO	-	-	0.12	0,31
TiO ₂	-	-	0.02	0.11
L.O.I*	-	12.20	0.25	-

* Loss on ignition

Table 2. Porcelain compositions studied in the experimental studies.

Sample Code	Raw materials (wt%)			
	Kaolin	Quartz	Potassium-feldspar	Borosilicate Glass
B ₀	50	25	25	0
B ₁	50	25	20	5
B ₂	50	25	15	10
B ₃	50	25	10	15
B ₄	50	25	0	25

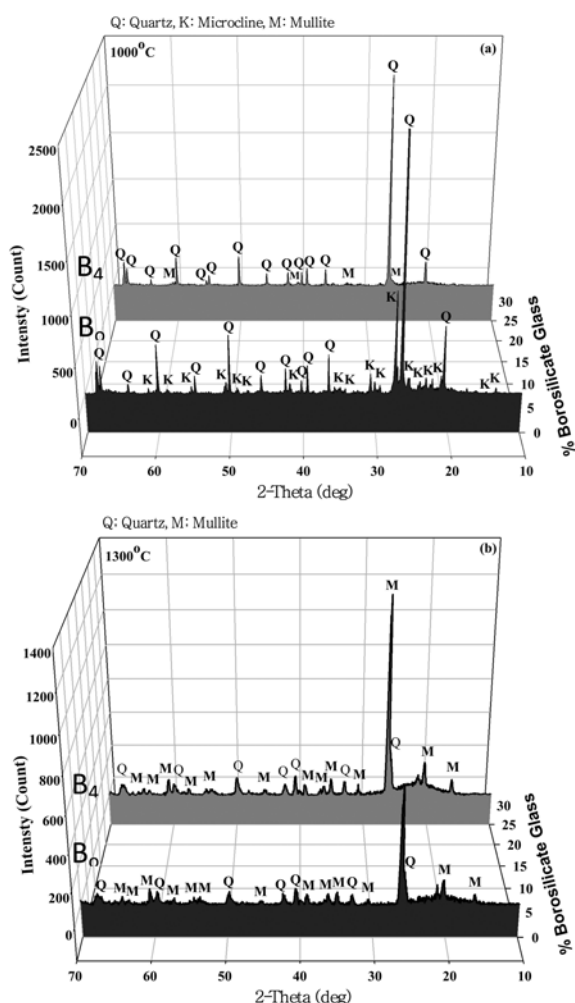


Fig. 1. XRD patterns of (a) B₀ and B₄ samples sintered at 1000 °C 1 h and (b) B₀ and B₄ samples sintered at 1300 °C 1 h.

Microstructural investigations from SEM analyses of B₀ and B₂ samples sintered at 1300 °C for 1 h revealed various features including very small cracks, undissolved quartz grains, mullite needles, glassy phases and porosity, as shown in Fig. 2 (a, b). This figure shows the typical microstructure of a commercial porcelain. In addition, SEM results confirmed the XRD analysis (as seen in Fig. 1). The small cracks and porosity are formed by shrinkage and thermal expansion. During firing, the borosilicate waste glass has a negative effect, which is a higher volume of shrinkage. Where there is more waste glass, the cracks become more prominent [8, 13-16].

Bulk density graphs of samples sintered at different temperatures and times were drawn as a function of sintering time. The effects of sintering temperature and sintering time on the densification of the samples are shown in Fig. 3. Generally, densifications increased with an increase in the sintering time. However, sintering temperatures of 1000 °C and 1100 °C were not enough for densification. This situation is confirmed by Fig. 4. The SEM micrographs of the fracture surface of all compositions sintered at 1000 °C for 1 hour are compared in Fig. 4. Here, in the samples sintered at 1000 °C were

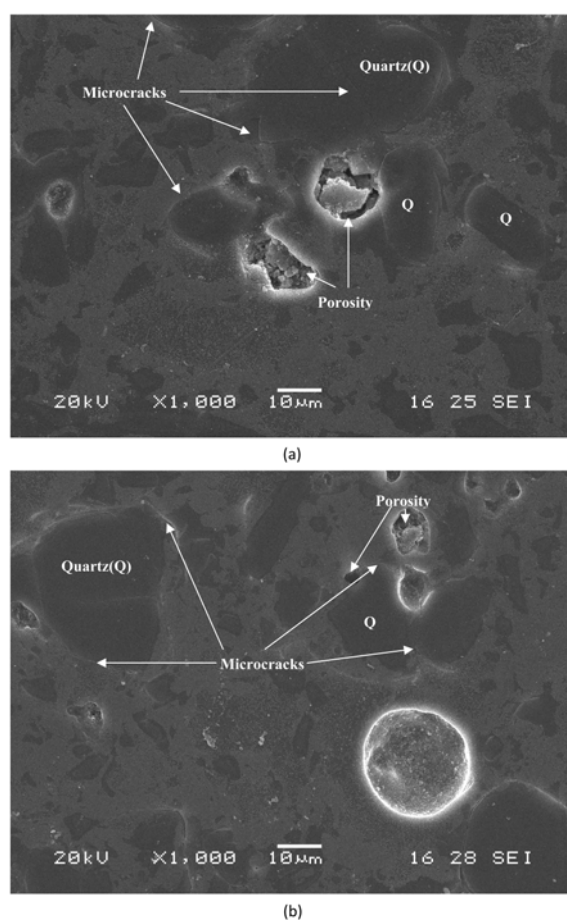


Fig. 2. SEM micrographs of (a) B₀ and (b) B₂ compositions sintered at 1300 °C for 1 hour.

seen porous microstructures. A dense structure was formed when the sintering temperature was increased to 1300 °C (as seen Fig. 5). Sintering temperatures at 1000 °C and 1100 °C for 1, 2, 3 and 5 h raised the bulk density of the samples when the waste glass addition was increased. The vitreous phase contains more Na₂O and B₂O₃ with lower amounts of Al₂O₃ and K₂O in the waste glass. These oxides bring about a lower viscosity of the liquid phase at sintering temperatures in the materials containing waste glass [8-16]. The oxide compositions of the samples are given in Table 3. The amounts of Na₂O and B₂O₃ increase with an increase in the amount of waste glass, while the amounts of Al₂O₃ and K₂O decrease. The glassy phase produced from these oxides has a lower viscosity and flows easily to fill open pores. Therefore, an increased density was caused by increasing the addition of waste glass at 1000 °C and 1100 °C (Fig. 3 (a) and (b)). However, as borosilicate waste glass is added, the bulk density of samples dramatically decreased at sintering temperatures of 1200 °C and 1300 °C (as seen in Fig 3 (c) and (d)). During sintering, glass waste accelerates the densification process, with some positive effects (lower open porosity) as well as negative effects (higher values of shrinkage and closed porosity with lower values of bulk density,

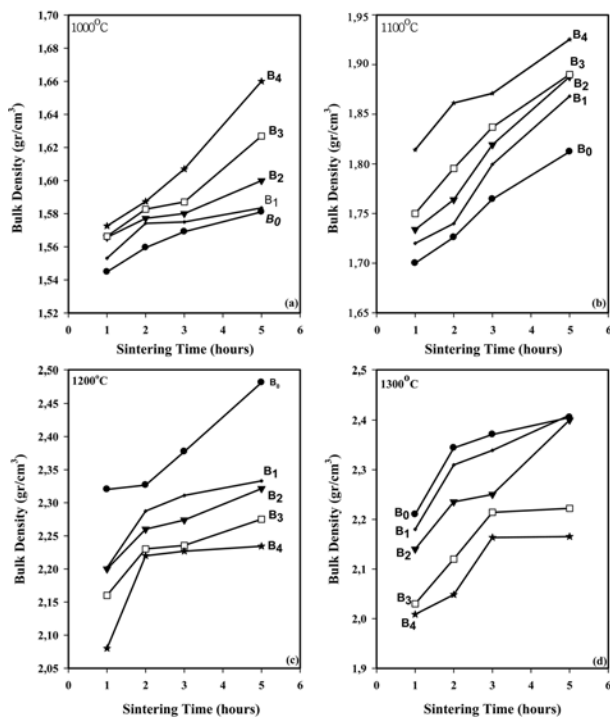


Fig. 3. Calculated densification curves as a function of sintering time at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C and (d) 1300 °C.

Table 3. Oxide compositions of the experimental samples.

Oxides (wt.%)	Sample Codes				
	B ₀	B ₁	B ₂	B ₃	B ₄
SiO ₂	69.71	70.33	70.95	71.58	72.82
Al ₂ O ₃	24.98	24.16	23.34	22.53	20.90
B ₂ O ₃	-	0.66	1.31	1.97	3.29
CaO	0.10	0.09	0.08	0.07	0,05
MgO	0.03	0.04	0.05	0.06	0,08
Na ₂ O	0.80	0.90	1,00	1.09	1.21
K ₂ O	3.93	3.36	2.79	2.22	1.08
Fe ₂ O ₃	0.43	0.43	0.44	0.45	0.46
TiO ₂	0.02	0.02	0.02	0.03	0.02

mechanical and tribological properties). These differences were limited and tolerable to a sintering temperature to 1100 °C, but in the sintering temperature range higher than 1100 °C, the bulk density of the samples dramatically decreased with an increase in the borosilicate glass waste.

Sintering kinetics

The activation energies of densification process were calculated from Eq. (1) and Eq. (2). Firstly, bulk density (D) and log t curves were drawn. The reaction rate constant (K) in Eq. (1) was calculated from the slope of this graphic. Then, log K versus 1/T graphs were plotted to calculate the sintering activation energy for all compositions and these graphs are given in Fig. 6 and Fig. 7 (a-d). The sintering activation energy values were

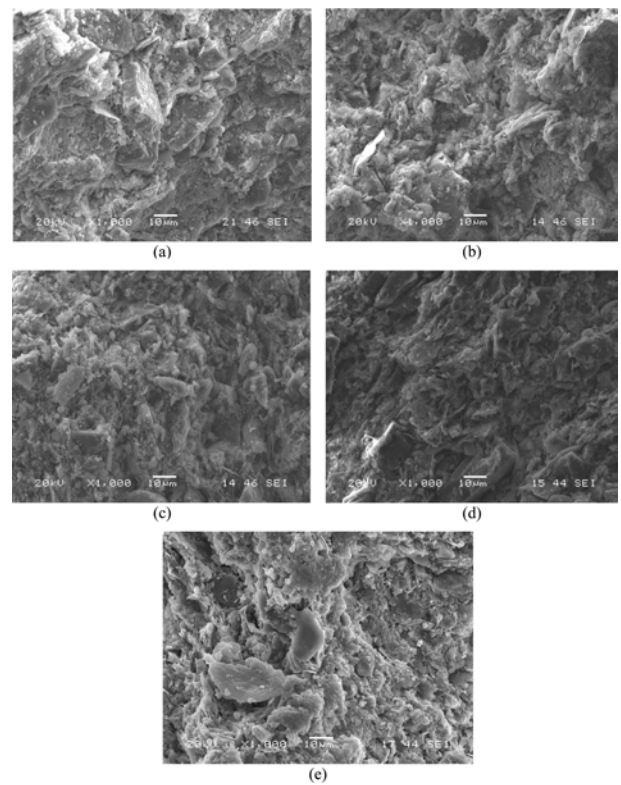


Fig. 4. SEM micrographs of B₀ (a), B₁ (b), B₂ (c), B₃ (d), B₄ (e) samples at 1000 °C/1 h, respectively.

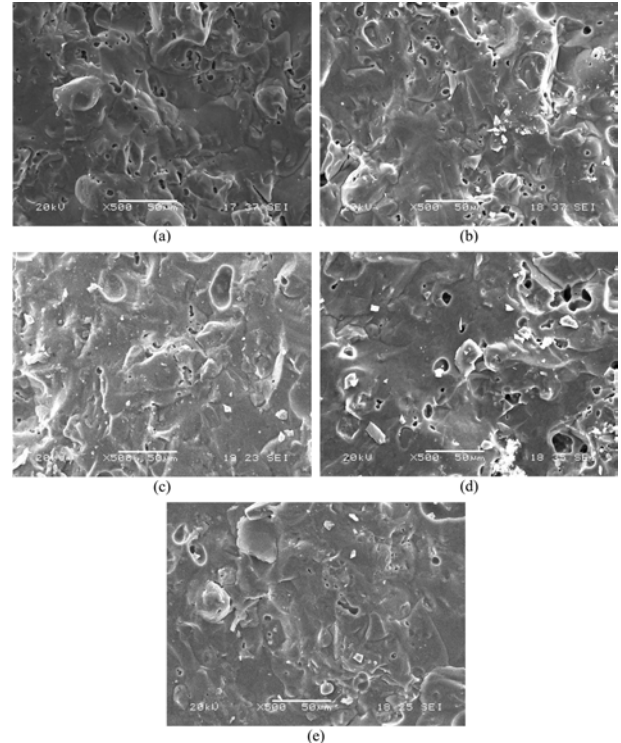


Fig. 5. SEM micrographs of B₀ (a), B₁ (b), B₂ (c), B₃ (d), B₄ (e) samples at 1300 °C/1 h, respectively.

calculated for the initial stage of sintering of the different compositions from these graphs. These values are seen in Table 4. The activation energies of B₀, B₁,

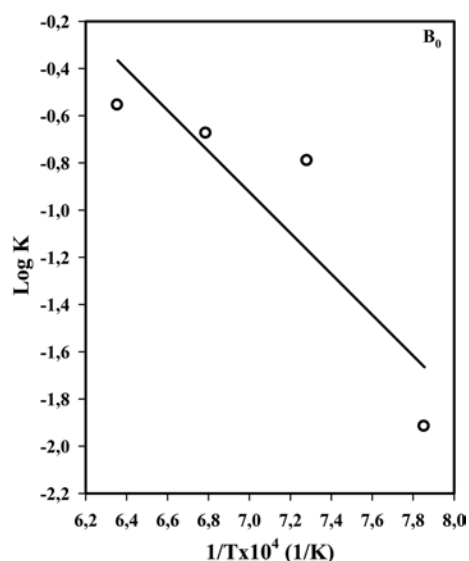


Fig. 6. log K and 1/T graphs for B₀ compositions.

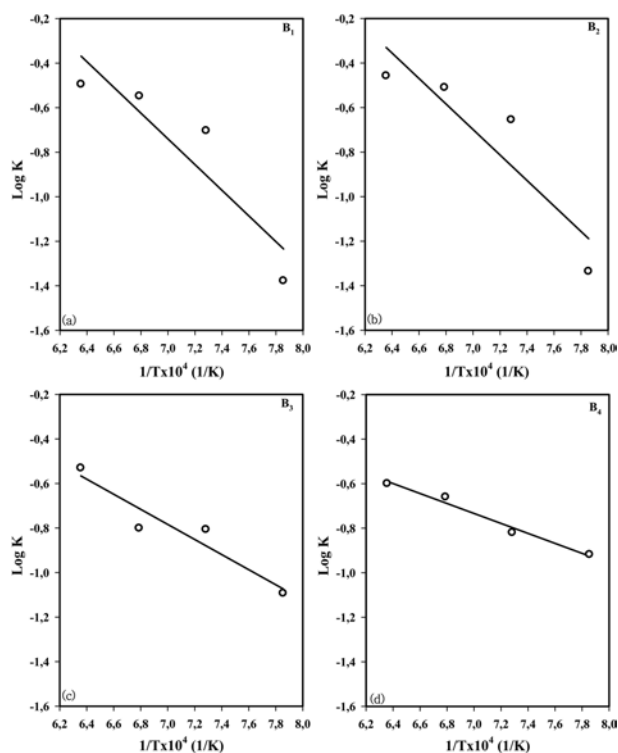


Fig. 7. log K and 1/T graphs for (a) B₁, (b) B₂, (c) B₃ and (d) B₄ compositions.

B₂, B₃ and B₄ compositions were found to be 166, 110.73, 109.85, 65, 43 kJ/mol, respectively. As can be seen from the table, the activation energy decreased with the addition of borosilicate glass waste. The components of the frits, mainly alkaline and alkaline-earth oxides, are diffused into the liquid phase, altering the most important physical properties (viscosity and surface tension) for densification. The positive influence of the glass-ceramic additions in promoting the sintering stands out when the onset temperature of densification and the sintering rate are considered: both are improved

Table 4. Activation energy values for sintering of all porcelain compositions.

Compositions	-Q/R	Activation energy, Q (kJ/mol)
B ₀	-19982	166.00
B ₁	-13309	110.73
B ₂	-13203	109.85
B ₃	-7807	65.00
B ₄	-5161	43.00

with respect to the reference body. In particular, the sintering rate of porcelain stoneware tiles depends on the properties of the liquid phase at high temperature (i.e. surface tension/viscosity ratio) [17]. Increasing the sintering time and temperature can reduce the viscosity of the glassy phase contained in the matrix, resulting in an increase in viscous flow and densification of the porcelain body by lowering the activation energy [9]. This is also associated with a high rate of sintering due to the increased waste glass addition and glassy phase formation, leading to a decline in the volume of the overall porosity and an improvement in the densification, resulting in easier diffusion and a reduced activation energy. The content of alkali oxides such as K₂O, Na₂O and B₂O₃ is very high in borosilicate glass waste as compared to potassium-feldspar. These oxides decrease the melting temperature of the powder mixture and facilitate fusibility, leading to liquid phase sintering [8, 18].

The sintering activation energy of the basic porcelain composition is 166 kJ/mol while the sintering activation energy of the B₄ composition is 43 kJ/mol. The increased borosilicate glass waste addition increased the glassy phase formation. This leads to a decline in the porosity and an increase in the densification. In addition to, the decrease in the activation energy facilitates diffusion. As a result, the low activation energy causes to the densification of the porcelain body, easily.

Conclusions

The effect of borosilicate glass waste additions on the sintering properties of porcelain bodies was studied between 1000 °C and 1300 °C in air. In our study, we selected a basic porcelain composition consisting of 50% kaolin, 25% potassium-feldspar and 25% quartz. The sintering activation energy of this composition has been calculated as 166 kJ/mol. Demirkiran [9] et al. have calculated the sintering activation energy of a composition with 45 wt.% kaolin, 30 wt.% potassium-feldspar and 25 wt.% quartz as 137.618 kJ/mol. This composition is very similar to our selected basic porcelain composition. Replacement of potassium-feldspar with borosilicate glass waste resulted in a reduced activation energy required to initiate sintering in porcelain samples. The activation energies of the B₁, B₂, B₃ and B₄ compositions were found to be 110.73, 109.85, 65,

43 kJ/mol, respectively. In other words, the starting temperature for sintering was reduced by the additional fluxing oxides such as B_2O_3 and Na_2O which eased the vitrification by reducing the viscosity of the liquid phase during sintering.

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