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The sintering kinetics of porcelain bodies made from waste glass and fly ash

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Abstract

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 work is to study the possibility of the use of glass powder waste and fly ash together for manufacturing porcelain. Instead of quartz, fly ash was used at the selected porcelain composition. The waste glass was added partially and fully in replacement of potassium-feldspar. Samples were fired in an electric furnace with a heating rate of 10 °C/min at 1100, 1150 and 1200 °C for a period of 1, 2, 3 and 5 h. 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 result. At 10, 15, 20 and 25 wt.% glass waste addition, the apparent activation energies were calculated to be 145, 113.5, 70.4 and 53.74 kJ/mol, respectively. It was found that the sintering activation energy decreased with increasing waste glass addition.

Keywords: D. Porcelain; Waste glass; Sintering kinetics

1. Introduction

One of the most important problems regarding industrial and urban wastes concerns its impact on the safety of people and the environment. The hazardous nature of some wastes requires that suitable treatments be found to render these materials inert. In addition, the use of non-hazardous wastes also needs to be carefully evaluated, taking into account the possibility of recycling, not only in the processes of origin, but also in other industrial activities. Such recycling makes it possible to reach important goals related to the storage of waste, conserving limited supplies of natural raw materials and consequently, safeguarding the environment. To take advantage of the available opportunities and correctly use wastes, it is necessary to understand whether they contain materials suitable for such processes and the products for which they are to be used [1].

Porcelain is a ceramic material with a very compact structure; it is impervious, sometimes glazed and made up of crystalline phases surrounded by a glassy matrix. It is composed of small amounts of clay and kaolin, a high percentage of feldspars as fluxes and some quartz sand. The roles of each of these raw materials in the physico-mechanical behaviour of such triaxial porcelain bodies have been studied in detail [2]. In the case of most commercial porcelain compositions, the glass formation boundary lies in the mullite phase field, so any excess of alumina crystallizes from the glass as mullite. If the glass formation boundary intersects the cristobalite phase field, it is proposed that cristobalite will form. The amount of glass formed during firing is determined by the amount of flux ($R_2O + RO$) and the soak temperature during heat treatment and becomes constant once steady conditions have been reached. The flux level also precisely determines the alumina solubility in the glassy phase, and the Al_2O_3:($R_2O + RO$) ratio has been determined to be constant over the range of firing temperatures applicable to all commercial porcelain compositions [3].

Fly ash containing a large amount of SiO_2 and Al_2O_3 can be a good raw material for porcelain. Therefore, researchers have utilized fly ash, a by-product of thermal power plants, as an alternative source of alumino-silicate raw material by replacing a portion of naturally occurring kaolinitic clays and quartz in

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porcelain tile compositions [2]. In addition, glass waste, when incorporated into a mixture, has a good potential as a new fluxing agent in replacement of traditional feldspar and makes it possible to obtain a vitreous microstructure during the sintering of porcelain [4].

The aim of this study is to investigate the effects of fly ash and glass powder waste additions on the sintering properties of porcelain bodies. An attempt was also made to study the densification behaviour of samples with different compositions and different sintering temperatures and sintering times by using bulk density, scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques.

2. Experimental procedure

A basic porcelain composition consisting of 50% kaolin, 25% potassium-feldspar and 25% quartz was selected. Instead of quartz, fly ash was used at the selected porcelain composition. Also, waste glass was added to the mixture for forming the glass phase instead of potassium-feldspar. The fly ash used in the present study was supplied by Seyit Ömer Power Plant, Turkey. The waste powder glass is a waste material obtained from glass pieces (soda-lime-silica glass). Kaolin and potassium-feldspar were supplied from Çelvit Company, Turkey. The chemical compositions of the raw materials are given in Table 1. Four compositions, marked as P-1, P-2, P-3 and P-4, 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/min at 1100, 1150 and 1200 °C for a period 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 Cu Kα radiation. For microstructural observation, SEM with an EDS attachment of the fracture surfaces was used.

Table 1
Chemical composition of raw materials.

	Raw materials (wt.%)			
	Waste glass	Kaolin	Potassium-feldspar	Fly ash
SiO_2	72.00	48.00	65.10	44.98
Al_2O_3	2.00	37.00	19.50	19.57
Fe_2O_3	–	0.75	0.12	8.11
CaO	12.00	–	0.37	16.55
K_2O	–	1.85	11.00	1.41
Na_2O	14.00	–	3.00	0.21
MgO	–	–	0.12	2.07
TiO_2	–	–	0.02	–
L.O.I.[a]	–	12.20	0.25	6.61

[a] Loss on ignition.

Table 2
Porcelain compositions studied in experimental studies.

Sample codes	Raw materials (wt.%)			
	Kaolin	Fly ash	Potassium-feldspar	Waste glass
P-1	50	25	15	10
P-2	50	25	10	15
P-3	50	25	5	20
P-4	50	25	0	25

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

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

where D is the density, C a characteristic constant of the powders, K 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 the gas constant, T is the absolute temperature and A is a constant [5,6].

3. Results and discussion

3.1. Microstructure characterisation

Microstructural investigations from SEM and EDS analyses of sintered samples revealed various features including very small cracks, undissolved quartz grains, mullite needles, glassy phases and porosity, as shown in Fig. 1. The size of porosity determined by SEM is generally 10–20 μm for the sintered samples. These results are consistent with the results of Islam et al. [7]. Their studies showed quartz grains, mullite needles, glassy phases and very small cracks in the microstructure by SEM. In addition, they reported that the small cracks, cavities and porosity are formed by shrinkage and thermal expansion. During firing, the waste glass has a negative effect, which is a higher volume of shrinkage [8]. Where there is more waste glass, the cracks become more prominent.

In order to understand the microstructural changes and correlate the results, XRD was performed. The X-ray powder diffraction patterns of all compositions sintered at different temperatures and for different periods of time showed the presence of mullite, quartz and anorthite phases (Fig. 2(a) and (b)). Additionally, XRD patterns consisting of mullite and quartz peaks confirmed the SEM results (as seen in Fig. 1). These results are consistent with the results of Dana et al. [2] and Luz and Ribeiro [4]. Quartz is a residual mineral from the original raw materials, and mullite forms during the firing process. Porcelain stoneware bodies generally contain a single mullite phase, $3Al_2O_3{\cdot}2SiO_2$, evolution pathway: the dehydroxylated kaolin, metakaolin, transforms into a nonequilibrium unstable type

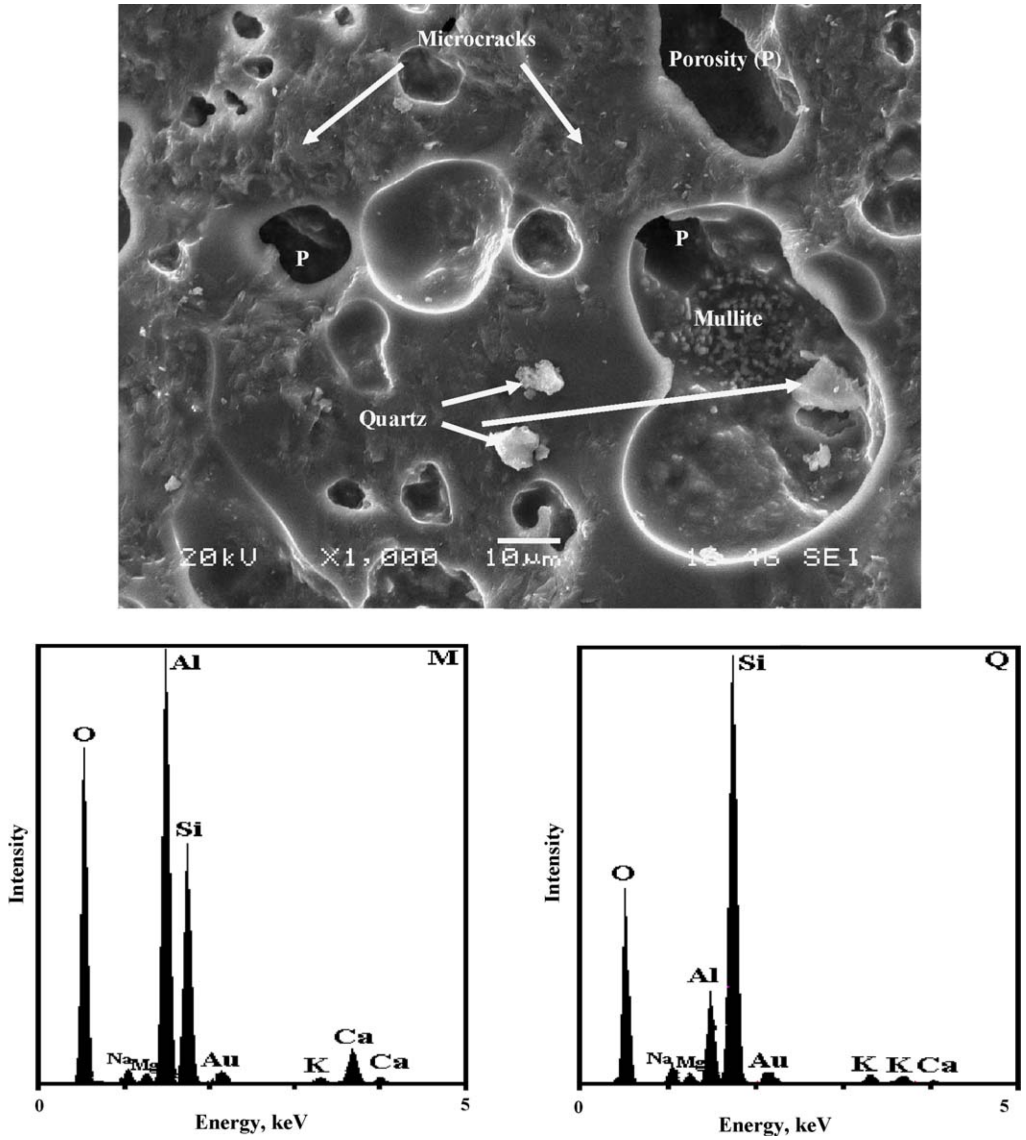

Fig. 1. SEM micrograph and EDS analyses of P-1 composition sintered at 1200 °C for 1 h.

structure, which converts to mullite above 1075 °C [4,9]. For the compositions containing glass powder and fly ash, some modifications in the intensity and position of peaks of the XRD diffraction patterns indicate the presence of anorthite [4]. The intensities of the quartz and anorthite peaks decrease with increasing waste glass addition (Fig. 2(a)) and sintering temperature (Fig. 2(b)), while the intensity of the mullite peak rises with increasing waste glass addition and sintering temperature.

The effects of sintering temperature and sintering time on the densification of the samples are given in Fig. 3(a) and (b). In this figure, the effects of sintering temperature and time for all compositions were compared to the effects of extreme sintering conditions. Similarly, the SEM micrographs of the fracture surfaces of all compositions sintered at 1100 °C and 1200 °C for 1 h were compared in Fig. 4(a)–(h). Densification increases with increasing sintering temperature and sintering time. However, a sintering temperature of 1100 °C did not have any significant effect on densification. The sintering at this temperature resulted in a porous microstructure (Fig. 4(a)–(d)). This effect was very pronounced in sintering at 1200 °C. As can be seen from the micrographs given in Fig. 4(e)–(h), the prolonged sintering at 1200 °C results in a dense structure. The sintering at 1100 °C and 1200 °C for 1, 2, 3 and 5 h raised the bulk density of the samples as the waste glass addition increased from 10 wt.% to 15 wt.%. In waste glass, the vitreous phase contains more Na_2O and CaO with lower amounts of Al_2O_3, K_2O and sometimes SiO_2. These variations bring about a lower viscosity of the liquid phase at sintering temperatures in the materials containing waste glass [8]. The oxide compositions of the experimental samples are given in Table 3. As seen from Table 3, the amounts of Na_2O and CaO increase with increasing amounts of waste glass, while the amounts of K_2O and Al_2O_3 decrease. This cause the formation of a glass phase, which has a lower viscosity and flows easily to fill open pores [10]. However, as more waste glass is added, the bulk density of the samples dramatically decreased. During firing, glass waste accelerates the densification process, with some positive effects

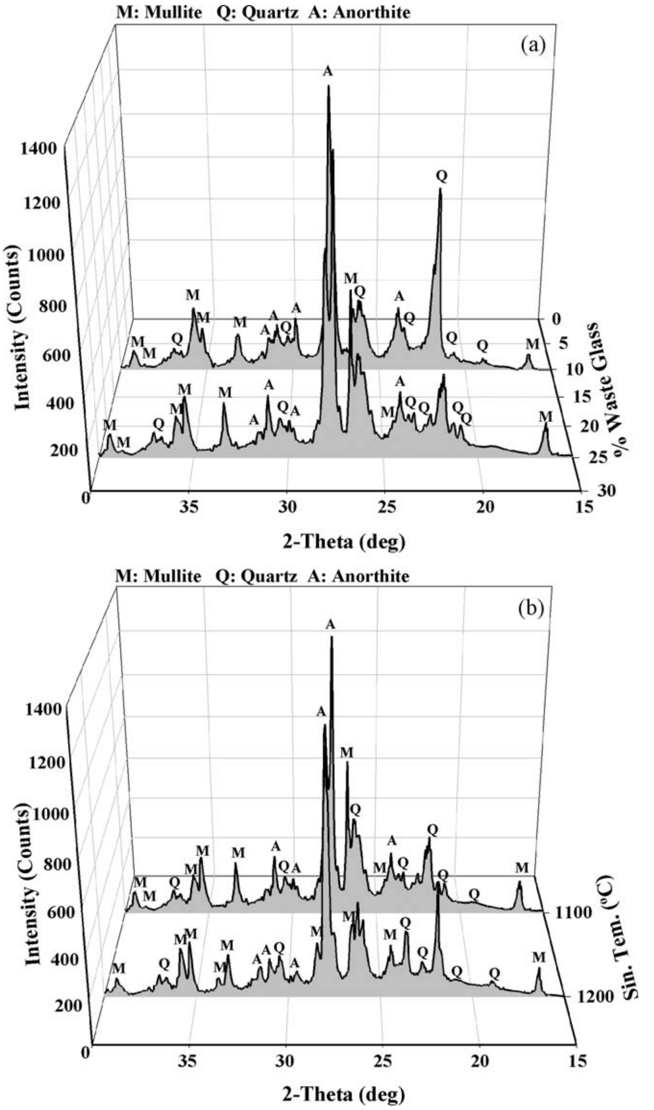

Fig. 2. XRD patterns of (a) P-1 and P-4 samples sintered at 1100 °C 1 h and (b) P-4 samples sintered at 1100 °C and 1200 °C.

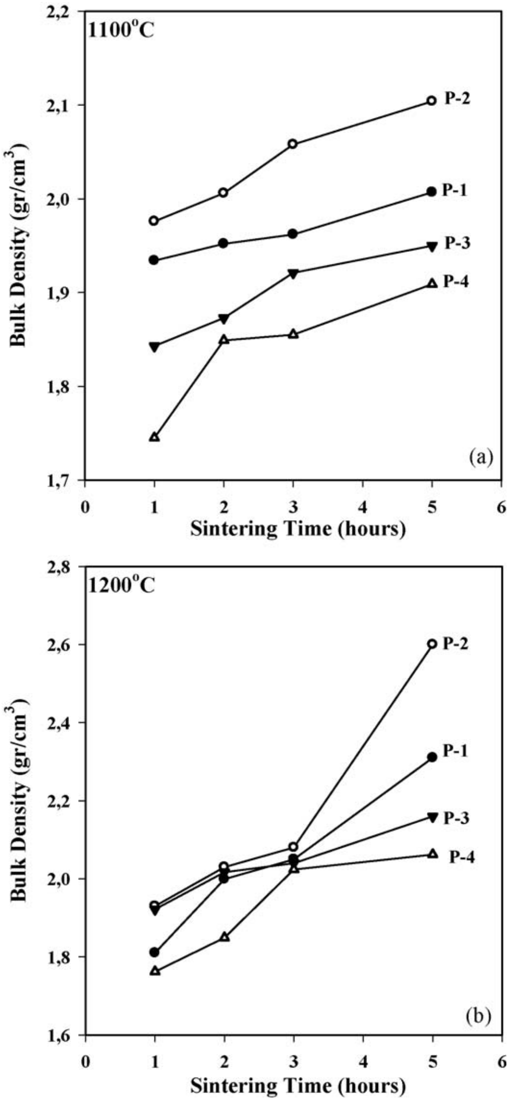

Fig. 3. Calculated densification curves as a function of sintering time at (a) 1100 °C and (b) 1200 °C.

(lower open porosity) as well as negative effects (higher values of shrinkage and closed porosity, lower values of bulk density, mechanical and tribological properties). These differences were limited and tolerable with the addition of 15 wt.% waste glass, but as more waste glass is added, the bulk density of the samples dramatically decreased. In summary, soda-lime glass seems basically to accelerate the densification process, increasing the firing shrinkage and decreasing the open porosity in respect of 10 wt.% added samples, especially when waste addition is as high as 15 wt.%. At all events, this accelerated kinetics brings about the formation of a large amount of closed porosity and, slightly lower values of bulk density. These results are consistent with the results of Matteucci et al. [8].

Table 3
Oxide compositions of the experimental samples.

Oxides (wt.%)	Sample codes			
	P-1	P-2	P-3	P-4
SiO_2	56.80	57.14	57.49	58.74
Al_2O_3	28.84	27.88	26.93	25.97
CaO	5.87	6.50	7.13	7.76
MgO	0.58	0.58	0.57	0.56
Na_2O	2.07	2.66	3.26	3.85
K_2O	3.19	2.59	1.99	1.39
F_2O_3	2.64	2.63	2.62	2.62
TiO_2	0.01	0.01	0.01	0.01

3.2. Sintering kinetics

The reaction rate constant in Eq. (1) can be calculated from the slope of D (bulk density) versus log t (logarithmic scale of sintering time). Then, log K versus $1/T$ graphs were plotted to calculate the sintering activation energy for all compositions (Fig. 5(a)–(d)). From these graphs, the sintering activation energy values were calculated for the initial stage of sintering of different compositions (Table 4). Sintering is largely driven by an increase in viscous flow due to the existence of a glassy phase. Viscous flow sintering development is limited by its

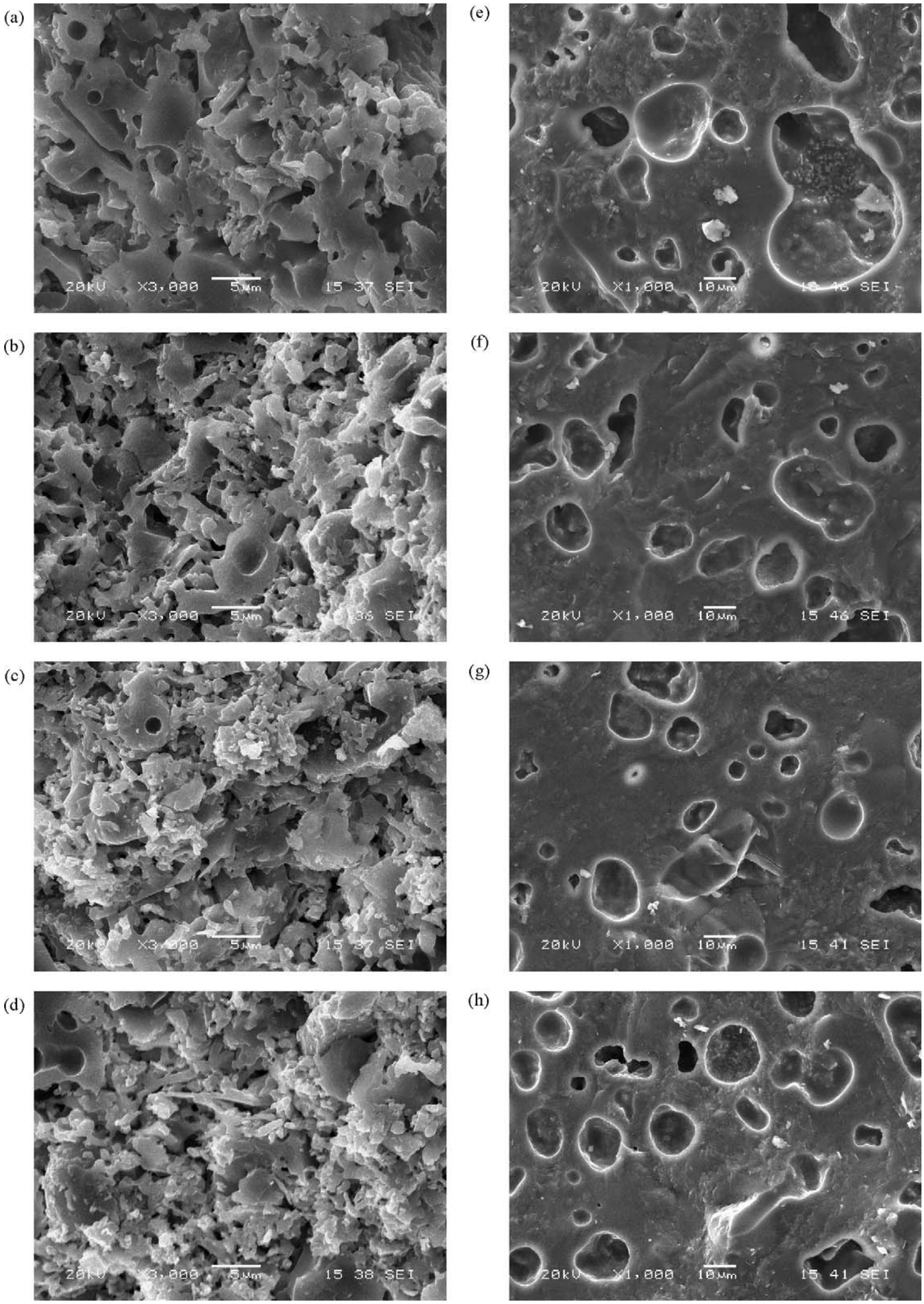

Fig. 4. SEM micrographs of 10, 15, 20 and 25 wt.% waste glass added samples at 1000 °C/1 h (a–d) and at 1200 °C/1 h (e–h), respectively.

viscosity and enhanced by diffusion [11]. Increasing 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 [5]. 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 overall porosity and an improvement in densification, resulting in easier diffusion and a reduced activation energy.

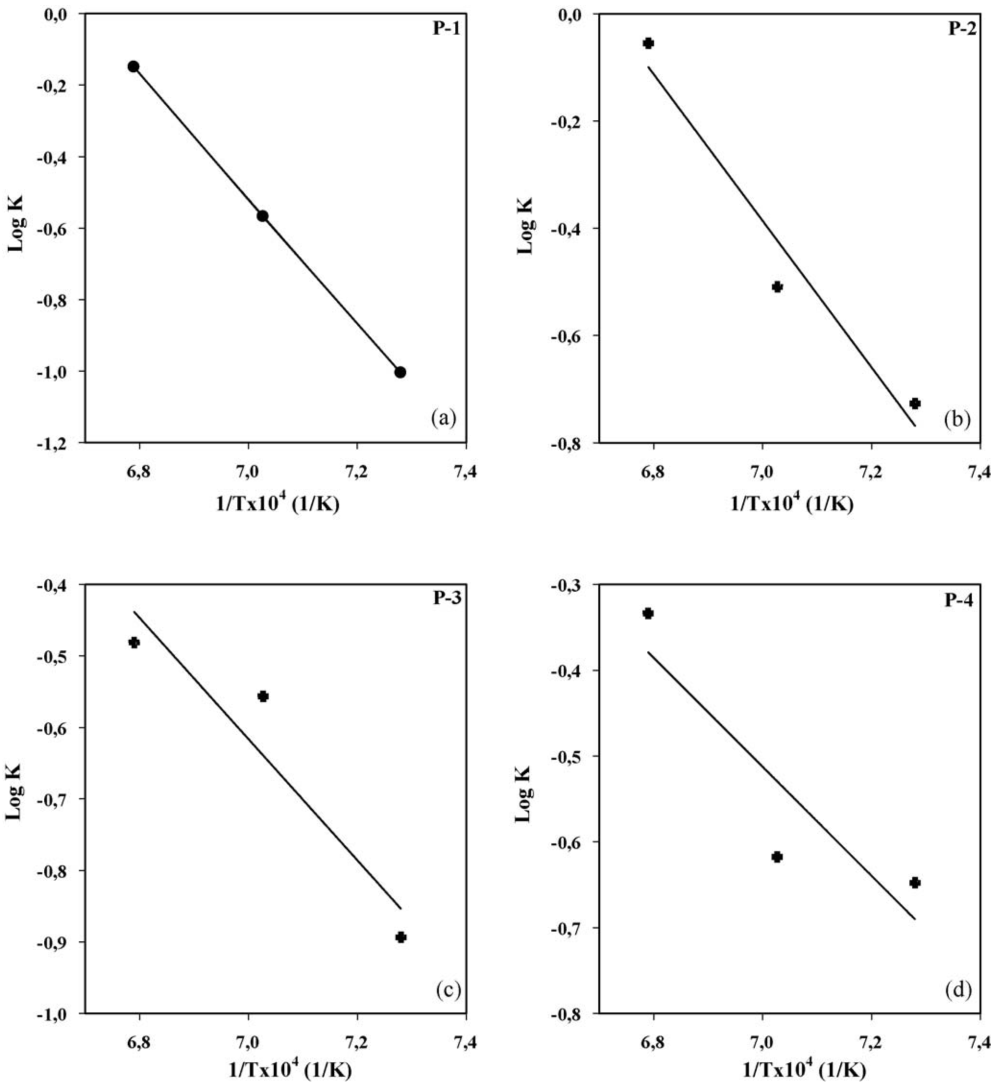

Fig. 5. log K versus $1/T$ graphs for (a) P-1, (b) P-2, (c) P-3 and (d) P-4 compositions.

The activation energy is the energy required to initiate a chemical reaction. Based on the sintering kinetic studies, the activation energies of the P-1, P-2, P-3 and P-4 compositions were found to be 145, 113.5, 70.4 and 53.74 kJ/mol, respectively. Namely, the sintering activation energy decreases as waste glass replaces potassium-feldspar. This may be caused by inclusions of oxide in the raw materials. The content of alkali oxides such as K_2O, Na_2O and CaO is very high in 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.

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

Compositions	$-Q/R$	Activation energy, Q (kJ/mol)
P-1	−17447	145,00
P-2	−13657	113,50
P-3	−8473	70,40
P-4	−6347	53,74

4. Conclusion

The effect of waste glass additions on the sintering properties of fly ash in porcelain bodies was studied between 1100 °C and 1200 °C in air. In our study, we selected a basic porcelain composition consisting of 50% kaolin, 30% potassium-feldspar and 25% quartz, and fly ash was used instead of quartz at the selected porcelain composition. Demirkıran 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. The sintering activation energy value of 145 kJ/mol found for a composition of 10 wt.% waste glass addition (P-1) is very close to the value of 137.618 kJ/mol quoted by Demirkıran et al. Replacement of potassium-feldspar with waste glass resulted in a reduced activation energy required to initiate sintering in porcelain samples. The activation energies of the P-2, P-3 and P-4 compositions were found to be 113.5, 70.4 and 53.74 kJ/mol, respectively.

Therefore, the densification rate could be increased. As a consequence of the lower activation energy, it may be possible to produce the porcelain at 1200 °C instead of 1300–1350 °C. Moreover, it may be possible to use waste glass and fly ash instead of quartz and potassium-feldspar as raw materials in porcelain compositions.

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