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The effect of hydrothermal hot-pressing parameters on the fabrication of porous ceramics using waste glass

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Abstract

The effect of varying hydrothermal hot-pressing (HHP) parameters on the expansion of waste glass powder was investigated by conventional heat treatment. Glass ceramic porous materials were prepared by hydrothermal hot pressing under standard conditions at 200 °C, for 2 h at a constant uniaxial pressure of 20 MPa, while varying experimental variables such as glass particle size, water content, reaction interval, temperature and heating rate. SEM investigation showed the presence of a new glass phase, which incorporated water in its structure. The degree of reactivity attainable between glass particles and water seems to control the expansion process during heating of HHP glass compacts. It was found that the expansion process is independent of experimental parameters such as reaction time, temperature and heating rate, but does depend on the particle size and water content. During the heat treatment, the glass foaming process was preceded by decomposition of the new glass phase in the HHP compacts. A minimum apparent density of 0.40 g cm⁻³ was obtained on specimens prepared with low water content (5 wt%) and medium particle size (39–45 μm). X-ray diffraction patterns of the expanded glasses revealed the formation of SiO₂ (α-cristobalite and quartz) and CaSiO₃ (wollastonite).

1. Introduction

Porous materials, particularly porous glasses, have been developed due to their wide range of properties and applications such as filters, molecular sieves, thermal insulator and building

materials [1, 2]. In general, porous materials with open and/or closed pores are currently fabricated by a combination of solid state sintering and the decomposition of organic polymer compounds and/or calcium carbonate, during a firing process. The actual processing routes allow production of a wide range of porous ceramics with different pore sizes and controlled morphology. Other alternative methods for the preparation of porous materials are glass phase transformation, gel casting, sol-gel and phase separation [1–5].

Over the last decade, new routes for preparing porous glasses have been under further investigation. One of these involves the reaction of glass with water under supercritical conditions when water becomes extremely reactive, due to the increased dissociation potential and the high mobility of molecules and ions. Sigoli *et al* [6] have found that glasses of the ternary $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system show promise for the preparation of porous silica materials by means of a phase separation process, which is accelerated under supercritical water conditions, because glass hydration of silicates decreases the glass transition temperature, T_g , resulting in a decrease of the thermal treatment temperature required to achieve phase transformation. In this way Sigoli *et al* [6] produced a silica matrix containing interconnected homogeneously distributed macropores in one step at 450 °C for 180 min in saturated water vapour, and an α -cristobalite porous matrix was obtained by a heat treatment at 950 °C.

On the other hand, the present authors have recently reported an alternative route for the preparation of porous materials from waste glass through compaction by hydrothermal hot pressing (hereafter referred to as HHP), at a much lower temperature of 200 °C for 1 h with 10 wt% water content under a loading pressure of 20 MPa. It was found that densification proceeds due to the reaction of water and glass, which results in the formation of a new glass phase that incorporates water in its structure [7, 8]. Heat treatment of the HHP compacted glass at temperatures between 650 and 750 °C resulted in a marked expansion. It was found that this is due to water release from the new glass phase; the thermal expansion of water vapour caused a significant volumetric expansion. By means of this route, porous materials with low thermal conductivity (0.21 W mK^{-1}) were prepared [8]. Details of the structure and production mechanism of the porous glass have yet to be clarified, however, there also remains a lack of data related to the influence of the experimental hydrothermal hot-pressing parameters such as glass particle size, glass powder particle size, heating rate, temperature, water content and time on properties of low density porous glass materials.

2. Experimental procedure

2.1. Hydrothermal hot pressing of waste glass

The waste blue glass powder used elsewhere [7] was utilized again to prepared HHP glass compacts. Chemical analysis of the waste glass showed that it consisted basically of SiO_2 (69.58 wt%), Na_2O (14.61 wt%) and CaO (10.9 wt%), and other oxides in minor amounts. Experiments were conducted using glass powder with three different particle sizes, small ($<38 \mu\text{m}$), medium (39–45 μm) and large (63–75 μm). The glass powder (5 g) was well mixed with various contents of water (5, 10 and 20 wt%). The mixture was placed into the cylindrical chamber of an autoclave for HHP experiments, with an inner diameter of 20 mm. The standard HHP conditions selected for the preparation of glass compacts are as follows: temperature of 200 °C, reaction interval of 2 h and 10 wt% of water. All experiments were conducted at a uniaxial loading pressure of 20 MPa. Details of the variation of the HHP experimental parameters are summarized in table 1 together with the total number of compacts prepared.

Table 1. Summary of the experimental HHP conditions used for the preparation of glass compacts and area measurements of the reaction products after HHP treatment.

Simple ID	Temperature (°C)	Water content (wt%)	Particle size (μm)	Reaction interval (min)	Heating rate (deg min^{-1})	Area measurements	
						Glass particles (%)	New glass phase (%)
FM1		5				84.55	15.15
FM2		10	<38	120	5	28.20	71.80
FM3		20				27.15	72.85
FM4			<38			28.20	71.80
FM5	200	10	38–45	120	5	39.25	60.75
FM6			63–75			49.46	50.54
FM7				30		33.18	66.82
FM8		10	<38	60	5	28.27	71.73
FM9				180		29.94	70.06
FM10	150					62.57	37.43
		10	<38	120	5		
FM12	250					11.48	88.52
FM13	200	10	<38	120	1	25.82	74.18

2.2. Heat treatments of HHP compacts

The expansion of the HHP glass compacts was conducted by a conventional firing in air. In order to determine the effect of the heating rate on the expansion, two different heating rates were considered, 1 and 5°C min^{-1} . All the compacts were expanded at various temperatures (650–800 °C) for an interval of 1 h. After the heating treatment, the expanded specimens were cooled down to room temperature inside the furnace.

2.3. Characterization

Aspects relating to the reactivity of glass particles with water were revealed by a scanning electron microscope (SEM, Philips XL30 ESEM) equipped with an energy dispersive x-ray (EDX) device on polished compact surfaces. The reaction products (new glass phase) were measured with an area image analyser (Image Pro Plus software). Powder x-ray diffraction analyses were also employed to determine the crystalline phases of the expanded specimens using an x-ray diffractometer (Rigaku, Rotaflex) with graphite-monochromatized Cu $K\alpha$ radiation at 40 kV and 100 mA. The apparent density of the foamed glasses was determined by Archimedes' principle using a helium pycnometer (Multipycnometer Quantachrome), using a cell with a volume of 135 cm^3 ; prior to measurement the cell was calibrated with a standard sphere of 56.5592 cm^3 . The specimens were weighed and the volume was measured at a helium pressure of 0.117 MPa. The expanded specimens were cut and ground to investigate aspects related to the inner microstructure by SEM.

3. Results and discussion

3.1. Reactivity of glass with water under HHP conditions

Initial attempts to investigate the reactivity of water with glass particles were carried out by varying the particle size, water content, reaction interval and heating rate from the standard HHP conditions, while keeping constant the temperature, time and pressure (200 °C for 2 h at a constant uniaxial pressure of 20 MPa).

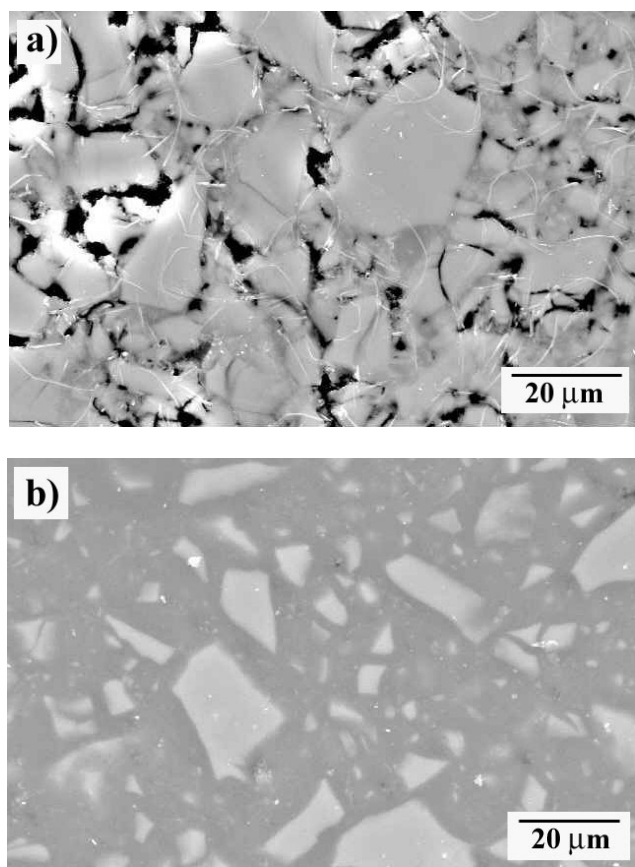


Figure 1. SEM micrographs of the surface of the hydrothermal compacts prepared at 200 °C for 2 h with a loading pressure of 20 MPa, with (a) 5 wt% water and (b) 20 wt% water.

Figure 1 shows typical microstructures of HHP compacts prepared at 200 °C for 2 h with a glass particle size of $<38 \mu\text{m}$ and varying water contents. The SEM micrographs of the compact prepared with 5 wt% water clearly revealed that a small amount of a new glass phase (continuous dark phase, figure 1(a)) was formed during the HHP treatment. At 10 wt%, the content of this phase in the compact was further increased and the glass particles were severely reduced in size. The reduction in the size of the original glass particles might be associated with glass dissolution in water, leading to the formation of the new glass phase. Indeed, the present authors have previously found that the new glass phase has the same constituents as in the original waste glass, but incorporates some water in its structure [7]. At higher water contents (20 wt%), no further reaction was observed in comparison to that which occurred at lower water content. The microstructure is similar to that observed on the compact prepared with 10 wt% water; however, a few cracks were generated inside the compacted glass.

Figure 2 shows the effect of the reaction temperature on the dissolution of glass particles. The amount of the new glass phase obtained at 150 °C was lower in comparison with that formed in the specimen treated at 250 °C. At 150 °C, only a few glass particles ($<20 \mu\text{m}$) were found on the surface of this specimen. It was found that on all the compacts the new phase was homogeneously distributed within the microstructure of the dense glass HHP compacts. Table 1 shows the effect of varying some of the HHP parameters. These results agree with the

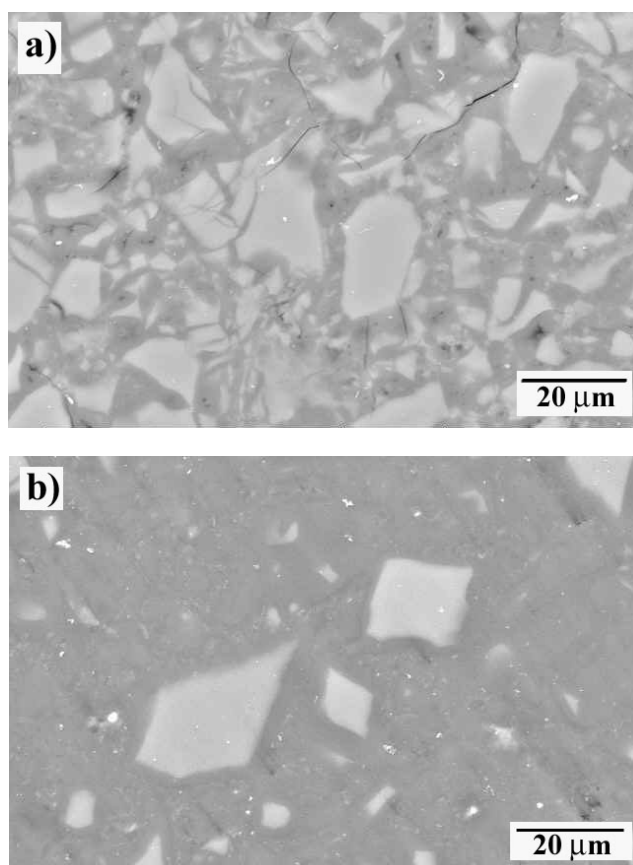


Figure 2. Aspects of the reaction between water and glass particles conducted under HHP conditions at a loading pressure of 20 MPa for 2 h with 10 wt% of water content at different temperatures: (a) 150 °C and (b) 200 °C.

microstructures determined by SEM, and show that the maximum amount of the new ‘glass water’ on the glass was 88.52%, obtained at a reaction temperature of 250 °C. Hence, the increase of the following parameters resulted in the formation of >60% new glass phase: temperature, reaction interval and water content. In contrast, a decrease in the amount of the ‘glass water’ was observed with an increase in the glass particle size.

The above results might be explained by the fact that water diffusion in glass takes place during HHP treatment. It is well known that under supercritical conditions water becomes extremely reactive because of the increased dissociation potential and the high mobility of molecules and ions. Hence, we suggest that under HHP conditions lower than the supercritical water state, the new glass phase that incorporates water is formed due to dissolution of the glass into the water. This inference is supported by the fact that the original glass particles were further reduced in size, as well as the glass reactivity being accelerated by increasing the reaction temperature, time and water content [6, 9].

3.2. Effect of the experimental HHP parameters on the expansion of glass

Since the HHP glass compacts incorporate molecules of water homogeneously distributed in the structure of the new glass phase, water release might produce the expansion of glass at relative high temperatures. Likewise, a process employed for producing ceramic foams involves the

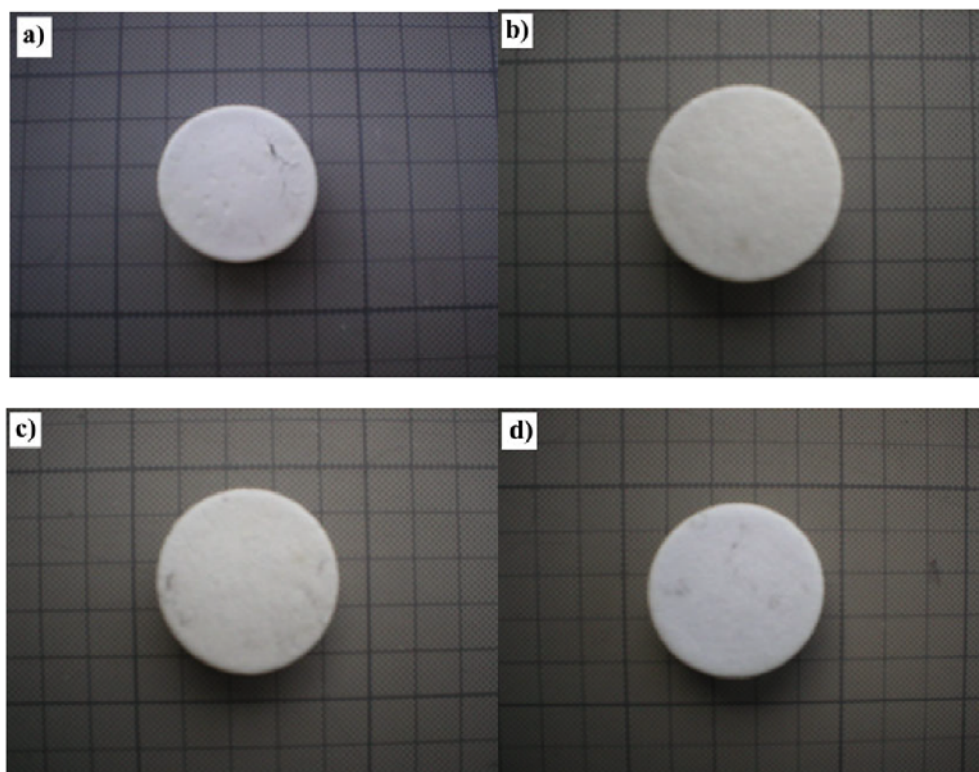


Figure 3. Low magnification micrographs of glass compacts HHP prepared at 200 °C for 2 h with a loading pressure of 20 MPa and 10 wt% of water, which were then expanded by conventional firing in air at different temperatures: (a) 650 °C, (b) 700 °C, (c) 750 °C and (d) 800 °C. Grid division = 10 mm.

use of foaming agents that decompose at high temperature, producing a gas that expands the material [5]. This inference was proved by the naked eye observations conducted on HHP specimens ID FM5 (table 1) after heat treatments conducted at different temperatures (650–800 °C). The results are shown in figure 3. In general, macroscopic observations of the heat-treated samples revealed that the expansion process proceeds without severe distortions of the disc shape. Furthermore, a gradual increase in size of the specimens is clearly observed when treated at intermediate temperatures (700 or 750 °C; figures 3(a)–(c)). When the specimens were treated at 800 °C, bulk shrinkage occurred of both the diameter and thickness of the specimen (figure 3(d)); this fact might be associated with the pore collapse and the partial release of the inner pressure of water vapour.

Figure 4 shows the effect of hydrothermal hot-pressing parameters on the apparent density of expanded glass materials. The samples were obtained under standard HHP conditions at 200 °C for 2 h and 20 MPa of confining pressure, with different particle sizes (figure 4(a)) and water contents (figure 4(b)). The lowest apparent density (0.40 g cm^{-3}) was achieved by treating the HHP compacts between 700 and 750 °C, using an intermediate particle size of 39–45 μm , while the compacts prepared with smaller ($<38 \mu\text{m}$) and larger (63–75 μm) particle sizes had more limited expansion and the minimum apparent density achieved by these specimens was above 0.60 g cm^{-3} . These results might be explained by the fact that the expansion of glass is limited by the quantity and a homogeneous distribution of the new glass phase which incorporates water and causes the expansion process. After all the HHP treatments

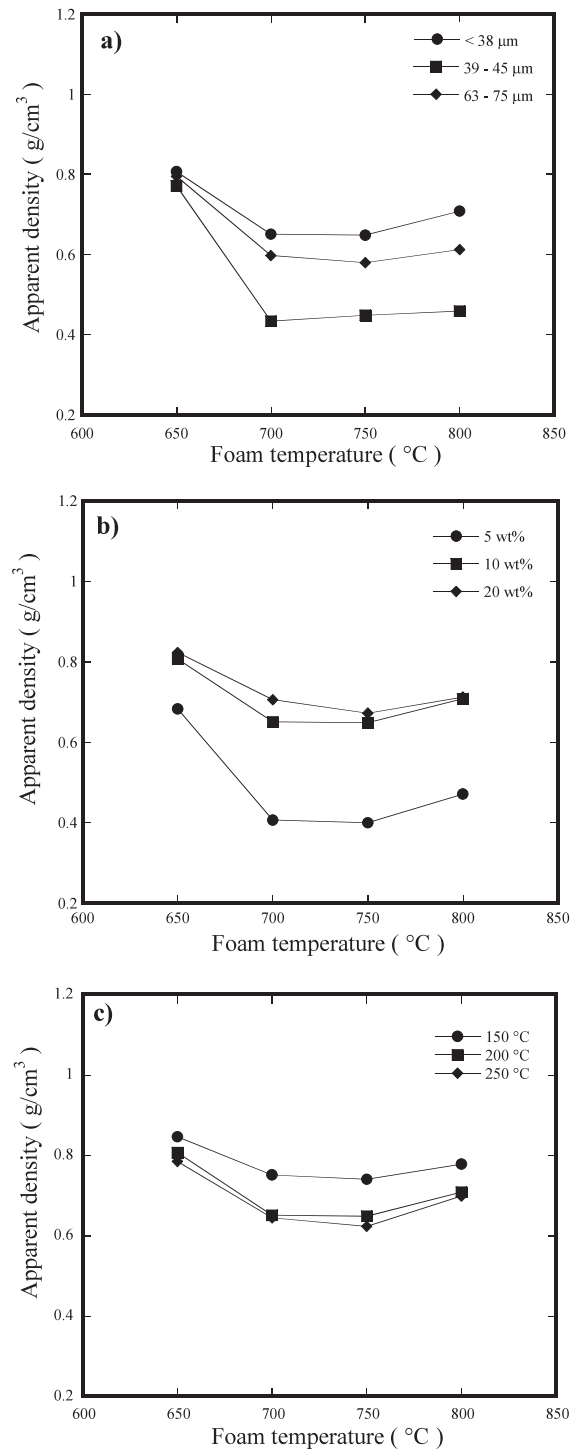


Figure 4. Variation of apparent density of HHP glasses expanded at different heating temperatures for 1 h. The glass compacts were prepared at standard conditions, of 200 °C for 2 h with a loading pressure of 20 MPa and 10 wt% water, varying experimental parameters such as (a) particle size, (b) water content and (c) reaction temperature.

conducted with 10 wt% water (irrespective of the particle size), no trace of the remaining water was seen after opening the HHP vessel. Therefore, we believe that the 10 wt% of water was diffused into the structure of the new glass phase in all cases. The fraction of water incorporated in the new glass phase, however, must be higher in the compacts prepared with intermediate (sample ID FM5) and large (sample ID FM6) particle sizes, because the portion of this new phase in the compacts is lower in comparison with that seen in the compact prepared with glass particles $<38 \mu\text{m}$. It has been reported that the viscosity of a glass decreases due to water diffusion, and a gradual variation of glass viscosity might result from the amount of water incorporated in the glass structure [6]. Hence, it is likely that a loss of the internal gas pressure due to the damage of the inner porosity might cause a lower expansion of the glass compact. Likewise, the presence of a large number of original glass particles may retard the expansion process, because the original particles must be softened by the interaction with the new glass phase, in order to allow the expansion process to proceed [8].

A similar trend to that described above was observed in the case of the effect of the water content (figure 4(b)). The results in figure 4(b) show that the lowest apparent density is preferentially obtained by using low water contents (5 wt%). On the other hand, it is clear that the compacts prepared with large amounts of water exhibit a broadly similar density behaviour. In previous work the present authors found that the content of water that reacts with glass particles and that becomes incorporated in the new glass phase is limited to approximately 12 wt% under hydrothermal conditions [7]. Hence, the HHP compacts prepared with 20 wt% of water had similar apparent density to those prepared with lower water contents of 10 wt%. In the case of the compact prepared with 5 wt% of water, the significant expansion obtained after the heat treatment might be associated with the presence of the residual porosity, which contains the expelled water vapour, preventing a further release of the foaming gas phase during the heat treatment.

On the other hand, HHP parameters such as reaction temperature, time and heating rate did not have a significant influence on the expansion process. Figure 4(c) shows the typical variation of the apparent density of expanded glasses which were prepared under HHP conditions at different temperatures. In general, the values of the apparent density of the compacts vary from 0.62 to 0.80 g cm^{-3} , and the specimens prepared at temperatures above 200°C expanded remarkably in comparison with those prepared at lower temperature (150°C). Thus, we suggest that the limited expansion obtained at lower temperature is associated with a decrease in the degree of reaction between water and glass. The large number of original glass particles remaining might limit the attainable apparent density reduction, because the glass particles are much less soft than the new glass phase when heated. Therefore, from the present results, we conclude that the degree of reactivity between glass and water under HHP conditions may be controlled to lead to an optimum control expansion of HHP glass compacts to produce very low apparent density and thermal conductivity products [8].

3.3. Characteristics of the glass expansion process

X-ray diffraction analyses conducted on the expanded samples showed that during the treatments conducted at temperatures between 650 and 750°C the glass undergoes a crystallization of various silicate phases (figure 5). Figure 5 includes the x-ray diffraction pattern for the HHP compacted glass, which constitutes only an amorphous phase. The HHP glass devitrification process begins at a lower temperature of 650°C , leading to the formation of an hydrated silicate known as montmorillonite $((\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2\text{SiO}_2\text{O}_{10}(\text{OH}) \cdot n\text{H}_2\text{O})$. At higher temperature ($>700^\circ\text{C}$), this phase was reduced in content and the crystalline phases of SiO_2 (quartz and α -cristobalite) and CaSiO_3 (wollastonite) were preferentially formed in

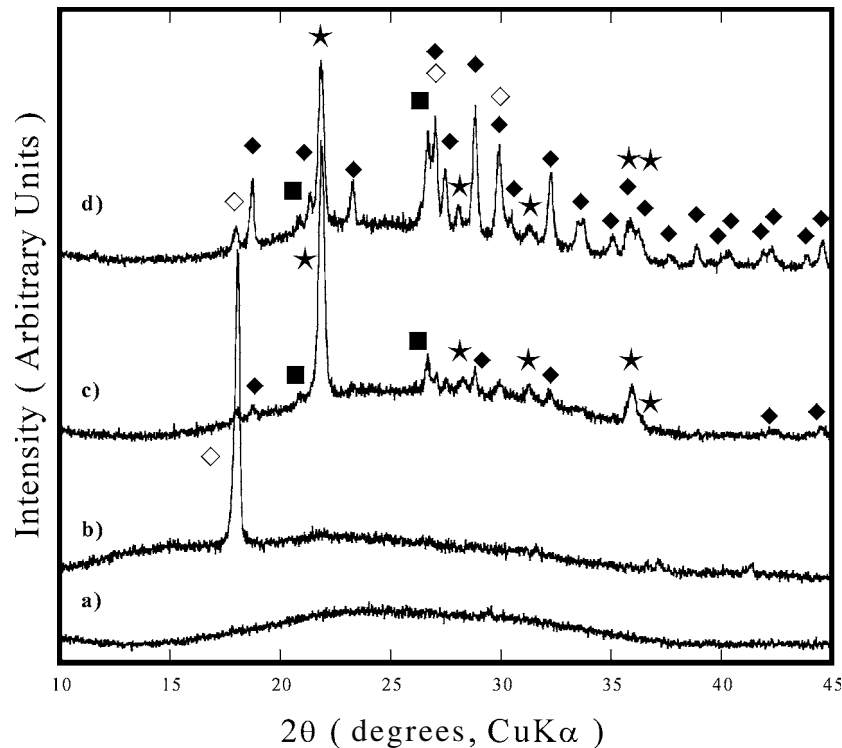


Figure 5. X-ray diffraction patterns of (a) HHP compact, and those of the glasses expanded at (b) 650 °C, (c) 700 °C and (d) 750 °C in air, respectively. Crystalline phases: ◇, $(\text{Na}, \text{Ca})_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_2\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ montmorillonite; ★, SiO_2 cristobalite; ◆, CaSiO_3 wollastonite; ■, SiO_2 quartz.

the expanded samples. Recently, Tomozawa [10] has reported that glass properties such as viscosity and crystallization temperature, T_g , are commonly decreased when water diffuses into the glass structure. Hence, the HHP compacted glass must undergo a decrease in the crystallization temperature simultaneously with the expansion process, due to the presence of molecular water.

Typical microstructures within the expanded samples are shown by SEM micrographs in figure 6. The glass compacts were prepared under HHP conditions of 200 °C for 2 h with 10 wt% of water content and varying glass particle sizes. In general, a typical microstructure consisting of cellular hollows homogeneously distributed was obtained on all the expanded glasses, after heat treatment at 700 °C for 1 h. Furthermore, the specimen prepared with the smallest particle size ($<38 \mu\text{m}$, figure 6(a)) showed the formation of some large hollows ($300 \mu\text{m}$) interconnected with small cavities. In contrast, the specimens prepared with intermediate ($39\text{--}45 \mu\text{m}$, figure 6(b)) and large ($63\text{--}75 \mu\text{m}$, figure 6(c)) glass particle sizes are characterized by a large number of semi-spherical hollows with an average size of 125 and $\sim 90 \mu\text{m}$, respectively. Small cavities also remain between the walls of the hollows, mainly on the specimen prepared with intermediate size glass particles. These results are in accordance with the apparent density trends obtained for each sample (figure 4(a)). Hence, we suggest that the collapse of the spherical hollows observed in sample FM2 is attributable to the excess of the new glass phase (71.82%), which is well distributed in the bulk specimen. Thus, during the hollow collapse a sudden drop of pressure might retard the bulk expansion of the specimen [11].

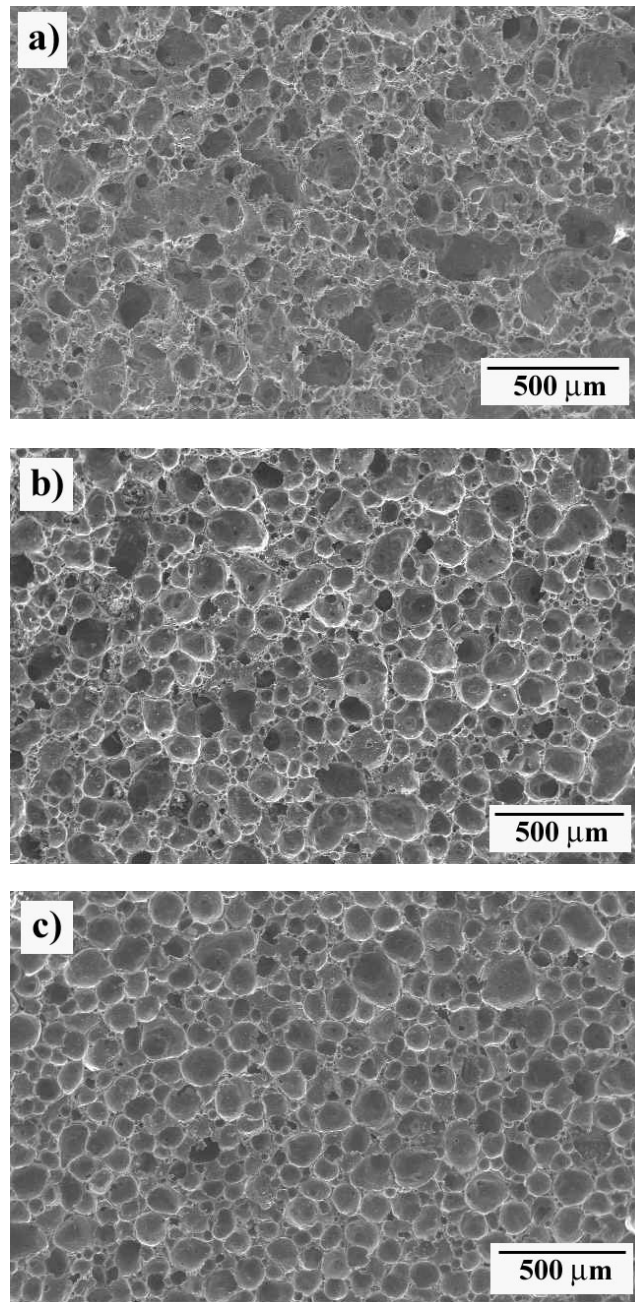


Figure 6. SEM micrographs of glass specimens expanded at 700 for 1 h; samples prepared by HHP with a particle size of (a) $<38 \mu\text{m}$, (b) $39\text{--}45 \mu\text{m}$ and (c) $63\text{--}75 \mu\text{m}$ at 200°C for 2 h with 10 wt% of water content.

The optimum amount of the new glass phase in the HHP compact is nearly 60%, which leads to the preparation of low apparent density porous glass materials with controlled microstructures after heat treatment.

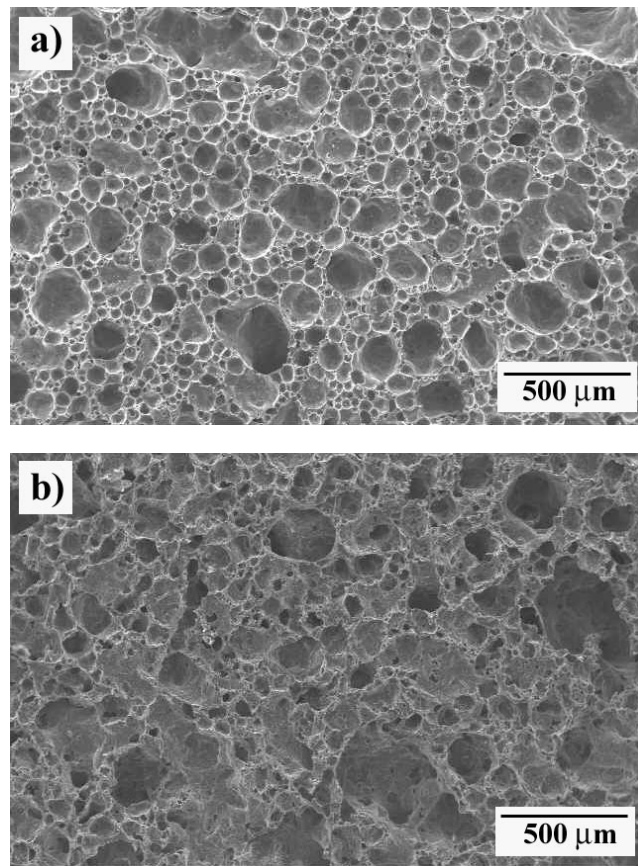


Figure 7. SEM micrographs of glass specimens expanded at 700 for 1 h; samples prepared by HHP with various water contents of (a) 5 wt% and (b) 20 wt%, at 200 °C for 2 h with a glass particle size < 38 μm.

Figure 7 shows the effect of the water content on the microstructure of the expanded HHP specimens (samples ID FM10 and FM12), which were obtained under the standard conditions referred to in the experimental procedure. Thus, the specimens prepared with low water content (5 wt%, figure 7(a)) and which have the lowest apparent density (0.39 g cm^{-3}) are characterized by two different types of hollow, one larger semi-spherical ($\sim 300 \text{ μm}$) and a great number of spherical small holes with an average diameter of 50 μm . In this particular case, it is expected that this peculiar microstructure is produced due to the partial reaction of the glass particles with water and the presence of closed pores (figure 1(a)). Since the new glass phase is heterogeneously distributed within the glass compact, very small spherical hollows were produced at particular locations in the specimen that exhibits a low amount of the phase that achieves foaming. In contrast, the coalescence of hollows and the interconnection with surrounding cavities leads to the formation of very large irregular pores ($\sim 400 \text{ μm}$) in specimens prepared with large water contents ($> 10 \text{ wt\%}$), figure 7(b).

In general, according to previous studies already published [8], the formation of cellular hollows is explained as follows. The original compacts prepared by HHP contained water, which had diffused into the glass network structure. Thus, when the compacts were heated at high temperatures, the water might be diffused out from the surface of the compacts. Likewise,

glass becomes soft when it is heated at high temperatures, and this softening might be also affected by the presence of water diffused in the glass network, because water decreases glass viscosity [6, 10, 11]. The release of water from the glass structural network at high temperatures produced water vapour bubbles in the softened glass, just like boiling water. The size of the bubbles increases with the increase in temperature due to thermal expansion of the vapour in the bubbles and further softening of the glass. Thus, the volume of the compacts was increased remarkably by high temperature treatment. Treatment at high temperatures ($>750^{\circ}\text{C}$) produces the collapse of the cellular hollows, perhaps because the glass viscosity becomes too low.

4. Conclusions

In the present work, it was found that the reactivity of glass particles and water under HHP conditions leads to the ability to create very light porous glass ceramic materials, which float in water. The expansion of HHP glass compacts was further influenced by the HHP treatment parameters of water content, particle size rather than temperature, reaction interval and heating rate. Variations of these parameters lead to control of the reaction of glass and water during the hydrothermal treatment, which results in the formation of a new glass phase that incorporates water. Thus, the optimum HHP conditions for the preparation by subsequent heating of low apparent density porous glasses (0.40 g cm^{-3}) were a glass particle size of $39\text{--}45\ \mu\text{m}$ and $5\text{ wt}\%$ water. The heating of the HHP glass compacts resulted in the expansion of the glass due to a simultaneous release of water and glass softening. It seems this process is further influenced by the amount of water originally incorporated in the glass structure, because high water contents might lead to hollow collapse that limited the glass foaming process. Simultaneously, a crystallization of glass occurred during the heat treatment due to a decrease in the T_g , which is affected by the water incorporated in the structure of the new glass phase. Thus, major crystalline phases of SiO_2 (α -cristobalite and quartz) and CaSiO_3 (wollastonite) were found in the porous glass after heat treatment in air.

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