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Synthesis of spherical shape borate-based bioactive glass powders prepared by ultrasonic spray pyrolysis

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Abstract

Spherical shape borate-based bioactive glass powders with fine size were directly prepared by high temperature spray pyrolysis. The powders prepared at temperatures between 1200 and 1400 °C had mixed phase with small amounts of fine crystal and an amorphous rich phase. Glass powders with amorphous phase were prepared at a temperature of 1500 °C. The mean size of the glass powders prepared by spray pyrolysis was 0.76 μm. The glass powders prepared at a temperature of 1200 °C had two distinct exothermic peaks (T_{c1} and T_{c2}) at temperatures of 588 and 695 °C indicating crystallization. The glass transition temperature (T_g) of the powders prepared at a temperature of 1200 °C was 480 °C. Phase-separated crystalline phases with spherical shape were observed from the surface of the pellet sintered at a temperature of 550 °C. Crystallization of the pellet was completely occurred at temperatures of 750 and 800 °C. The pellets sintered at temperatures below 700 °C had single crystalline phase of $CaNa_3B_5O_{10}$. The pellet sintered at a temperature of 800 °C had two crystalline phases of $CaNa_3B_5O_{10}$ and CaB_2O_4.
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1. Introduction

Bone reconstruction is mandatory in several clinical issues involving orthopaedics and dentistry. The replacement and repair of bone have traditionally been accomplished through the use of artificial implants, autografts, and allografts. Since the discovery of bioactive glass by Hench, many bioactive glasses and glass–ceramics, which exhibit the ability to bond to living bone through a hydroxyapaptite (HA) layer formed onto their surfaces, have been synthesized and developed for medical applications [1–5]. One of the main characteristics of the bioactive glasses and glass–ceramics is their highly reactive surface when this material is soaked in human plasma or an analogous solution [6]. HA generally forms rapidly onto surfaces of glasses and glass–ceramics, which favour releasing of Ca ions, than onto crystalline materials [6].

A borate glass, based on B_2O_3 network as opposed to the SiO_2 network for silicate glasses, has been shown to undergo more rapid and complete conversion to HA in a dilute aqueous phosphate solution [7,8]. Bioactive glasses and glass–ceramics are mainly prepared by conventional melting process. In the conventional melting process, control of compositions of glasses and glass–ceramics is difficult because of volatility of some volatile components. Contamination of the product could be occurred in melting and crushing processes. Therefore, sol–gel process was introduced to the preparation of bioactive glasses and glass–ceramics. In the sol–gel process, thermal treatment of the samples is inevitable to completely decompose the precursors and to remove the remaining solvent. In the conventional melting and sol–gel processes, control of the morphologies and mean sizes of bioactive glass–ceramics is difficult.

Recently, spray pyrolysis was applied to produce the glass powders with various compositions [9–12]. The glass powders prepared by spray pyrolysis had submicron size, spherical shape and non-aggregation characteristics. In this study, the spherical shape borate-based bioactive glass powders were directly prepared by spray pyrolysis. The optimum preparation conditions for borate-based glass powders with amorphous phase were investigated. The structure and crystallization behavior of the prepared borate-based glass powders were also investigated.

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2. Experimental procedure

Borate-based bioactive glass, designated 45S5B1, with the composition (in mol%): 24.4 Na_2O, 26.9 CaO, 2.6 P_2O_5, and 46.1 B_2O_3, were prepared by high temperature spray pyrolysis. Fig. 1 shows the schematic diagram of the spray pyrolysis process. The spray pyrolysis equipment used consisted of six ultrasonic spray generators that operated at 1.7 MHz, a 1000-mm-long tubular alumina reactor of 50-mm ID, and a bag filter. The 45S5B1 powders were prepared at temperatures between 1000 and 1400 °C. The spray solutions were obtained by adding Na_2CO_3 (Junsei, 99%), $Ca(NO_3)_2{\cdot}4H_2O$ (Kanto, 99%), and $NH_4H_2PO_4$ (Aldrich, 98%), H_3BO_3 (Kanto, 99%) to distilled water. The overall solution concentration was 0.5 M. The spray solution of salts was atomized with ultrasonic spray generators and introduced into a hot reaction column, where the droplets were dried, decomposed, and melted. The flow rate of air used as a carrier gas was 20 L/min. The production rate of glass powders was 5 g/h. The pellets compressed of precursor powders obtained by spray pyrolysis were heat-treated at temperatures between 500 and 800 °C at constant heating rates of 10 °C/min for 3 h in air atmosphere.

The crystal structures of the prepared powders and sintered pellets were investigated by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation ($\lambda = 1.5418$ Å). The thermal properties of the prepared glass powders were measured using a thermo-analyzer (TG-DSC, Netzsch, STA409C) in the temperature range from 40 to 900 °C. Fourier transform infrared (FT-IR) transmittance spectra were recorded between 400 and 2000 cm^{-1}. The morphological characteristics of the prepared powders and pellets sintered at various temperatures were investigated using scanning electron microscopy (SEM, JEOL, JSM-6060). The mean sizes and size distributions of the glass powders were investigated using a light-scattering powder-size analyzer (Otsuka Electronics, DLS PAR-III).

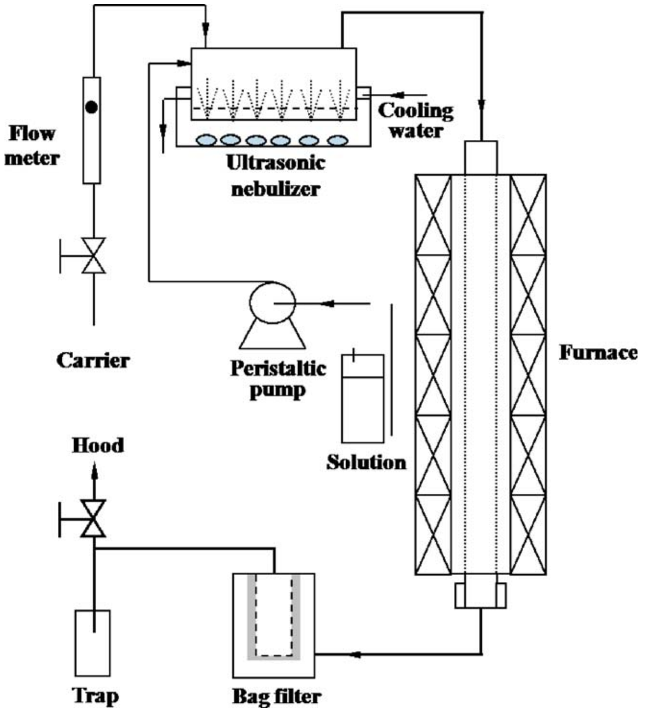


Fig. 1. The schematic diagram of the ultrasonic spray pyrolysis process.

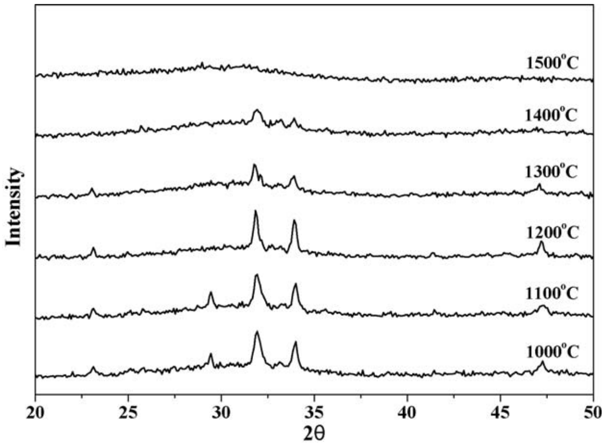
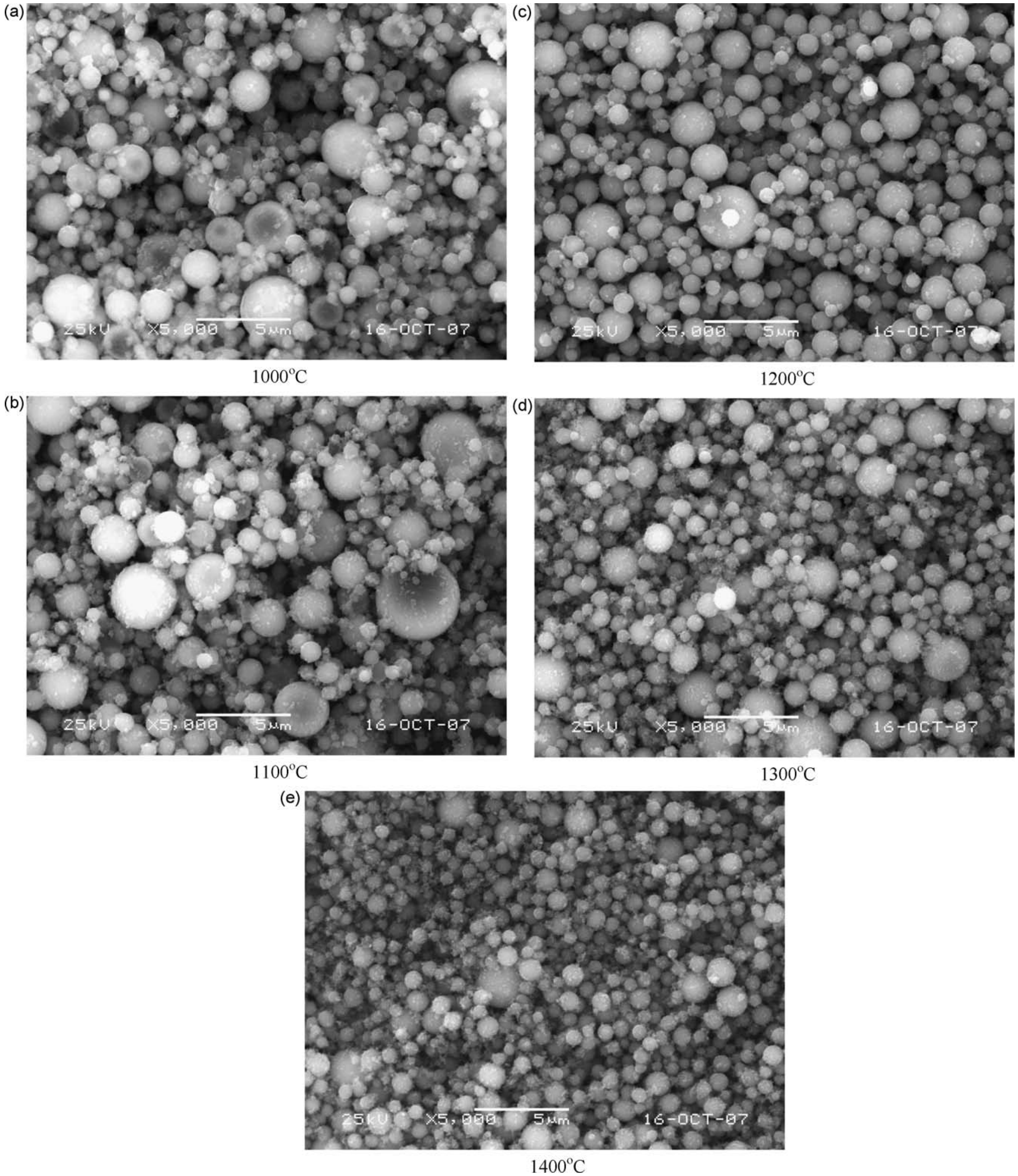


Fig. 2. XRD patterns of the powders prepared by spray pyrolysis at different temperatures.

3. Results and discussion

The crystal structures and morphologies of powders prepared at various temperatures are shown in Figs. 2 and 3. Fig. 2 shows the XRD patterns of the powders prepared by spray pyrolysis. The powders prepared at temperatures below 1400 °C had crystalline phases, in which transition to the glass phase did not completely occur because of short residence time of the powders inside the tubular alumina reactor. On the other hand, the sharpness of the XRD peaks decreased with increasing the preparation temperatures. Glass powders with amorphous phase were prepared at 1500 °C, in which the residence time of the powders was 0.5 s. The broad peak in the XRD pattern represents the character of glass material. In the conventional melting process, 45S5B1 glass powders with amorphous phase were obtained at a low melting temperature of 1000 °C because of long heating time above 1 h. Fig. 3 shows the SEM images of the glass powders prepared by spray pyrolysis at various preparation temperatures. The powders prepared at a low temperature of 1000 °C did not melt and had hollow morphologies. The hollowness of the prepared powders decreased with increasing the preparation temperatures. Thus, the powders prepared at high temperatures above 1200 °C had a spherical shape and dense structure. Melting of the glass powders occurred at high preparation temperatures above 1200 °C even at the short residence times of the powders inside the hot wall reactor. The size distributions of the glass powders shown in Fig. 3(a) and (c), which were measured by the light-scattering method, are shown in Fig. 4. The mean sizes of the 45S5B1 glass powders shown in Fig. 3(a) and (c) were 0.99 and 0.76 μm. The glass powders prepared at temperatures of 1300 and 1500 °C had bimodal size distributions of nano-sized and micron-sized powders. One micron-sized particle was formed from one droplet by drying, decomposition and melting



1000°C

1200°C

1100°C

1300°C

1400°C

Fig. 3. SEM images of the powders prepared by spray pyrolysis at temperatures between 1000 and 1400 °C.

processes. However, the nano-sized powders were formed by chemical vapor deposition (CVD) process. Evaporation of the glass powders occurred at high preparation temperature. Nano-sized powders were formed from the evaporated vapors by CVD process.

Fig. 5 shows the EDX spectrum of the powders prepared at a preparation temperature of 1200 °C. In the EDX analysis, a boron component was not detected. Thus, the composition of the powders, except for boron, was compared with that of the spray solution. The ratio of Na/Ca/P was identified to be 9.17:5.21:1, which was very close to the original starting ratio of Na/Ca/P in mixture of the spray solution. Thus, the change of composition by evaporation of some components comprising the glass powder did not occur even at a high temperature of

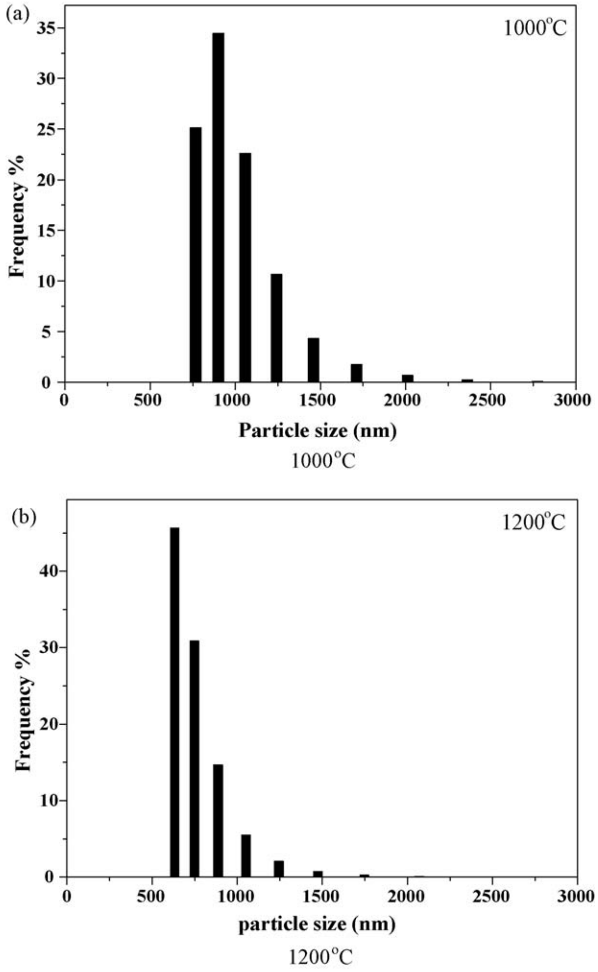


Fig. 4. Size distributions of the powders prepared by spray pyrolysis at temperatures of 1000 and 1200 °C.

1200 °C because of the short residence time of the glass powders inside the hot wall reactor.

The FT-IR spectra of the glass powders prepared by spray pyrolysis are shown in Fig. 6. In the FT-IR analysis, mainly the peaks for [BO_3], [BO_4] and [PO_4] units in 45S5B1 bioactive glass can be identified [13]. The glass powders prepared by spray pyrolysis at temperatures of 1000 and 1200 °C had similar absorption spectra to those of the glass powders prepared by the conventional methods [13,14]. The absorption bands in the 1200–1500 and 1150–1300 cm^{-1} range were due to B–O stretching of trigonal [BO_3] units, while the absorption bands in the 800–1200 and 600–800 cm^{-1} ranges were related to B–O stretching of tetrahedral [BO_4] units and bond-bending motion of B–O–B groups, respectively [14].

Figs. 7 and 8 show the TG/DSC curves of the powders prepared at temperatures of 1000 and 1200 °C. The TG curve of

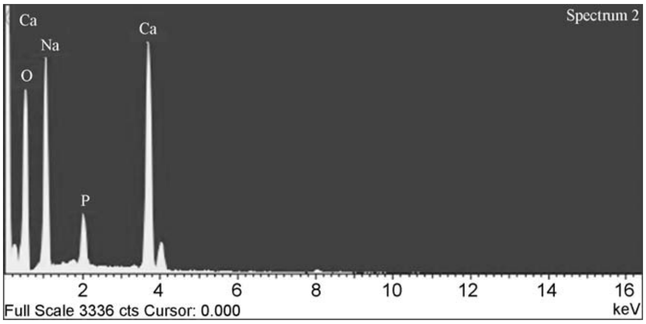


Fig. 5. EDX spectrum of the glass powders prepared by spray pyrolysis at a temperature of 1200 °C.

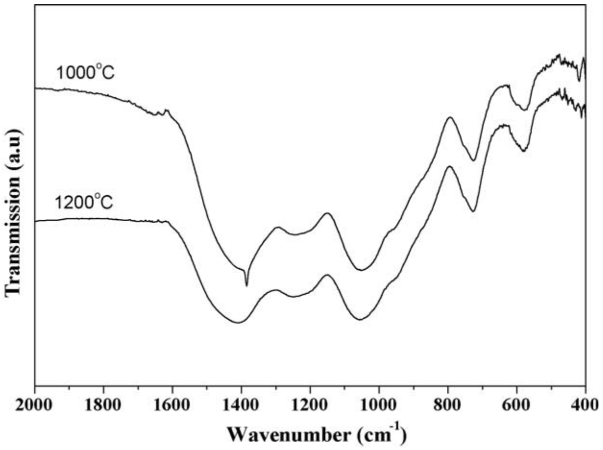


Fig. 6. FT-IR spectra of the powders prepared by spray pyrolysis at temperatures of 1000 and 1200 °C.

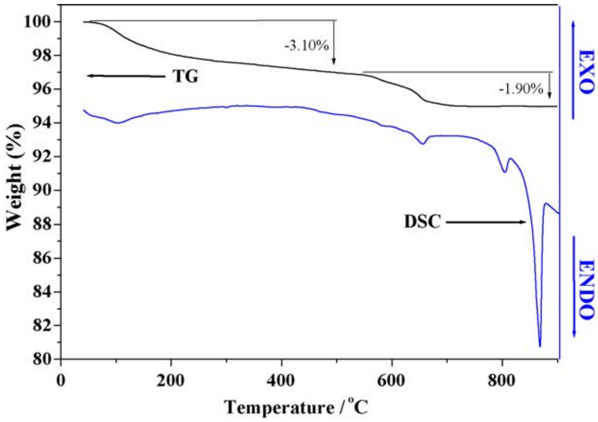


Fig. 7. TG/DSC curves of the glass powders prepared by spray pyrolysis at a temperature of 1000 °C.

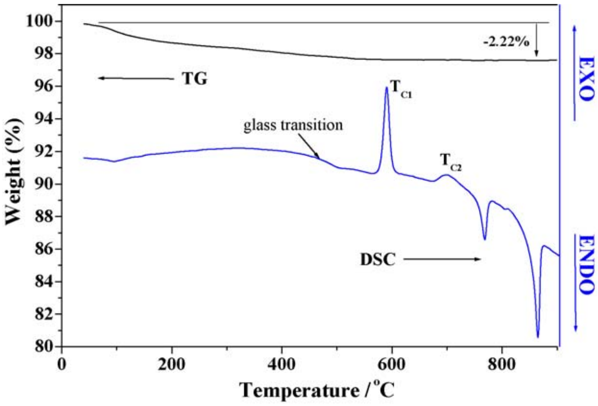
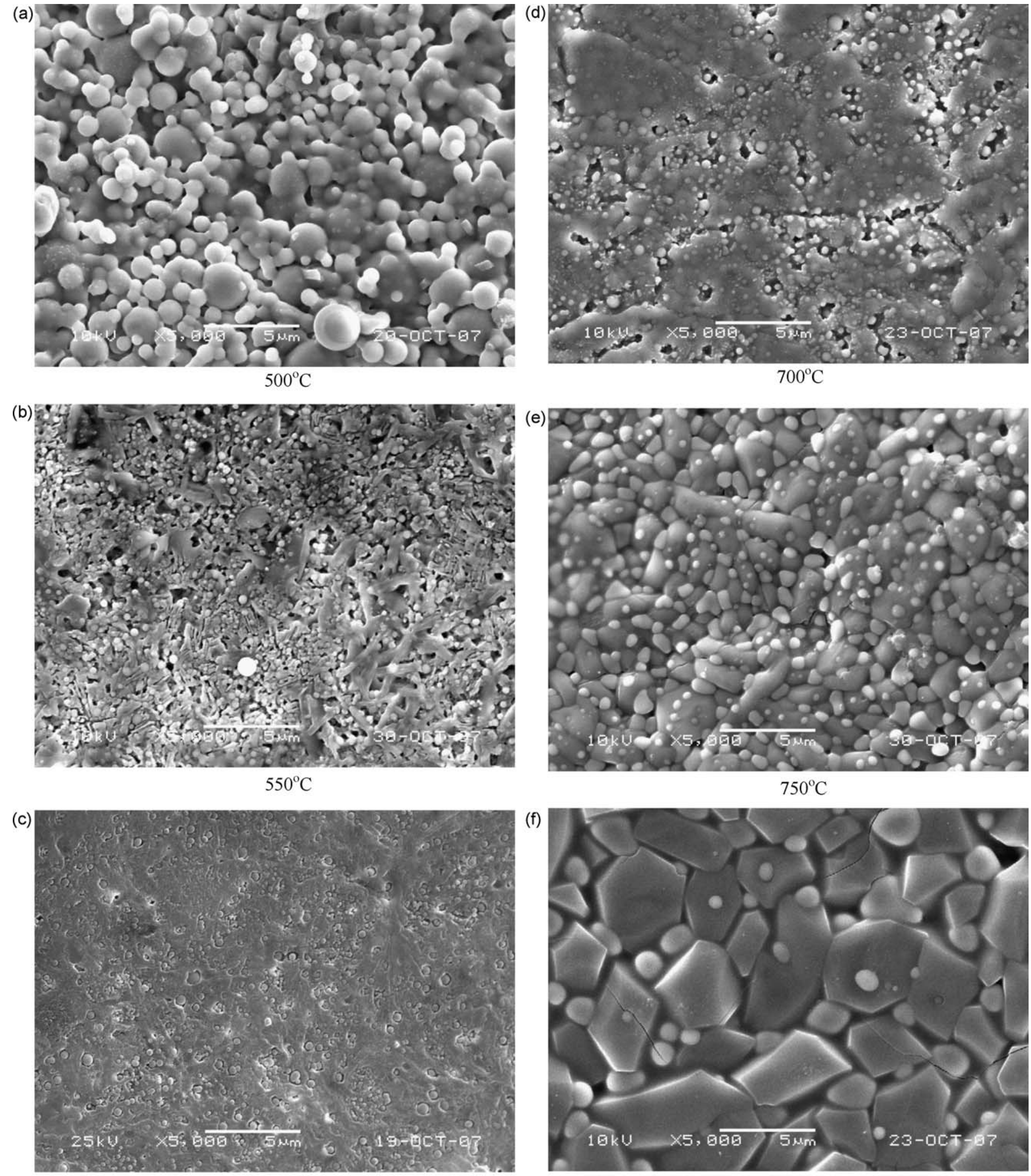


Fig. 8. TG/DSC curves of the glass powders prepared by spray pyrolysis at a temperature of 1200 °C.



500°C

700°C

550°C

750°C

600°C

800°C

Fig. 9. SEM images of the surface of the pellets sintered at temperatures between 500 and 800 °C.

the powders prepared at a temperature of 1000 °C show two weight losses at temperatures below 900 °C. The first pronounced weight loss region from 40 to 200 °C resulted from the loss of adsorbed water. The second weight loss region from 555 to 665 °C resulted from the decomposition of residual precursors. The complete decomposition of the precursors did not occur at a low preparation temperature of 1000 °C. The total weight loss of the powders prepared at a temperature of 1000 °C was 5.00% in the TG curve. On the other hand, the TG curve of the powders prepared at a temperature of 1200 °C shows one-step weight loss at temperatures below 900 °C. Decomposition of the precursors completely occurred at a preparation temperature of 1200 °C to form the glass powders. The total weight loss of the powders prepared at a temperature of 1200 °C was 2.22% in the TG curve. DSC curve of the powders prepared at a temperature of 1200 °C had two distinct exothermic peaks (T_{c1} and T_{c2}) at temperatures of 588 and 695 °C indicating crystallization. It indicates that there are two distinct phase transformations in this glass system. On the other hand, the exothermic peaks were not observed in the DSC curve of the powders prepared at a temperature of 1000 °C. The glass transition temperature (T_g) of the powders prepared at a temperature of 1200 °C was 480 °C. The glass powders prepared by spray pyrolysis had similar glass transition and crystallization temperatures to those of the glass powders prepared by conventional melting process [13].

To determine the crystalline phases formed in the heat-treated glass, glass pellets were sintered at different temperatures at constant heating rates of 10 °C/min for 3 h. The pellets compressed of glass powders prepared by spray pyrolysis at a temperature of 1200 °C were sintered at various temperatures. Fig. 9 shows the SEM images of the surfaces of the pellets sintered at temperatures between 500 and 800 °C. Melting of the glass powders occurred at a sintering temperature of 500 °C, in which crystalline phases were not observed from the SEM image. Phase-separated crystalline phases with spherical shape were observed from the SEM image of the pellet sintered at a temperature of 550 °C. The number and mean size of the crystals increased with increasing the temperature in the range from 550 to 700 °C. The SEM images of the pellets sintered at temperatures between 550 and 700 °C showed mixed structure of amorphous glass and crystalline phases. Crystallization of the glass was completely occurred at temperatures of 750 and 800 °C. The SEM images of the pellets sintered at temperatures of 750 and 800 °C showed the two types of crystalline phases with fine and large grain sizes. The grain sizes of the two crystalline phases increased with increasing temperatures. The two crystalline phases were well mixed.

Fig. 10 shows the XRD patterns of the pellets sintered at various temperatures. The pellets sintered at temperatures below 700 °C had single crystalline phase of $CaNa_3B_5O_{10}$. The $CaNa_3B_5O_{10}$ phase grew with increasing the sintering temperature up to 700 °C. However, the mean grain sizes calculated from the Scherrer's equation from the half width of the XRD peak were small. Crystalline phases with spherical shape as shown in Fig. 8(b)–(d) were $CaNa_3B_5O_{10}$ phase. The sharp peaks of the CaB_2O_4 phase appeared at a temperature of 800 °C. The XRD pattern of the pellet sintered at a temperature of 800 °C had two crystalline phases of $CaNa_3B_5O_{10}$ and CaB_2O_4. The crystalline phases of small and large size grains as shown in Fig. 9(e) and (f) were CaB_2O_4 and $CaNa_3B_5O_{10}$, respectively.

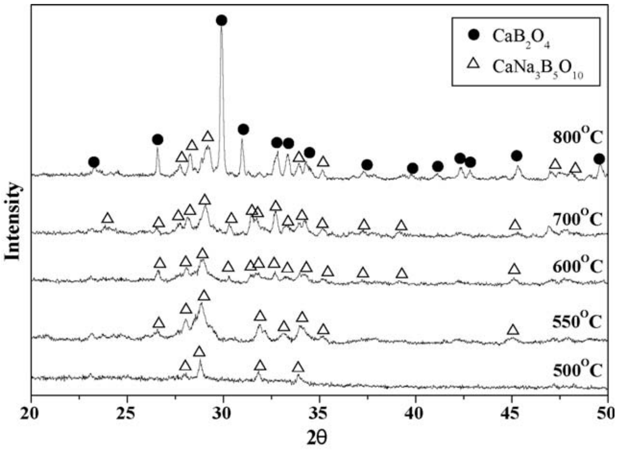


Fig. 10. XRD patterns of the pellets sintered at temperatures between 500 and 800 °C.

4. Conclusion

Spherical shape borate-based bioactive glass powders, designated 45S5B1, for the replacement and repair of bone were prepared by spray pyrolysis. The optimum preparation temperature to prepare the bioactive glass powders with a spherical shape and dense inner structure was 1200 °C. The glass powders prepared at temperatures of 1300 and 1500 °C had bimodal size distributions of nano-sized and micron-sized powders. The two distinct phase transformations in this bioactive glass system were observed. Melting of the prepared glass powders occurred at a heat temperature of 500 °C. The number and mean size of the crystals increased with increasing the temperature in the range from 550 to 700 °C. The pellet heat treated at a temperature of 800 °C had two crystalline phases of $CaNa_3B_5O_{10}$ and CaB_2O_4.

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