The effect of drying method on the surface structure of mesoporous sol-gel derived bioactive glass-ceramic

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Abstract. Mesoporous bioactive glass ceramic in the system of 60SiO₂-36CaO-4P₂O₅ (mol.%) named 58S was synthesized using the sol-gel process. The effect of different drying methods (oven-drying, freeze drying, and vacuum drying) on the structure of 58S bioactive glass ceramic was investigated. Samples were characterized by scanning electron microscopy (SEM) and nitrogen sorption porosimetry (BET). SEM images of the samples after drying and then calcination indicated crystals formed in the 58S glass. The nitrogen isotherm of all samples calcinated at 600 °C revealed a mesoporous structure for 58S glass-ceramics. BET surface area of freeze-dried sample after calcination was greater than that of the oven and vacuum dried specimens. Drying methods had significant effect on morphology, surface area, and shape of pores.

1. Introduction

Bioactive glasses were the first group of synthetic biomaterials which showed a bone-bonding ability [1]. If implanted in the body, a bone-like apatite phase forms on their surface, which forms a strong bond with bone. Apart from bioactivity, they are also biocompatible and biodegradable [1], [2]. Bioactive glasses can be synthesized either by melting or sol-gel process [2].

Sol-gel is a wet-chemical process in which inorganic materials as well as organic-inorganic hybrids are synthesized from liquid sources at low temperatures. This method is particularly attractive for preparing glasses with a high tendency to crystallize and relatively high melting temperature [3].

Other advantages of the sol-gel process over the melting technique for making bioactive glasses are higher bioactivity, higher surface area, wider range of bioactive compositions, and interconnectivity between pores [1], [4]. Through the sol-gel, a solid porous network in a liquid forms due to the hydrolysis of alkoxides. Next polycondensation creates a gel. In order to remove the liquid phase which fills the porosity of the solid network, a drying step is required. Drying the gel by heating at low temperature results in a xerogel, while freeze drying makes cryogel. The methods of liquid extraction within the structure can induce different levels of capillary stresses on the solid network [5] which may change the surface structure. The aim of this study is to compare the surface structure of a gel which is dried using oven drying, freeze drying, and vacuum drying with using the drying mechanisms of evaporation, sublimation, and boiling, respectively.

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2. Experimental procedure and characterization methods

The chemical composition of 58S glass, 60SiO₂-36CaO-4P₂O₅ (mol.%), was chosen based on the sol-gel calcium silicate bioglass [1]. To synthesize 50g of 58S bioactive glass, 100.940 g Tetraethyl orthosilicate (TEOS, product No. 86578 from Sigma Aldrich) was added into the mixture of distilled water, ethanol absolute (product No. 214 from Ajax Finechem Chemicals), and nitric acid 69% (HNO₃, product No. 101799 from Merck) with the molar ratio of (HNO₃+H₂O+EtOH)/(TEOS+TEP)=8 in TEOS:H₂O:EtOH:HNO₃=0.48:4:0.34:0.02. The pH of the solution was adjusted to 0.84. The solution was magnetically stirred for 1h at room temperature to hydrolyze TEOS. Next, 11.767 g triethyl phosphate (TEP, No. 30505 from BDH Chemicals Ltd Poole England) and 68.654 g calcium nitrate tetrahydrate (Ca(NO₃)₂.4H₂O, product No. CA015 from Chem-supply) were added into the solution sequentially, with an interval of 1h between each addition. The final solution (clear sol) was stirred for an additional 1 hour, then poured into a glass petri dish, and stored at room temperature until they formed a clear gel. The clear gel was dried using different methods of oven-drying, freeze drying, and vacuum drying, named O-58S, F-58S, and V-58S, respectively. In the case of oven-drying, the gel was aged at 70 °C for 24h and then dried at 120 °C for 24h. Vacuum drying was employed for 36h. In the case of freeze drying, the gel was placed into the liquid nitrogen and then freeze drying was carried out for 24h on a Labconco FreeZone Plus 6. The dried gels were subsequently calcined in air by heating them at 2°C/min to 600 °C and holding for 3h. After calcination, the glass-ceramics were ground and until are passed through a 74 microns sieve.

The structure and morphology of the 58S bioactive glass-ceramics were observed using scanning electron microscopy on a Zeiss 1555 VP-FESEM working at 5 kV, 5.2-5.6 WD, with an In-Lens detector. The samples were Pt-coated before imaging. Nitrogen adsorption-desorption isotherm measurements were accomplished on Micromeritics ASAP 2020 at 77 K using a relative pressure from 0 to 0.99 to determine the specific surface area, pore size, and pore volume.

3. Results and discussion

The morphology and structure of 58S bioactive glass-ceramics after different drying methods are shown in Figure 1. Comparing the SEM images reveals that the O-58S glass-ceramic contains an agglomeration of particles, the F-58S is cracked and the V-58S has a highly rough surface. It is apparent from Figure 1(a) and (b) that particles have become agglomerated through the thermal drying. In contrast, freeze-drying creates a different morphology with some cracks evident within the particles, Figure 1(c) and (d). These cracks may have occurred during the sublimation process. In other words, after freezing, sublimation of the solvent may lead to cracking. At room temperature, the gel is able to flow into the space created by the removed of the solvent and therefore cracking does not occur. The same flow is not possible when the gel is frozen and therefore cracking occurs. Finally SEM images of the vacuum dried gel, Figure 1(e) and (f) show a rough, porous surface which may be attributed to the way that the solvent molecules leave the gel under vacuum.
Figure 1. SEM images of samples after (a) and (b) oven drying, (c) and (d) freeze drying, and (e) and (f) vacuum drying. Images (b), (d) and (f) are higher magnification images of (a), (c) and (e), respectively.

Figure 2 shows the SEM images of O-58S, F-58S, and V-58S after calcination at 600 °C for 3h. Comparing the morphologies of the material after calcination indicates that the drying method causes a significant change in the surface structure. The O-58S was partially crystallized (Figure 2(a) and (b)) with flake like crystals. For the F-58S sample, there were areas that look similar to the O-58S but at some regions were different such as shown in Figure 2(c) and (d). Vacuum drying, Figure 2(e) and (f), results in a similar flake like crystalline morphology to oven drying. However, the crystals of V-58S are more interlocked and smaller. From these results, it is apparent that the method of solvent extraction from the gel affects the surface porosity size and shape as well as agglomeration of particles.

Figure 2. SEM images of samples after calcination at 600 °C for 3h. (a) and (b) oven drying, (c) and (d) freeze drying, and (e) and (f) vacuum drying. Images (b), (d) and (f) are higher magnification images of (a), (c) and (e), respectively.

Figure 3 shows the nitrogen sorption isotherms of O-58S, F-58S, and V-58S after calcination at 600 °C for 3h. The nitrogen sorption isotherms of all samples are identified as type IV according to IUPAC classification, with a hysteresis loop which is representative of mesoporous materials [6]. Table 1
summarizes BET surface area, pore volume, and pore size of O-58S, F-58S, and V-58S after calcination. Calcined F-58S had the highest BET surface area with lowest pore size amongst the samples. Based on the results of nitrogen sorption isotherms, there is a significant difference amongst the BET surface area of samples, although all of them represented mesoporous structure.

![Graph showing nitrogen sorption isotherms of O-58S, F-58S, and V-58S calcinated at 600 °C for 3h.](image)

Figure 3. Nitrogen sorption isotherms of O-58S, F-58S, and V-58S calcinated at 600 °C for 3h.

Table 1. BET surface area, pore volume, and pore size of O-58S, F-58S, and V-58S calcinated at 600 °C for 3h.

|                  | O-58S after calcination | F-58S after calcination | V-58S after calcination |
|------------------|-------------------------|-------------------------|-------------------------|
| BET surface area (m²/g) | 161                     | 209                     | 140                     |
| Pore volume (cm³/g)       | 0.29                    | 0.21                    | 0.15                    |
| Pore size (nm)             | 7.20                    | 3.97                    | 4.12                    |

4. Conclusions
Mesoporous bioactive glass ceramics in the system of 60SiO₂·36CaO·4P₂O₅ (mol.%)(i.e. 58S) have been synthesized using the sol-gel process. The effect of different drying methods (oven-drying, freeze drying, and vacuum drying) on the structure of 58S bioactive glass ceramic was investigated. SEM images of the samples after drying revealed an agglomeration of the particles for oven-dried sample, cracks in the freeze-dried material, and a highly rough surface on the vacuum dried particles. After calcination, both the oven and vacuum dried material were partially crystallized with flake like crystals, while freeze-drying produced a different crystalline morphology. The nitrogen isotherms of all samples calcinated at 600 °C indicated that a mesoporous structure formed. The BET surface area of the freeze-dried materials after calcination was greater than after either oven or vacuum drying. Hence, it is apparent that the method of solvent extraction from the gel has significant effect on morphology and surface properties for the resultant bioactive glass ceramic.

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