Supplementary Information

Self-crystallisation, an unexpected property of 45S5 Bioglass®

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Experimental Procedures

The 45S5 Bioglass® was obtained by a traditional melting and quenching method[1], using a Carbolite Gero HTF 1800 furnace. Commercial reagents (Sigma Aldrich) $CaCO_3$, Na_2CO_3, SiO_2 and $CaHPO_4 \bullet 2H_2O$, were melted in a platinum crucible at 1400°C, followed by quenching in water. The resultant glass was dried, ground and sieved (<53μm). Apatite-wollastonite glass powder with the composition (wt%) 4.6 MgO, 44.7 CaO, 34.0 SiO_2, 16.2 P_2O_5 and 0.5 CaF_2 was received from Glass Technology Service (GTS) Ltd (Sheffield, UK). Apatite-wollastonite glass powder was sieved below 53μm.

45S5 Bioglass® and apatite-wollastonite scaffolds were obtained using the sponge replication method[2]. Briefly, polyurethane foams impregnated with the 45S5 Bioglass® slurry[1] were heat treated at 1100°C for 2h, while polyurethane foams impregnated with the apatite-wollastonite slurry were heat treated at 1250°C for 1h. During heat treatment the foam burned out (leaving a porous structure instead), and the glass crystallised, forming a glass-ceramic. All samples were kept in sealed plastic bags in the laboratory during the Covid pandemic (2020), at room temperature. They were further analysed one year after their fabrication (2021).

The temperature and relative humidity in the lab varied between 14-20°C and 50-80%, respectively, depending on the weather.

The microstructure of the bioglass powders and glass-ceramic scaffolds was observed using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). Low vacuum Hitachi TM3030 Tabletop SEM and high vacuum Tescan Lyra 3 SEM were used to observe the structure of glass powders and glass-ceramic scaffolds. Samples were gold coated. Plate- and acicular-shape crystals were observed only on the surface of 45S5 Bioglass® powder and scaffolds, respectively. There was no crystal growth on the surface of apatite-wollastonite glass powder or glass-ceramic scaffolds after one year in storage.

The crystalline phases were identified by X-ray diffraction (XRD), using a Philips PW3710 diffractometer with Cu Kα radiation. The patterns were recorded using 2θ range of 10–70°, step size of 0.02° and time per step of 2s/step. HighScore software was used to identify the crystalline phases. The values of crystallite size were calculated from line broadening of fitted diffraction patterns, using the Scherrer equation (Scherrer's constant was considered K=0.9)[3]. The XRD spectra were compared with the diffraction patterns for the same samples before storage (immediately after synthesis).

Dissolution tests for 45S5 Bioglass® powders and glass-ceramic scaffolds were carried out at room temperature. The samples were immersed in distilled water for 15 minutes and observed on SEM. The needle-shape crystals present on the surface of

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1 D. Vukajlovic, O. Bretcanu, K. Novakovic, Open Ceramics, 2021, 8, 100174

2 Q. Z. Chen, I. D. Thompson, A. R. Boccaccini, Biomaterials, 2006, 27, 2414–2425

3 J. I. Langford, A. J. C. Wilson, Journal of Applied Crystallography, 1978, 11, 102-113

glass-ceramic scaffolds completely dissolved. The plate-shape crystals present on the surface of 45S5 Bioglass® were still observed after the dissolution test.

Supplementary data

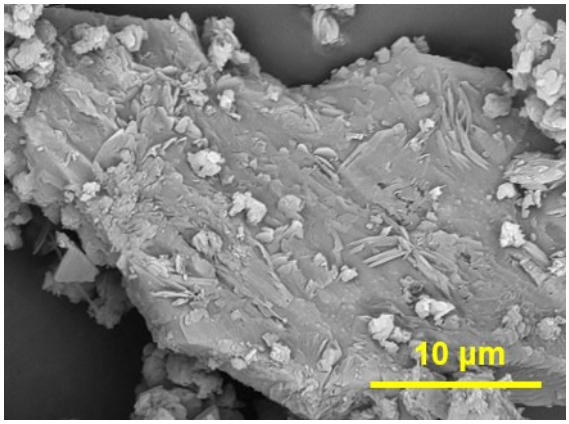

Figure S1 SEM image of 45S5 Bioglass® powder after one year in storage

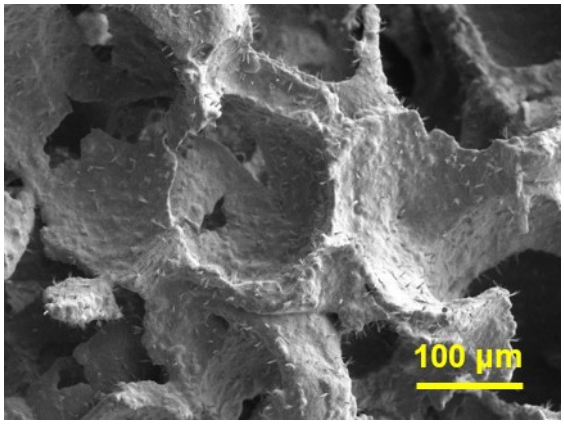

Figure S2 SEM image of 45S5 Bioglass® scaffold after one year in storage

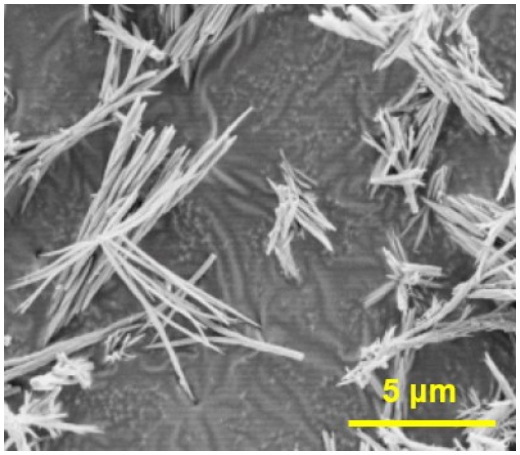

Figure S3 SEM image of acicular-shape crystals grown on the surface of a sol-gel derived bioactive glass after 36h hydrothermal processing at 170°C (adapted from [4])

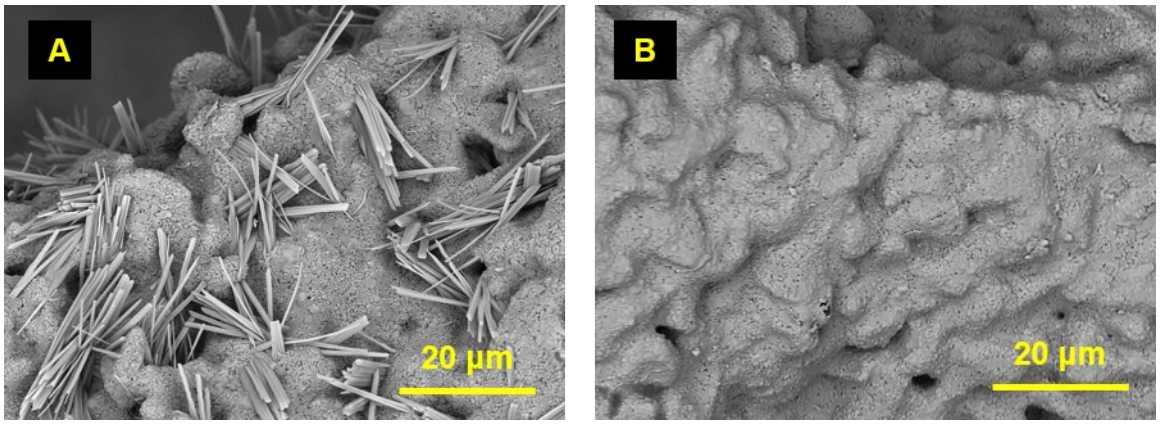

Figure S4 SEM images of 45S5 Bioglass® scaffolds after one year in storage before (A) and after (B) immersion in distilled water for 15min at room temperature

4 D. Mondal, A. Zaharia, K. Mequanint, A. S. Rizkalla, Journal of Functional Biomaterials, 2020, 11 (2), 35