

# 多孔性生醫玻璃陶瓷材料之研製 = Investigations of porous bioglass-ceramic materials

洪佳豐、何文福;吳世經

E-mail: 9706897@mail.dyu.edu.tw

## 摘要

本實驗以MgO-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>之成分系統的玻璃為材料，用硬酯酸為成孔劑，經模壓成形再進行燒結，研製了多孔性生醫玻璃陶瓷，期能作為組織工程支架材料用途。本實驗之玻璃主要化學成分為：MgO 3.0%、CaO 35.0%、Al<sub>2</sub>O<sub>3</sub> 8.6%、SiO<sub>2</sub> 41.4%、P<sub>2</sub>O<sub>5</sub> 12.0%。實驗結果顯示，玻璃分別經過960 °C、1小時及1060 °C、1小時的結晶熱處理後，主要晶相種類以XRD測定結果為：磷灰石、鈣長石兩種結晶相。在添加三種不同含量及粒徑大小的硬酯酸經由960 °C、1小時燒結後，分別用SEM、阿基米德原理量測孔隙大小、開放型孔隙度。以添加50vol%的硬酯酸發泡劑，其大孔隙分別為448 ± 67 μm、251 ± 42 μm、59 ± 12 μm，而開放型孔隙度則為29.94 ± 1.14%、27.67 ± 0.94%、18.67 ± 0.97%。所有樣品的孔隙度範圍從26.96 ± 1.03%至45.89 ± 0.17%，而孔隙度為26.96 ± 1.03%之樣品，其彈性模數與彎曲強度接近於人類的皮質骨。其餘的樣品之機械性質只介於皮質骨與海綿骨之間。浸泡人工體液30天後，樣品表面大量形成新的晶體，而且細胞活性評估的結果顯示，以SA50P1所形成的多孔性生醫玻璃陶瓷具有極佳之生物適應性。綜合上述實驗之結果顯示，此多孔性生醫玻璃陶瓷可作為組織工程之支架材料。

關鍵詞：支架材料；多孔性生醫玻璃陶瓷；硬酯酸；燒結；孔隙大小；機械性質

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## 參考文獻

- [1] J. B. Park, " Biomaterials science and engineering ", Plenum Press, New York and London, (1988).
- [2] K. Sayler, R. Holmes, and D. Johns, " Replamineform porous hydroxyapatite as bone substitutes in craniofacial osseous reconstruction ", Journal of Dental Research, 56B (1977) 173.

- [3] F. H. Lin, and M. H. Hon, " Sintering of  $\beta$ -Tricalcium Phosphate Bioceramics with  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  ", Journal of Materials Science Letters, 6 (1987) 501 – 503.
- [4] H. Yuan, Z. Yang, Y. Li, X. Zhang, J. D. de Brujin, and K. de Groot, " Osteoinduction by calcium phosphate biomaterials ", Journal of Materials Science: Materials in Medicine, 9 (1998) 723 – 726.
- [5] S. C. Wu, C. L. Wang, and M. H. Hon, " Effects of Ca/P ratio on the crystallization of  $\text{MgO-CaO-Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5$  glass-ceramics ", Journal of Ceramic Society of Japan, 103 (1995) 99 – 103.
- [6] 俞耀庭, " 生物医用材料 ", 新文京開發出版股份有限公司, (2004).
- [7] L. L. Hench, " Bioceramics: From Concept to Clinic ", Journal of the American Ceramic Society, 74 (1991) 1487 – 1510.
- [8] R. H. Doremus, " Review: Bioceramics ", Journal of Materials Science, 27 (1992) 285 – 297.
- [9] F. H. Lin, C. C. Lin, H. C. Liu, Y. Y. Huang, C. Y. Wang, and C. M. Lu, " Sintered porous DP-bioactive glass and hydroxyapatite as bone substitute ", Biomaterials, 15 (1994) 1087 – 1098.
- [10] J. M. Dorlot, P. Christel, and A. Meunier, " Alumina HIP Prosthesis, Bioceramics: Proceeding of International Symposium on Ceramic in Medicine ", Tokyo, Ishi. Euro American, (1988) 236 – 301.
- [11] G. Heimke, " Use of alumina ceramic in medicine ", Bioceramics Volumn, 3rd, Terre Haute, Ind., Rose Hulman Institute of Technology, (1992) 19 – 30.
- [12] G. A. Graves, R.L. Henrich, H. G. Stain, and P. K. Baijpal, " Resorbable ceramic implants in bioceramic ", Engineering in Medicine, New York, Interscience Publisher, (1972) 91 – I 15.
- [13] M. Jarcho, " Calcium phosphate ceramics as hard tissue prosthetics ", Clinical Orthopaedics and Related Research, 157 (1981) 259 – 278.
- [14] D. S. Metsger, T. D. Driskell, and J. R. Paulsrud, " Tricalcium phosphate ceramic—a resorbable bone implant: review and current status ", The Journal of the American Dental Association, 105 (1982) 1035 – 1038.
- [15] G. Willmann, " Medical grade hydroxyapatite: state of the art ", British Ceramic Transactions, 95 (1996) 212 – 216.
- [16] R. Z. LeGeros, " Biodegradation and bioresorption of calcium phosphate ceramics ", Clinical Materials, 14 (1993) 65 – 88.
- [17] L. L. Hench, R. J. Splinter, W. C. Allen, and T. K. Greenlee, " Bonding mechanism at the interface of ceramic prosthetic materials ", Journal of Biomedical Materials Research, 2 (1971) 117 – 141.
- [18] H. Broemer, K. Deutscher, B. Blencke, E. Pfeil, and V. Strunz, " Properties of the bioactive implant material ' Ceravital ' ", Science of Ceramics, 9 (1977) 219 – 225.
- [19] T. Kokubo, S. Ito, S. Sakka, and T. Yamamuro, " Formation of a high-strength bioactive glass-ceramic in the system  $\text{MgO-CaO-SiO}_2-\text{P}_2\text{O}_5$  ", Journal of Materials Science, 21 (1986) 536 – 540.
- [20] W. Vogel, " Chemistry of glass ", American Ceramic Society, (1985) 251.
- [21] F. H. Lin, and M. H. Hon, " A study on the bioglass ceramics in the  $\text{NaO-CaO-SiO}_2-\text{P}_2\text{O}_5$  system ", Journal of Materials Science, 23 (1989) 4295 – 4299.
- [22] C. M. Stanford, " Application of oral implants to the general dental practice ", The Journal of the American Dental Association, 136 (2005) 1092 – 1100.
- [23] N. Melba, V. Sergio, M. Salvador, and P. G. Maria, " New macroporous calcium phosphate glass ceramic for guided bone regeneration ", Biomaterials, 25 (2004) 4233 – 4241.
- [24] C. T. Lawrencin, S. F. El Amin, S. E. Ibim, D. A. Willoughby, M. Attavia, H. R. Allcock, and A. A. Ambrosio, " A highly porous 3-dimensional polyphosphazene polymer matrix for skeletal tissue regeneration ", Journal of Biomedical Materials Research, 30 (1996) 133 – 138.
- [25] A. G. Mikos, G. Sarakinis, S. M. Leite, J. P. Vacanti, and R. Langer, " Laminated 3-dimensional biodegradable foams for use in tissue engineering ", Biomaterials, 14 (1993) 323 – 330.
- [26] D. M. Liu, " Fabrication of hydroxyapatite ceramic with controlled porosity ", Journal of Material Science: Materials in Medicine, 8 (1997) 227 – 232.
- [27] D. W. Hutmacher, " Scaffolds in tissue engineering bone and cartilage ", Biomaterials, 21 (2000) 2529 – 2543.
- [28] J. S. Temenoff, and A. G. Mikos, " Injectable biodegradable materials for orthopaedic tissue engineering ", Biomaterials, 21 (2000) 2405 – 2412.
- [29] Y. Abe, M. Hosoe, and T. Kasuga, " High strength  $\text{Ca(PO}_3)_2$  glass-ceramics prepared by unidirectional crystallization ", Journal of the American Ceramic Society, 65 (1982) 189 – 190.
- [30] A. F. Lemos, and J. M. F. Ferreira, " Porous bioactive calcium carbonate implants processed by starch consolidation ", Materials Science and Engineering: C, 11 (2000) 35 – 40.
- [31] O. Lyckfeldt, and J. M. F. Ferreira, " Processing of porous ceramics by a new direct consolidation technique ", Journal of the European Ceramic Society, 18 (1998) 131 – 140.
- [32] J. Saggio-Woyansky, C. E. Scott, and W. P. Minnear, " Processing of porous ceramics ", American Ceramic Society bulletin, 71 (1992) 1674 – 1682.
- [33] K. de Groot, C. P. A. T Klein, J. G. C. Wolke, and J. M. A. De Blieck-Hogervorst, " Chemistry of calcium phosphate bioceramics ",

Handbook of Bioactive Ceramics, 2 (1990) 3 – 16.

- [34] O. Gauthier, J. M. Bouler, E. Aguado, P. Pilet, and G. Daculsi, “ Macroporous biphasic calcium phosphate ceramics: influence of macropore diameter and macroporosity percentages on bone ingrowth ” , *Biomaterials*, 19 (1998) 133 – 139.
- [35] J. Bobyn, R. Pilliar, H. Cameron, and G. Weatherly, “ The optimal pore size for the fixation of porous surfaced metal implants by the ingrowth of bone ” , *Clinical Orthopaedics and Related Research*, 150 (1980) 263 – 270.
- [36] W. Cao, and L. L. Hench, “ Bioactive materials ” , *Ceramics International*, 22 (1996) 493 – 507.
- [37] H. A. Elbatal, M. A. Azooz, E. M. A. Khalil, A. S. Monem, and Y. M. Hamdy, “ Characterization of some bioglass-ceramics ” , *Materials Chemistry and Physics*. 80 (2003) 599 – 609.
- [38] A. El-Ghannam, P. Ducheyne, and I. M. Shapiro, “ Bioactive material template for in vitro synthesis of bone ” , *Journal of Biomedical Materials Research*, 29 (1995) 359 – 370.
- [39] M. S. Hernández-Crespo, M. Romero , and J. Ma. Rinco'n, “ Nucleation and crystal growth of glasses produced by a generic plasma arc-process ” , *Journal of the European Ceramic Society*, 26 (2006) 1679 – 1685.
- [40] A. K. Varshneya, D. J. Mauro, B. Rangarajan, and B. F. Bowden, “ Deformation and Cracking in Ge – Sb – Se Chalcogenide Glasses During Indentation ” , *Journal of the American Ceramic Society*, 90 (2007) 177 – 183.
- [41] P. F. James and W. Shi, “ Crystal nucleation kinetics in a 40CaO-40P<sub>2</sub>O<sub>5</sub>-20B<sub>2</sub>O<sub>3</sub> glass — a study of heterogeneously catalysed crystallization ” , *Journal of Materials Science*, 28 (1993) 2260 – 2266.
- [42] 吳振名, “ 玻璃陶瓷 ” , 陶瓷技術手冊 (下) , 經濟部技術處發行, (1994).
- [43] M. J. Davis, and I. Mitra, “ A Combinatorial Chemistry Study of YAG Nucleation ” , *Journal of the American Ceramic Society*, 86 (2003) 1540 – 1546.
- [44] W. H. Zachariasen, “ The atomic arrangement in glass ” , *Journal of the American Ceramic Society*, 54 (1932) 3841.
- [45] A. Sakamoto, F. Sato, and S. Yamamoto, “ Structural relaxation and optical properties in transparent nanocrystalline ?-quartz glass-ceramic ” , *Journal of Non-Crystalline Solids*, 352 (2006) 514 – 518.
- [46] P. F. James, “ Glass ceramics: New compositions and uses ” , *Journal of Non-Crystalline Solids*, 181 (1995) 1 – 15.
- [47] K. Ishizaki, S. Komarneni, and M. Nanko, “ Porous Materials: Processing Technology and Applications ” , Kluwer Academic Publishers, (1998).
- [48] J. Szymura-Oleksiak, A. Słomiński, A. Cios, B. Mycek, Z. Paszkiewicz, S. Szklarczyk, and D. Stankiewicz, “ The kinetics of pentoxyfylline release in vivo from drug-loaded hydroxyapatite implants ” , *Ceramics International*, 27 (2001) 767 – 772.
- [49] Jean-Michel Bouler, Marylène Tre'cant, Joe"l Dele'crin, Jean Royer, Norbert Passuti, and Guy Daculsi, “ Macroporous biphasic calcium phosphate ceramics: Influence of five synthesis parameters on compressive strength ” , *Journal of Biomedical Materials Research*, 32 (1996) 603 – 609.
- [50] M. H. Prado da Silva, A. F. Lemos, I. R. Gibson, J. M. F. Ferreira, and J. D. Santos, “ Porous glass reinforced hydroxyapatite materials produced with different organic additives ” , *Journal of Non-Crystalline Solids*, 304 (2002) 286 – 292.
- [51] K. Maca, P. Dobsák, and A. R. Boccaccini, “ Fabrication of graded porous ceramics using alumina – carbon powder mixtures ” , *Ceramics International*, 27 (2001) 577 – 584.
- [52] J. J. Klawitter, A. M. Weinstein, F. W. Cooke, L. J. Peterson, B. M. Pennel, and R. V. McKinney, “ An evaluation of porous alumina ceramic dental implants ” , *Journal of Dental Research*, 56 (1977) 768 – 776.
- [53] H. Yuan, J. D. de Brujin, X. Zhang, C. A. van Blitterswijk, and K. de Groot, “ Bone Induction by Porous Glass Ceramic Made from Bioglass? (45S5) ” , *Journal of Biomedical Materials Research*, 58 (2001) 270 – 276.
- [54] M. Navarro, S. del Valle, S. Martinez, S. Zeppetelli, L. Ambrosio, J. A. Planell, and M. P. Ginebra, “ New macroporous calcium phosphate glass ceramic for guided bone regeneration ” , *Biomaterials*, 25 (2004) 4233 – 4241.
- [55] H. R. Ramay, and M. Zhang, “ Preparation of porous hydroxyapatite scaffolds by combination of the gel-casting and polymer sponge methods ” , *Biomaterials*, 24 (2003) 3293 – 3302.
- [56] M. Milosevski, J. Bossert, D. Milosevski, and N. Gruevska, “ Preparation and properties of dense and porous calcium phosphate ” , *Ceramics International*, 25 (1999) 693 – 696.
- [57] D. C. Tancred, B. A. O. McCormack, and A. J. Carr, “ A synthetic bone implant macroscopically identical to cancellous bone ” , *Biomaterials*, 19 (1998) 2303 – 2311.
- [58] 曲遠方, “ 功能陶瓷材料 ” , 曉園出版社有限公司, (2006).
- [59] 肖定全, “ 陶瓷材料 ” , 新文京開發出版有限公司, (2003).
- [60] 汪建民、朱秋龍, “ 粉末冶金 ” , 中華民國粉末冶金協會, (1999).
- [61] F. F. Lange, “ Sinterability of Agglomerated Powders ” , *Journal of the American Ceramic Society*, 67 (1984) 83 – 89.
- [62] M. F. Yan, R. M. Cannon, U. Chowdhry, and H. K. Bowen, “ Effect of grain size distribution on sintered density ” , *Materials Science and Engineering A*, 60 (1983) 275 – 281.
- [63] H. P. Cohoon, and C. J. Christensen, “ Sintering and Grain Growth of Alpha-Alumina ” , *Journal of the American Ceramic Society*, 39

- (1956) 337 – 344.
- [64] R. L. Coble, “ Sintering Crystalline Solids: II, Experimental Test of Diffusion Models in Powder Compacts ” , Journal of Applied Physics, 32 (1961) 793 – 799.
- [65] 徐仁輝, “ 粉末冶金概論 ” , 新文京開發出版有限公司, (2002).
- [66] 王明光、王敏昭, “ 實用儀器分析 ” , 合記圖書出版社, (2003).
- [67] E. N. Ozguu"r, and T. A. Cuu"neyt, “ Manufacture of Macroporous Calcium Hydroxyapatite Bioceramics ” , Journal of the European Ceramic Society, 19 (1999) 2569 – 2572.
- [68] Q. Z. Chen, I. D. Thompson, and A. R. Boccaccini, “ 45S5 Bioglass? -derived glass – ceramic scaffolds for bone tissue engineering ” , Biomaterials, 27 (2006) 2414 – 2425.
- [69] 葉郁仁、林鴻儒、郭俊榕、楊俊佑、吳侑峻, “ 應用於骨組織工程Alginate/HAP多孔海綿體之製備及活體外與活體內相關性質之研究 ” , 中華民國生物醫學工程學會, 2002年年會論文集, (2002).
- [70] A. Tampieri, G. Celotti, S. Sprio, A. Delcogliano, and S. Franzese, “ Porosity-graded hydroxyapatite ceramics to replace natural bone ” , Biomaterials, 22 (2001) 1365 – 1370.
- [71] R. Xin, Y. Leng, J. Chen, and Q. Zhang, “ A comparative of calcium phosphate formation on bioceramics in vitro and in vivo ” , Biomaterials, 26 (2005) 6477 – 6486.
- [72] S. J. Ding, C. W. Wang, C. H. Chen, and H. C. Chang, “ In vitro degradation behavior of porous calcium phosphates under diametral compression loading ” , Ceramics International, 31 (2005) 691 – 696.
- [73] T. Kokubo, S. Ito, Z. T. Huang, T. Hayashi, S. Sakka, T. Kitsugi, and T. Yamamuro, “ Ca, P-rich layer formed on high-strength bioactive glass-ceramic A-W ” , Journal of Biomedical Materials Research, 24 (1990) 331 – 341.
- [74] K. S. Jaw, C. K. Hsu, and J. S. Lee, “ The thermal decomposition behaviors of stearic acid, paraffin wax and polyvinyl butyral ” , Thermochimica Acta, 367-368 (2001) 165 – 168.
- [75] R. M. German, “ Particle packing characteristics ” , NJ: Metal Powder Industries Federation, (1989) 404 – 407.
- [76] C. L. Martin, and D. Bouvard, “ Isostatic compaction of bimodal powder mixtures and composites ” , International Journal of Mechanical Sciences, 24 (2004) 907 – 927.
- [77] R. K. McGeary, “ Mechanical packing of spherical particles ” , Journal of American Ceramic Society, 44 (1961) 513 – 522.
- [78] Y. Cai, and L. Zhou, “ Effect of thermal treatment on the microstructure and mechanical properties of gel-derived bioglasses ” , Materials Chemistry and Physics, 94 (2005) 283 – 287.
- [79] J. R. Joones, L. M. Ehrenfried, and L. L. Hench, “ Optimising bioactive glass scaffolds for bone tissue engineering ” , Biomaterials, 27 (2006) 964 – 973.
- [80] J. B. Park and R. S. Lakes, Biomaterials 2nd, Plenum Press, New York, (1992).
- [81] Ayhan Mergen, and ve Ziya Aslanoglu, “ Low-temperature fabrication of anorthite ceramics from kaolinite and calcium carbonate with boron oxide addition ” , Ceramics International, 29 (2003) 667 – 670.
- [82] W. Gong, A. Abdelouas, and W. Lutze, “ Porous bioactive glass and glass-ceramics made by reaction sintering under pressure ” , Journal of Biomedical Materials Research, 54 (2001) 320 – 327.
- [83] I. D. Xynos, M. V. Hukkanen, J. J. Batten, L. D. Buttery, L. L. Hench, and J. M. Polak, “ Bioglass 45S5 stimulates osteoblast turnover and enhances bone formation In vitro: implications and applications for bone tissue engineering ” , Calcified Tissue International, 67 (2000) 321 – 329.
- [84] A. R. El-Ghannam, “ Advanced bioceramic composite for bone tissue engineering: design principles and structure – bioactivity relationship ” , Journal of Biomedical Materials Research, 69 (2004) 490 – 501.