

球磨處理對生醫用多孔鈦合金性質之影響研究

張天佑、何文福

E-mail: 321852@mail.dyu.edu.tw

摘要

近年來最常被研究探討的多孔金屬材料即是鈦金屬及其合金，因為鈦及其合金具有極佳的生物相容性與生物活性以及較低的彈性模數，由於具有以上這些優良的性質，因此，鈦金屬及其合金已被普遍應用於生醫材料上。本實驗目的針對TiMo合金系統中，將純元素Ti與Mo粉末藉由機械合金法(mechanical alloying, MA)，以達到非晶質之合金粉末。並利用碳酸氫氨(NH₄HCO₃)作為成孔劑，而本研究中成孔劑之所以選擇碳酸氫氨(NH₄HCO₃)，其原因是碳酸氫氨具有低熔點之特性故在脫除上較為簡易。本實驗將不同球磨處理時間，分別以BM3、BM15、BM30表示。經由背向式電子顯微觀察發現，在BM3處理後，粉末尚未達到均質化，再經過BM15及BM30之處理後，粉末以達到均質化階段。將球磨過的合金粉末進行多孔TiMo支架的製作，並利用真空熱處理爐進行真空燒結，真空度為D1 Pa，燒結溫度至A1 並分別持溫B1、B2、B3及B4小時。在XRD相分析方面，多孔TiMo合金經過不同燒結階段後，並無任何純元素鈦及鉬的存在，同時此時將會產生新的合金相 (Ti, Mo)。在抗壓強度方面，本實驗以不同的持溫下製作出多孔TiMo支架分別為B1、B2、B3及B4小時，結果提出，隨著燒結時間的增加，有助於提高多孔TiMo支架之抗壓強度，並配合抗壓強度之結果，本實驗選擇BM15之合金粉末以及燒結B1小時之多孔樣品作為後續表面改質之研究，因此組條件之抗壓強度及彈性模數分別為25.02 MPa, 1.72 GPa，非常適合鬆質骨植入材之應用。另外在孔徑分佈方面，不同球磨時間以及不同燒結階段之多孔樣品皆以100-200 μm之孔徑居多，但在第BM30之處理後，由於粉末的粒徑分佈趨向均一，在模壓成形後，導致粉末與粉末之間會有孔隙存在，進而影響孔徑大小之差異。因此在BM30處理後之多孔樣品，我們可以清楚的看到在400 μm以上之孔徑有明顯變多之趨勢。多孔試片經由表面改質(鹼處理及鹼水處理)後，發現試片表面將會形成一網狀多孔結構，藉由HR-XRD分析顯示為Na₂Ti₆O₁₃鈦酸鈉水凝膠層(sodium titanate hydrogel)，且經FE-SEM觀察發現鹼水處理的網孔比鹼處理來的小，然而為了觀察孔洞對磷灰石生成的影響故以實心試片作為對照組。隨後將實心及多孔試片進行人工模擬體液(simulated body fluid, SBF)之浸泡，其結果顯示鹼處理及鹼水處理後之多孔試片於SBF-14天的浸泡中發現孔洞內部已開始生成磷灰石。而後續觀察浸泡21天，發現鹼處理及鹼水處理之多孔試片，不論是孔洞內及孔洞外皆以佈滿磷灰石，而後續經由EDS分析發現，不論是鹼處理及鹼水處理Ca與P的含量相當高。由此結果得知，多孔TiMo支架經由表面改質後對於多孔植入材而言具有良好的生物活性。

關鍵詞：機械合金法、多孔鈦合金、多孔金屬材料、粉末冶金、力學性能、表面改質、生物相容性、生物活性

目錄

封面內頁 簽名頁 授權書.....	iii 中文摘要.....
..... iv 英文摘要.....	vi 誌謝.....
.....viii 目錄.....	x 圖目錄.....
..... xv 表目錄.....	xix 第一章前言.....
.....1 1.1生醫材料.....	1 1.1.1生醫材料之定義.....
.....1 1.1.2生醫材料之發展.....	1 1.1.3生醫材料之分類.....
.....3 1.2鈦與鈦合金之基本性質.....	5 1.2.1純鈦.....
.....5 1.2.2鈦合金.....	5 1.3生醫用多孔金屬材料.....
.....6 1.3.1生醫用多孔金屬材料之研究與發展.....	6 1.4近年來生醫用多孔鈦合金之發展.....
.....11 1.4.1多孔鈦金屬及其合金.....	11 1.4.2多孔鈦鎢合金.....
.....12 1.4.3Ti-6Al-4V及Ti-6Al-7Nb合金.....	12 1.4.4多孔Ni-Ti形狀記憶合金.....
.....13 1.4.5Ti-13Nb-13Zr合金.....	15 1.4.6多孔Ti-15Mo合金.....
.....15 1.4.7多孔Ti-16Sn-4Nb合金.....	16 1.5生醫用多孔植入材之性質.....
.....16 1.5.1低彈性模數.....	16 1.5.2生物相容性.....
.....17 1.5.3生物活性.....	17 1.6機械合金法製程的影響.....
.....18 1.7粉末冶金法.....	19 1.8製程控制劑(Process Control Agent)之影響.....
.....19 1.9生醫用多孔陶瓷材料.....	19 第二章文獻回顧.....
.....21 2.1不同燒結溫度對多孔金屬材料機械性質及多孔結構之影響.....	21 2.2不同孔隙率對多孔金屬材料機械性質之影響.....
.....22 2.3不同添加量之碳酸氫氨(NH ₄ HCO ₃)對多孔TiMo合金之影響.....	24 2.4不同的燒結時間.....

對多孔金屬材料多孔結構之影響...24	2.5不同的相對密度對多孔金屬材料機械性質之影響...25	2.6多孔金屬材料表面粗糙度之重要性.....26	2.7機械合金化對多孔金屬材料之影響.....27	2.8表面處理對多孔金屬材料之影響.....28
第三章材料及實驗方法.....31				
3.1實驗材料.....31	3.1.1實驗流程.....31	3.1.2材料與試片準備.....31	3.2.1機械合金化處理.....33	3.2.2粒徑大小與分佈.....36
3.2.3混粉及造粒.....37	3.2.4試片的準備.....38	(1)壓製生胚.....38	(2)生胚脫脂及燒結.....42	3.3抗壓強度測試.....43
3.4XRD相分析.....44	3.5SEM觀察.....45	3.5.1橫截面之觀察.....45	3.5.2孔徑計算.....45	3.6表面改質.....46
3.7HRXRD分析.....47	3.8人工模擬體液(simulated body fluid, SBF)浸泡之測試.....47	3.8.1人工模擬體液的調配.....47	3.8.2SBF浸泡.....49	第四章結果與討論.....50
4.1粉末形態觀察.....50	4.1.1顯微結構觀察.....50	4.1.2TiMo合金粉末球磨不同時間之SEM/EDS元素分析.....53	4.1.3粒徑分析.....54	4.1.4不同球磨時間TiMo合金粉末之BSE電子顯微觀察.....58
4.1.5TiMo合金粉末XRD繞射分析.....60	4.2起始粉末探討.....62	4.2.1球磨粉末及生胚性質.....62	4.3機械性質分析.....62	4.3.1不同燒結時間對彈性模數及相對密度之影響.....62
4.3.2不同燒結時間對抗壓強度之影響.....64	4.4顯微結構觀察與分析.....70	4.4.1孔徑大小分析.....70	4.4.2孔隙率分析.....76	4.4.3橫截面之觀察.....78
4.4.4XRD相分析.....82	4.4.5多孔TiMo支架之燒結後BSE電子顯微觀察.....86	4.4.6多孔TiMo支架以SEM/EDS之元素分析.....90	4.5前處理.....92	4.6FE-SEM觀察.....92
4.7HR-XRD分析.....95	4.8人工模擬體液(simulated body fluid, SBF)之浸泡.....98	4.8.1SEM觀察.....98	4.8.2EDS分析.....98	第五章結論.....106
參考文獻.....106				

參考文獻

- [1]Helmus MN, Tweden K, Materials selection Encyclopedic Handbook of Biomaterials and Bioengineering. Part A: Materials 1(1):27-59, 1995.
- [2]Suchanek W, Yoshimura M, Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants. Journal of Materials Research 13:94-117, 1998.
- [3]Ratner B.D., Hoffman A.S, Schoen F.J. and Lemons J.E., in: Biomaterials Science: An Introduction to Materials in Medicine, Academic Press, London, p.37, 1996.
- [4]Wang K, The use of titanium for medical applications in the USA. Materials Science and Engineering A 213:134-137, 2006.
- [5]Yamamuro M, Igarashi H, Katayama Y, Tsuganezawa T, Terashi A, Owan C, Three-Dimensional Anisotropy Contrast (3DAC) Magnetic Resonance Imaging of the Human Brain: Application to Assess Wallerian Degeneration. Internal Medicine 37:662-668, 1998.
- [6]Hierholzer S, Hierholzer G, Sauer KH, Paterson RS, Increased corrosion of stainless steel implants in infected plated fractures. Archives of Orthopaedic and Trauma Surgery 102(3):198-200, 1984.
- [7]Rae T, The action of cobalt, nickel and chromium on phagocytosis and bacterial killing by human polymorphonuclear leucocytes; its relevance to infection after total joint arthroplasty. Biomaterials 4(3):175-180, 1983.
- [8]Andriano KP, Tabata Y, Ikada Y, Heller J, In vitro and in vivo comparison of bulk and surface hydrolysis in absorbable polymer scaffolds for tissue engineering. Journal of Biomedical Materials Research 48(5):602-612, 1999.
- [9]Stefflik DE, McKinney RV, Sisk AL, Parr GR, Koth DL, Scanning electron microscopic studies of the oral tissue responses to dental implants. Department of Oral Pathology, Medical College of Georgia School of Dentistry 4(4):1021-1037, 1990.
- [10]王盈錦, 林峰輝, 胡孝光 等編著, 生物醫學材料, 國立編譯館, 1992.
- [11]Collings EW, In vitro apatite formation on chemically treated (P/M) Ti-13Nb-13Zr. Dental Materials 24(1):50-56, 1984.
- [12]Liu X, Chu PK, Ding C, Surface modification of titanium, titanium alloys, and related materials for biomedical applications. Materials Science and Engineering Reports 47:49-121, 2004.
- [13]Okazaki Y, Ito Y, Kyo K, Corrosion resistance and corrosion fatigue strength of new titanium alloys for medical implants without V and Al. Materials Science and Engineering 213:138-147, 1996.
- [14]Kawahara H, Cytotoxicity of implantable metals and alloy. Bulletin of the Japan Institute of Metals 31:1033-1039, 1992.
- [15]Zhentao Y, Lian Z, Influence of martensitic transformation on mechanical compatibility of biomedical type titanium alloy TLM. Materials Science and Engineering A 438-440:391-394, 2006.

- [16]Okazaki Y, Ito Y, Ito A, Tateishi T, New titanium alloys to be considered for medical implants. In: Brown SA, Lemons JE, editors. Medical applications of titanium and its alloys: The Material and Biological Issues. West Conshohocken, PA:ASTM, pp.45-59, 1996.
- [17]Nouri A, Chen XB, Hodgson PD, Wen CE, Preparation and characterisation of new titanium based alloys for orthopaedic and dental applications. *Advances in Materials Research* 15-17:71-76, 2007.
- [18]Pypen CMJM, Dessein K, Helsen JA, Gomes M, Leenders H, Bruijn JD, Comparison of the cytotoxicity of molybdenum as powder and as alloying element in a niobium – molybdenum alloy. *Journal of Materials Science Materials in Medicine* 9:761-765, 1998.
- [19]Kujala S, Ryhanen J, Danilov A, Tuukkanen J, Effect of porosity on the osteointegration and bone ingrowth of a weight-bearing nickel-titanium bone graft substitute. *Biomaterials* 24:4691-4697, 2003.
- [20]Yang SF, Leong KF, Du ZH, Chua CK, The design of scaffolds for use in tissue engineering. Part 1. Traditional factors. *Tissue Engineering* 7:679-690, 2001.
- [21]Gomes ME, Ribeiro AS, Malafaya PB, Reis RL, Cunha AM, A new approach based on injection moulding to produce biodegradable starch-based polymeric scaffolds: morphology, mechanical and degradation behaviour. *Biomaterials* 22:883-889, 2001.
- [22]Wen CE, Yamada Y, Shimojima K, Chino Y, Asahina T, Mabuchi M, Processing and mechanical properties of autogenous titanium implant materials. *Journal of Materials Science Materials in Medicine* 13: 397-401, 2002.
- [23]Fujibayashi S, Neo M, Kim H, Kokubo T, Nakamura T, Osteoinduction of porous bioactive titanium metal. *Biomaterials* 25:443-450, 2004.
- [24]Wen CE, Mabuchi M, Yamada Y, Shimojima K, Chino Y, Asahina T, Processing of biocompatible porous Ti and Mg. *Scripta Materialia* 45:1147-1153, 2001.
- [25]Wen CE, Yamada Y, Shimojima K, Chino Y, Hosokawa H, Mabuchi M, Novel titanium foam for bone tissue engineering. *Journal of Materials Research* 10:2633-2639, 2002.
- [26]Wen CE, Yamada Y, Shimojima K, Chino Y, Hosokawa H, Mabuchi M, Compressibility of porous magnesium foam: dependency on porosity and pore size. *Materials Letters* 58:357-360, 2004.
- [27]Livingston TL, Bioactive foam for bone tissue engineering: An in vivo study. University of Pennsylvania 1999.
- [28]Hing K.A., Best S.M. and Bonefield W., “ Characterization of porous hydroxyapatite ”, *Journal of Materials Science Materials in Medicine* 10(3):135-145, 1999.
- [29]De Oliverira JF, De Aguiar PF, Rossi AM, Soares GA, Effect of process parameters on the characteristics of porous calcium phosphate ceramics for bone tissue scaffolds. *International Social Artificial Organs* 27:406-411, 2003.
- [30]Vamsi Krishna B, Bose S, Bandyopadhyay A, Low stiffness porous Ti structures for load-bearing implants. *Acta Biomaterialia* 3:997-1006, 2007.
- [31]Plenk H, Prosthesis-Bone Interface. *Journal Biomedical Materials Research (Applied Biomaterials)* 43:350-355, 1998.
- [32]Clemow AJT, Weinstein AM, Klawitter JJ, Koeneman J, Anderson J, Interface mechanics of porous titanium implants. *Journal of Biomedical Materials Research* 15:73-82, 1981.
- [33]Evans FG, The mechanical properties of bone. *Artificial Limbs* 13:37-48, 1969.
- [34]Wang XH, Zhou YC, Microstructure and properties of Ti3AlC2 prepared by the solid – liquid reaction synthesis and simultaneous in-situ hot pressing process. *Acta Materialia* 50:3141-3149, 2002.
- [35]Gibson LJ, The Mechanical Behaviour of Cancellous Bone. *Journal of Biomechanics* 18:317-328, 1985.
- [36]Ontanon M, Aparicio C, Ginebra MP, Planell J, in: M. Elices (Ed.), *Structural Biological Materials. Design and Structure-Property Relationships*, Pergamon Press, Oxford, pp.31-72, 2000.
- [37]Takemoto M, Fujibayashi S, Neo M, Suzuki J, Kokubo T, Nakamura T, Mechanical properties and osteoconductivity of porous bioactive titanium. *Biomaterials* 26: 6014-6023, 2005.
- [38]Cameron JR, Skofronick JG, Grant RM, *Physics of the body*. 2nd ed. Madison, WI: Madison (WI): Medical Physics; 1999.
- [39]Martin RB, Burr DB, Sharkey NA, *Skeletal tissue mechanics*. New York: Springer; 1998.
- [40]Yang R, Guo ZX, Hong TF, Fabrication of porous titanium scaffold materials by a fugitive filler method. *Journal of Materials Science Materials in Medicine* 19:3489-3495, 2008.
- [41]Biswas A, Porous NiTi by thermal explosion mode of SHS: processing, mechanism and generation of single phase microstructure. *Acta Materialia* 53:1415-1425, 2005.
- [42]Li YH, Rong LJ, Li YY, Pore characteristics of porous NiTi alloy fabricated by combustion synthesis. *Journal of Alloys and Compounds* 325:259-262, 2001.
- [43]Wen CE, Yamada Y, Hodgson PD, Fabrication of novel metal alloy foams for biomedical applications. *Materials Forum Volume* 29:274-278, 2005.
- [44]Wang X, Li Y, Xiong J, Hodgson PD, Wen C, Porous TiNbZr alloy scaffolds for biomedical applications. *Acta Biomaterialia* 5:3616-3624, 2009.
- [45]Wen CE, Xiong JY, Li YC, Wang XJ, Hodgson PD, Mechanical properties and bioactive surface modification via alkali-heat treatment of a porous Ti-18Nb-4Sn alloy for biomedical applications. *Acta Biomaterialia* 4:1963-8, 2008.

- [46] Xiong JY, Li YC, Wang XJ, Hodgson PD, Wen CE, Titanium-nickel shape memory alloy foams for bone tissue engineering. *Journal of the Mechanical Behavior of Biomedical Materials* 1(3) 269-273, 2008.
- [47] Li YH, Rong LJ, Li YY, Compressive property of porous NiTi alloy synthesized by combustion synthesis. *Journal of Alloys and Compounds* 345:271-274, 2002.
- [48] Li YH, Chen RB, Qi GX, Wang ZT, Deng ZY, Powder sintering of porous Ti-15Mo alloy from TiH₂ and Mo powders. *Journal of Alloys and Compounds* 485:215-218, 2009.
- [49] Nouri A, Hodgson PD, Wen CE, Effect of Process Control Agent on the Porous Structure and Mechanical Properties of a Biomedical Ti-Sn-Nb Alloy Produced by Powder Metallurgy. *Acta Biomaterialia* 6:1630-1639, 2010.
- [50] Wen CE, Yamada Y, Shimojima K, Sakaguchi Y, Chino Y, Hosokawa H, Novel titanium foam for bone tissue engineering. *Journal of Materials Research* 17:2633-2639, 2002.
- [51] M?ller FA, Bottino MC, M?ller L, Henriques VAR, Lohbauere U, Bressiani AHA, Bressiani JC, In vitro apatite formation on chemically treated (P/M) Ti-13Nb-13Zr. *Dental Materials* 24: 50-56, 2008.
- [52] Zhu SL, Yang XJ, Fu DH, Zhang LY, Li CY, Cui ZD, Stress-strain behavior of porous NiTi alloys prepared by powders sintering. *Materials Science and Engineering A* 408:264-268, 2005.
- [53] Li BY, Rong LJ, Li YY, The influence of addition of TiH₂ in elemental powder sintering porous Ni-Ti alloys. *Materials Science and Engineering A* 281:169-175, 2000.
- [54] L?jering G, Williams JC, Titanium. Berlin:Springer-Verlag 2003.
- [55] Park JB, Lakes RS, Biomaterials: An introduction. New York: Plenum press, 1994.
- [56] Wang XJ, Li YC, Hodgson PD, Wen CE, Nano-and macro-scale characterisation of the mechanical properties of bovine bone. *Materials Forum* 31:156-159, 2007.
- [57] Heini P, M?ller L, K?rner C, Singer RF, M?ller FA, Cellular Ti-6Al-4V structures with interconnected macro porosity for bone implants fabricated by selective electron beam melting. *Acta Biomaterials* 4: 1536-1544, 2008.
- [58] Lopez-Heredia MA, Sohler J, Gaillard C, Quillard S, Dorget M, Layrolle P, Rapid prototyped porous titanium coated with calcium phosphate as a scaffold for bone tissue engineering. *Biomaterials* 29:2608-2615, 2008.
- [59] Ishizaki K, Komarneni S, Nanko M, Porous Materials: Process Technology and Applications. *Materials Technology Series Kluwer Academic Publishers* pp.56-65, 1998.
- [60] Oh IK, Nomura N, Masahashi N, Hanada S, Mechanical properties of porous titanium compacts prepared by powder sintering. *Scripta Materialia* 49:1197-1202, 2003.
- [61] Taddei BE, Henriques VAR, Silva CRM, Properties of Porous Ti-35Nb-7Zr-5Ta Processed by the Spacer Method for Use in Biomedical Applications. *Materials Science Forum Vol 591-593*, pp.224-234, 2008.
- [62] Dunand DC, Processing of Titanium Foams. *Advanced Engineering Materials* 6(6):369-376, 2004.
- [63] Li Y.H., Rao G.B., Rong L.J., Li Y.Y. and Ke W., " Effect of pores on corrosion characteristics of porous NiTi alloy in simulated body fluid ", *Materials Science and Engineering A* 363:356-359, 2003.
- [64] Li H, Yuan B, Gao Y, Chung CY, Zhu M, High-porosity NiTi superelastic alloys fabricated by low-pressure sintering using titanium hydride as pore-forming agent. *Journal of Materials Science* 44:875-881, 2009.
- [65] Steinemann SG, Evaluation of Biomaterials, edited by Winter GD, Leray JL, Groot de K (Wiley, New York) pp.1-3310, 1980.
- [66] Okazaki Y, Rao S, Ito Y, Tateishi T, Corrosion resistance, mechanical properties and cytocompatibility of new Ti alloys without Al and V. *Biomaterials* 19:1197-1215, 1998.
- [67] Niinomi M, Fatigue performance and cyto-toxicity of lowrigidity titanium alloy Ti-29Nb-13Ta-4.6Zr. *Biomaterials* 24:2673-2683, 2003.
- [68] Kasuga T, Nonami M, Niinomi M, Hattori T, Bioactive calcium phosphate invert glass-ceramic coating on -type Ti-29Nb-13Ta-4.6Zr alloy. *Biomaterials* 24:283-290, 2003.
- [69] Okazaki Y, Effect of friction on anodic polarization properties of metallic biomaterials. *Biomaterials* 23:2071-2077, 2002.
- [70] Inoue A, Stabilization of metallic supercooled liquid and bulk amorphous alloys. *Acta Materialia* 48:279-306, 2000.
- [71] Ma E, Amorphization in mechanically driven material systems. *Scripta Materialia* 49:941-946, 2003.
- [72] Li JP, De Wijn JR, Van Blitterswijk CA, De Groot K, Porous Ti-6Al-4V scaffold directly fabricating by rapid prototyping: preparation and in vitro experiment. *Biomaterials* 27: 1223-1235, 2006.
- [73] Li JP, Li SH, Van Blitterswijk CA, De Groot K, A novel porous Ti-6Al-4V: characterization and cell attachment. *Journal of Biomedical Materials Research A* 73:223-233, 2005.
- [74] Hollander DA, Von Walter M, Wirtz T, Sellei R, Schmidt-Rohlfing B, Paar O, Structural, mechanical and in vitro characterization of individually structured Ti-6Al-4V produced by direct laser forming. *Biomaterials* 27: 955-963, 2006.
- [75] Davidson JA, Mishra AK, Kovacs P, Poggie RA, New surface hardened low-modulus corrosion-resistant Ti-13Nb-13Zr alloy for total hip arthroplasty. *Bio-Medical Materials and Engineering* 4:231-243, 1994.
- [76] Geetha M, Mudali UK, Gogia AK, Asokamani R, Raj B, Influence of microstructure and alloying elements on corrosion behavior of

Ti-13Nb-13Zr alloy. *Corrosion Science* 46: 877-892, 2004.

- [77]Semiatin S.L., Seetharaman V. and Weiss I., " The thermomechanical processing of alpha/beta titanium alloys " , *JOM Journal of the Minerals, Metals and Materials Society* 49:33-39, 1997.
- [78]Okazaki Y, Nishimura E, Nakada E, Kobayashi K, Surface analysis of Ti-15Zr-4Nb-4Ta alloy after implantation in rat tibia. *Biomaterials* 22:599-607, 2001.
- [79]Kuroda D, Niinomi M, Morinaga M, Kato Y, Yashiro T, Design and mechanical properties of new type titanium alloys for implant materials. *Materials Science and Engineering A* 243:244-249, 1998.
- [80]Berthon G, Aluminium speciation in relation to aluminium bioavailability metabolism and toxicity, *Coordination Chemistry Reviews* 228:319-341, 2002.
- [81]Yu SY, Scully JR, Corrosion and passivity of Ti-13Nb-13Zr in comparison to other biomedical implant alloys. *Corrosion* 53:965-976, 1997.
- [82]Matsuno H, Yokohama A, Watari F, Uo M, Kawasaki T, Biocompatibility and osteogenesis of refractory metal implants, titanium, hafnium, niobium, tantalum and rhenium. *Biomaterials* 22:1253-1262, 2001.
- [83]Lipscomb I.P. and Nokes L.D.M., " The Application of Shape Memory Alloys in Medicine " , *Mechanical Engineering Publications Suffolk UK* p.154, 1996.
- [84]Hosoda H, Hunada S, Inoue K, Fukui T, Mishina Y, Suzuki T, Martensite transformation temperatures and mechanical properties of ternary NiTi alloys with offstoichiometric compositions. *Intermetallics* 6:291-301, 1998.
- [85]Chen MF, Yang XJ, Hu RX, Cui ZD, Man HC, Bioactive NiTi shape memory alloy used as bone bonding implants. *Materials Science and Engineering C* 24:497-502, 2004.
- [86]Gjunter VE, in: *Delay Law and New Class of Materials and Implants in Medicine*, STT, Northampton, p.11, 2000.
- [87]Itin VI, Gjunter VE, Shabalovskaya SA, Sachdeva RLC, Mechanical properties and shape memory of porous nitinol. *Materials Characterization* 32:179-187, 1994.
- [88]Li BY, Rong LJ, Li YY, Gjunter VE, Electric resistance phenomena in porous Ni-Ti shape-memory alloys produced by SHS. *Scripta Materialia* 44:823-827, 2001.
- [89]Ayers RA, Simske SJ, Bateman TA, Petkus A, Sachdeva RLC, Gjunter VE, Effect of nitinol implant porosity on cranial bone ingrowth and apposition after 6 weeks. *Journal of Biomedical Materials Research* 45(1):42-47, 1999.
- [90]Li BY, Rong LJ, Li YY, Gjunter VE, Synthesis of porous Ni-Ti shape-memory alloys by self-propagating high-temperature synthesis: reaction mechanism and anisotropy in pore structure. *Acta Materialia* 48:3895-3904, 2000.
- [91]Chu CL, Chung CY, Lin PH, Wang SD, Fabrication of porous NiTi shape memory alloy for hard tissue implants by combustion synthesis. *Materials Science and Engineering A* 366:114-119, 2004.
- [92]DC Lagoudas, EL Vandygriff, Processing and characterization of NiTi porous SMA by elevated pressure sintering. *Journal of Intelligent Material Systems and Structures* 13:837-850, 2002.
- [93]Yuan B, Chung CY, Zhu M, Microstructure and martensitic transformation behavior of porous Ni-Ti shape memory alloy prepared by hot isostatic pressing processing. *Materials Science and Engineering A* 382:181-187, 2004.
- [94]Zhu SL, Yang XJ, Hu F, Deng SH, Cui ZD, Processing of porous TiNi shape memory alloy from elemental powders by Ar-sintering. *Materials Letters* 58:2369-2373, 2004.
- [95]Zhao Y, Taya M, Kang Y, Kawasaki A, Compression behavior of porous NiTi shape memory alloy. *Acta Materialia* 53:337-343, 2005.
- [96]Elema H, De Groot JH, Nijenhuis AJ, Pennings AJ, Veth RPH, Klomp maker J, Jansen HWB, Use of porous biodegradable polymer implants in meniscus reconstruction. *Science* 268: 1082-1088, 1990.
- [97]Klomp maker J, Jansen HWB, Veth RPH, Nielsen HKL, De Groot JH, Pennings AJ, Porous implants for knee joint meniscus reconstruction: a preliminary study on the role of pore sizes in ingrowth and differentiation of fibrocartilage. *Clinical Mat* 14:1-11, 1993.
- [98]McNeese MD, Lagoudas DC, Pollock TC, Processing of TiNi from elemental powders by hot isostatic pressing. *Materials Science and Engineering A* 280:334-348, 2000.
- [99]Bram M, Ahmad-Khanlou A, Heckmann A, Fuchs B, Buchkremer HP, St?rger D, Powder metallurgical fabrication processes for NiTi shape memory alloy parts. *Materials Science and Engineering A* 337:254-263, 2002.
- [100]Shih CC, Lin SJ, Chen YL, Su YY, Lai ST, Wu GJ, Kwok CF, Chung KH, The cytotoxicity of corrosion products of nitinol stent wire on cultured smooth muscle cells. *Journal of Biomedical Materials Research* 52:395-403, 2000.
- [101]Wataha JC, O ' Dell NL, Singh BB, Ghazi M, Whitford GM, Lockwood PE, Relating nickelinduced tissue inflammation to nickel release in vivo. *Journal of Biomedical Materials Research Part B Applied Biomaterials* 58:537-544, 2001.
- [102]Otsuka K, Wayman CM, *Shape Memory Materials*. Cambridge University Press, Cambridge 13:1-14, 1998.
- [103]Baure G, Jardine AP, Modifying the mechanical properties of porous equiatomic nitinol for osteoimplants. In: *Proc. Int. Conf. on Shape Memory and Superelastic Technologies*. Kurhaus, BadenBaden, Germany, pp. 475-482, 2004.
- [104]Yamamuro T, Patterns of osteogenesis in relation to various biomaterials. *Journal Japanese of Society Biomaterials* 7:19-23, 1989.
- [105]Chu CL, Chung CY, Zhou J, Pu YP, Lin PH, Fabrication and characteristics of bioactive sodium titanate/titania graded film on NiTi shape

memory alloy. *Journal of Biomedical Materials Research* A75:595-602, 2005.

- [106]Gu YW, Li H, Tay BY, Lim CS, Yong MS, Khor KA, In vitro bioactivity and osteoblast response of porous NiTi synthesized by SHS using nanocrystalline NiTi reaction agent. *Journal of Biomedical Materials Research* A78:316-323, 2006.
- [107]Prymak O, Bogdanski D, K?雍ler M, Esenwein SA, Muhr G, Beckmann F, Morphological characterization and in vitro biocompatibility of a porous nickel-titanium alloy. *Biomaterials* 26:5801-5807, 2005.
- [108]Gibson LJ, Ashby MF, *Cellular Solids. Structure and Properties*, second edition, Cambridge University Press Cambridge, New York 1997.
- [109]Ho WF, Ju CP, Lin JHC, Structure and properties of cast binary Ti-Mo alloys. *Biomaterials* 20:2115-2122, 1999.
- [110]Rao S, Okazaki Y, Tateishi T, Cytocompatibility of New Ti Alloy without Al and V by Evaluating the Relative Growth Ratios of Fibroblasts L929 and Osteoblasts MC3T3-E1 cells. *Materials Science and Engineering C4*:311-314, 1997.
- [111]Helsen JA, Breme HJ, *Metals as Biomaterials*. Wiley, Baffins Lane, Chichester, England p.522, 1998.
- [112]Moyen BJ, Lahey Jr P.J., Weinberg EH, Harris WH, Effects on intact femora of dogs of the application and removal of metal plates. A metabolic and structural study comparing stiffer and more flexible plates. *Journal of Bone and Joint Surgery American* 60:940-947, 1978.
- [113]Vehof, Johan WM, Paul HM Spauwen, John A Jansen, Bone formation in calcium-phosphate-coated titanium mesh. *Biomaterials* 21:2003-2009, 2000.
- [114]Slenes K, Ackerman WC, Brotzman RW, Stoltzfux J, Gunaji M, *Surf Coat Technol* 68-69:pp.51-57, 1994.
- [115]Lemons JE, *Biomaterials biomechanics tissue healing and immediate-function dental implants*. *Journal of Oral Implantology* 30:318-324, 2004.
- [116]Ducheyne P, van Raemdonck W, Heughbaert JC, Heughbaert M, Structural analysis of hydroxyapatite coatings on titanium. *Biomaterials* 7:97-103, 1986.
- [117]Kim HM, Kokubo T, Fujibayashi S, Nishiguchi S, Nakamura T, Bioactive macroporous titanium surface layer on titanium substrate. *Journal of Biomedical Materials Research* 52:553-557, 2000.
- [118]Ishizawa H, Ogino M, Formation and characterization of anodic titanium oxide films containing Ca and P. *Journal of Biomedical Materials Research* 29:65-72, 1995.
- [119]Zhu XL, Kim KH, Jeong YS, Anodic oxide films containing Ca and P of titanium biomaterial. *Biomaterials* 22:2199-2206, 2001.
- [120]Han Y, Hong SH, Xu K, Structure and in vitro bioactivity of titania-based films by micro-arc oxidation. *Surface and Coatings Technology* 168:249-258, 2003.
- [121]Song WH, Jun YK, Han Y, Hong SH, Biomimetic apatite coatings on micro-arc oxidized titania. *Biomaterials* 25: 3341-3349, 2004.
- [122]Suryanarayana C, *Mechanical Alloying and Milling*. *Progress in Materials Science* 46:1-184, 2001.
- [123]L? L, Lai MO, *Mechanical Alloying*. Boston: Kluwer Academic Publishers, 154:361-370, 1998.
- [124]Soni PR, *Mechanical alloying: fundamentals and applications*. Cambridge: International Science Publishing, 1999.
- [125]Suryanarayana C, Froes FH, *Mechanical Alloying of Titanium-Base Alloys*. *Advanced Materials* 5:96-106, 1993.
- [126]Henriques VAR, Bellinati CE, Silva CRM, Production of Ti-6% Al-7% Nb alloy by powder metallurgy (P/M). *Journal of Materials Processing Technology* 118: 212-215, 2001.
- [127]Taddei EB, Henriques VAR, Silva CRM, Cairo CAA, Production of new titanium alloy for orthopedic implants. *Materials Science and Engineering C* 24:683-687, 2004.
- [128]Gilman PS, Benjamin JS, *Mechanical alloying*. *Annual Review of Materials Science* 13:279-300, 1983.
- [129]Tsuruga E, Takita H, Itoh H, Kuboki Y, Pore Size of Porous Hydroxyapatite as the Cell-Substratum Controls BMP-Induced. *Journal of Biochemistry* 121:317-324, 1997.
- [130]Sikavitsas VI, Temenoff JS, Mikos AG, *Biomaterials and bone mechanotransduction*. *Biomaterials* 22:2581-2593, 2001.
- [131]Athanasίου K, Agrawal C, Barber F, Burkhart S, Orthopaedic applications for PLA-PGA biodegradable polymers. *Arthroscopy* 14:726-737, 1998.
- [132]Gogolewski S, *Bioresorbable polymers in trauma and bone surgery*. *Injury* 31:28-32, 2000.
- [133]Murphy WL, Kohn DH, Mooney DJ, Growth of continuous bonelike mineral within porous poly(lactide-co-glycolide) scaffolds in vitro. *Journal of Biomedical Materials Research* 50:50-58, 2000.
- [134]Dong J, Kojima H, Uemura T, Kikuchi M, Tateishi T, Tanaka J, In vivo evaluation of a novel porous hydroxyapatite to sustain osteogenesis of transplanted bone marrow-derived osteoblastic cells. *Journal of Biomedical Materials Research* 57:208-216, 2001.
- [135]Rezwan K, Chen QZ, Blaker JJ, Boccaccini AR, *Biodegradable and bioactive porous polymer/inorganic composite scaffolds for bone tissue engineering*. *Biomaterials* 27:3413-3431, 2006.
- [136]Hing KA, Best SM, Tanner KE, Bonfield W, Revell PA, Mediation of bone ingrowth in porous hydroxyapatite bone graft substitutes. *Journal of Biomedical Materials Research* 68A:187-200, 2004.
- [137]De Long WG, Einhorn TA, Koval K, McKee M, Smith W, Sanders R, Bone grafts and bone graft substitutes in orthopaedic trauma surgery. *Journal of Bone and Joint Surgery* 89:649-658, 2007.
- [138]Yoshikawa H, Myoui A, *Bone tissue engineering with porous hydroxyapatite ceramics*. *Journal of Artificial Organs* 8:131-136, 2005.

- [139]Bertheville B, Porous single-phase NiTi processed under Ca reducing vapor for use as a bone graft substitute. *Biomaterials* 27:1246-1250, 2006.
- [140]Uchida M, Kim HM, Miyaji F, Kokubo T, Nakamura T, Apatite formation on zirconium metal treated with aqueous NaOH. *Biomaterials* 23:313-317, 2002.
- [141]Kokubo T, Kim HM, Kawashita M, Novel bioactive materials with different mechanical properties. *Biomaterials* 24:2161-2175, 2003.
- [142]Kokubo T, Apatite formation on surfaces of ceramics, metals and polymers in body environment. *Acta Materialia* 46:2519-2527, 1998.
- [143]Otsuki B, Takemoto M, Fujibayashi S, Neo M, Kokubo T, Nakamura T, Pore throat size and connectivity determine bone and tissue ingrowth into porous implants Three-dimensional micro-CT based structural analyses of porous bioactive titanium implants. *Biomaterials* 27:5892-5900, 2006.
- [144]Han Y, Cui K, Sun J, Microstructure and apatite-forming ability of the MAO-treated porous titanium. *Surface & Coatings Technology* 202:4248-4256, 2008.
- [145]Lin J.H, Chang CH, Chen YS, Lin GT, Formation of bone-like apatite on titanium filament by a simulated body fluid inducing process. *Surface & Coatings Technology* 200:3665-3669, 2006.
- [146]Kokubo T, Takadama H, How useful is SBF in predicting in vivo bone bioactivity. *Biomaterials* 27:2907-2915, 2006.
- [147]Wen C, Hodgson PD, Nouri A, Chen X, Li Y, Yamada Y, Synthesis of Ti-Sn-Nb alloy by powder metallurgy. *Materials Science and Engineering A* 485:562-570, 2008.
- [148]German RM, Particle packing characteristics. NJ: Metal Powder Industries Federation 404-407, 1989.
- [149]Martin CL, Bouvard D, Isostatic compaction of bimodal powder mixtures and composites. *International Journal of Mechanical Sciences* 24:907-927, 2004.
- [150]McGeary RK, Mechanical packing of spherical particles. *Journal of the American Ceramic Society* 44:513-522, 1961.
- [151]Zhang Y, Wei XY, Mao CH, Li TF, Yuan P, Du J, Preparation and pumping characteristics of Ti-7.5 wt.%Mo getter. *Journal of Alloys and Compounds* 485:200-203, 2009.
- [152]Takashi N, Tomiharu M, Kenji D, Hiroaki T, Pattanayak DK, Tadashi K, Effects of oxygen content of porous titanium metal on its apatite-forming ability and compressive strength. *Materials Science and Engineering C* 29:1974-1978, 2009.