

合金元素添加對生醫用鑄造三元鈦合金的結構及性質之影響研究

潘昌宏、何文福

E-mail: 9708021@mail.dyu.edu.tw

摘要

在本研究中，將探討TZX、TCX及TCFX之相/晶體構造、微結構、機械性質及研削性，並與商業純鈦做比較，期望能開發出適合作為牙科應用之鈦合金。TZX合金方面：實驗結果與對照組c.p. Ti做為比較。結果顯示，TZ合金添加少量的合金元素可以改善相/晶體結構、微結構、機械性質及研削性。雖然所有合金的研削量需用研削速度來加以控制，但是合金元素Nb、Mo、Cr及Fe在研削條件下明顯提升研削比。TZM合金與c.p. Ti做比較，微硬度增加(63%)、彎曲強度(40%)、彈性模數(30%)及彈性回復角(180%)，也發現有良好的研削性質。TZM合金，如果滿足牙科鑄造條件下，可用於牙科修復材使用。TCX合金方面：TC及TCX合金之彎曲強度均遠高於c.p. Ti，特別是TCN有最高之彎曲強度。三元合金的彎曲彈性模數均較c.p. Ti及TC合金高，其中以TCZ合金具有最高之彎曲彈性模數。此外，TC及TCX合金也具有較c.p. Ti更為良好之彈性回復能力。因此，本研究探討之TC與TCX合金具有良好的機械性質，且其相的結構也可使合金具有較好的加工性，相信在牙科鑄造用合金上將具有不錯的應用潛力。TCFX合金方面：實驗結果顯示，只有TCF5與TCF6展現出延性特徵。TCF5與TCF6未含有相，彈性模數遠低於含有相的TC1與TCFX。TCF5擁有最高抗彎強度/彈性模數比值25.1，高於商業純鈦(c.p. Ti) 195%與TC1合金132%。此外，TCF6也具有高比值24.6，遠高於c.p. Ti 189%與TC1合金128%。此外，彈性回復能力TCF5(31.5°)和TCF6(29.6°)合金均高於c.p. Ti(2.7°)，分別高達1067%和996%。從微結構發現，TCF5與TCF6涵蓋了許多滑移線。以目前尋求更好的植入材，低彈性模數、延性特徵、良好的彈性回復能力及適當的高強度或(高強度/彈性模數比值)相TCF5與TCF6合金將會是最好的選擇。研削結果顯示，TCFX合金微結構與Fe有關。當Fe含量超過0.5%時，等軸相完全保留下來，TC1、TCF2、TCF3及TCF4合金發現含有相。TCF3與TCF4合金含有大量相和極高的微硬度。TC1及TCFX合金顯示研削量與微硬度有相同趨勢。TC1、TCF2、TCF3及TCF4合金，尤其在500、750及1000 m/min時，研削量表現最佳。而且研削量比例隨著研削速率到1000 m/min為最高，到1200 m/min隨之減少。這項研究結果發現添加Fe可以增加鈦合金硬度及改善研削性。

關鍵詞：鈦合金；牙科合金；結構；機械性質；相；研削性；加工性；鈦合金；研削性；微結構；研削量

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.....	ix	圖目
錄.....	xv	表目
錄.....	xxii	第一章 緒
論.....	1	1.1 生醫材料的定義..... 1
材料種類.....	3	1.3 生物醫用金屬的發展..... 11
合金簡介.....	13	2.1 鈦資源的分佈及特點..... 13
鈦.....	15	2.2 純鈦物理性質..... 19
類.....	22	2.3.1 型鈦合金..... 23
金.....	24	2.3.3 型鈦合金..... 24
金.....	25	2.3.5 型鈦合金..... 26
響.....	29	2.4 合金元素對鈦的影響..... 29
用.....	30	2.4.1 Zr元素在合金中的作用..... 29
用.....	30	2.4.2 Cr元素在合金中的作用..... 29
用.....	32	2.4.3 Nb元素在合金中的作用..... 31
用.....	32	2.4.4 Mo元素在合金中的作用..... 31
用.....	34	2.4.5 Sn元素在合金中的作用..... 33
用.....	34	2.4.6 Fe元素在合金中的作用..... 33
展.....	36	2.5 醫用鈦及鈦合金發展..... 35
段.....	36	2.5.1 純鈦階段..... 36
段.....	36	2.5.2 型鈦合金階段..... 36
段.....	37	2.5.3 新型鈦合金階段..... 37
段.....	37	2.5.4 型鈦合金階段..... 37
Ti-12Mo-6Zr-2Fe.....	40	2.6 近年來生醫用鈦合金之發展..... 40
Ti-15Mo.....	41	2.6.1 型鈦合金階段..... 40
	40	2.6.2 Ti-13Nb-13Zr..... 41
	41	2.6.3 Ti-15Mo..... 41
	41	2.6.4 Ti-15Zr-4Nb-2Ta-0.2Pd..... 41

與Ti-15Sn-4Nb-2Ta-0.2Pd.....	42 2.6.5	Ti-35.3Nb-5.1Ta-7.1Zr	
與Ti-29Nb-13Ta-4.6Zr.....	42 2.7	鈦及其合金的應用.....	42 2.7.1 鈦合金
在航空上的應用.....	42 2.7.2	鈦合金在航海上的應用.....	43 2.7.3 鈦合金在日常生活領
域中的應用.....	45	第三章 理論及文獻回顧.....	46 3.1 口腔專用鑄造機的研究發
展.....	46 3.1.1	口腔專用鑄造機的發展.....	46 3.1.2 鑄造機分類及惰性氣體的影
體.....	46 3.1.3	包埋材對鑄造機的影響.....	47 3.2 鋁當量與鉬當量方程
式.....	49 3.3	鍵結次數(Bo)及d軌域能階(Md).....	50 3.4 麻田散體轉換及結
構.....	51 3.4.1	平衡下麻田散體轉換.....	52 3.4.2 非平衡下麻田散體轉
換.....	53 3.4.3	相形成的機構.....	54 3.5 相變化對鈦合金的影
響.....	56 3.6	微結構對鈦合金的影響.....	57 3.7 彈性模數的影響因
素.....	58 3.7.1	純金屬彈性模數影響的因素.....	59 3.7.2 鈦合金彈性模數影響的因
素.....	60 3.8	生物相容性.....	61 3.9 研究目
的.....	68	第四章 材料及實驗方法.....	69 4.1 實驗
流程.....	69 4.2	試料的準備.....	71 4.2.1 純
鈦.....	71 4.2.2	TZX合金.....	71 4.2.3 TCX合
金.....	72 4.2.4	TCFX合金.....	72 4.3 熔煉及鑄
造.....	73 4.4	相分析及顯微觀察.....	79 4.4.1 XRD繞射分
析.....	79 4.4.2	金相顯微結構觀察.....	79 4.4.3 晶粒尺寸(grain size)大小計
算.....	80 4.5	機械性質分析.....	81 4.5.1 微硬度測
試.....	81 4.5.2	三點彎曲試驗.....	82 4.5.3 彈性回復能
力.....	83 4.6	研削性測試.....	84 4.6.1 試片準
備.....	84 4.6.2	研削性測試系統設計並建立.....	85 4.6.3 實驗參數選
擇.....	86 4.6.4	研削性評估方法.....	87 4.6.5 試片測試方
式.....	89 4.6.6	金屬切屑(metal chip)收集.....	90 4.6.7 掃描式電子顯微鏡觀
察.....	90 4.6.8	光學顯微鏡觀察.....	90 第五章 結果與討
論.....	91 5.1	TZX 相分析及顯微觀察.....	91 5.1.1 熔煉及鑄
造.....	91 5.1.2	XRD繞射分析.....	93 5.1.3 金相顯微結構觀
察.....	95 5.2	TZX 機械性質分析.....	97 5.2.1 微硬度測
試.....	97 5.2.2	三點彎曲試驗.....	99 5.2.3 彈性模數分
析.....	101 5.2.4	彈性回復能力.....	102 5.3 TZX 研削性測
試.....	105 5.3.1	金屬及合金的密度計算.....	105 5.3.2 研削量及研削
比.....	106 5.3.3	SEM切屑觀察.....	109 5.3.4 光學顯微鏡觀察研削後試片
表面形態.....	115 5.4	TCX 相分析及顯微觀察.....	121 5.4.1 熔煉及鑄
造.....	121 5.4.2	XRD繞射分析.....	123 5.4.3 金相顯微結構觀
察.....	125 5.5	TCX 機械性質分析.....	127 5.5.1 微硬度測
試.....	127 5.5.2	三點彎曲試驗.....	129 5.5.3 彈性模數分
析.....	130 5.5.4	彈性回復能力.....	131 5.6 TCX 研削性測
試.....	134 5.6.1	金屬及合金的密度計算.....	134 5.6.2 研削量及研削
比.....	135 5.6.3	光學顯微鏡觀察研削後試片表面形態.....	137 5.7 TCFX 相分析及顯微觀
察.....	143 5.7.1	XRD繞射分析.....	143 5.7.2 金相顯微結構觀
察.....	147 5.7.3	晶粒尺寸大小.....	149 5.8 TCFX 機械性質分
析.....	155 5.8.1	微硬度測試.....	155 5.8.2 三點彎曲試
驗.....	158 5.8.3	合金變形表面金相分析.....	164 5.8.4 彈性模數分
析.....	167 5.8.5	彈性回復能力.....	168 5.9 TCFX 研削性測
試.....	170 5.9.1	金屬及合金的密度計算.....	170 5.9.2 研削量及研削
比.....	171 5.9.3	SEM切屑觀察.....	174 5.9.4 光學顯微鏡觀察研削後試片
表面形態.....	182	第六章 結論.....	188 參考文
獻.....	194	附錄.....	

參考文獻

[1] Horlington M. Biomaterials: present and future. Materials World. 1995. p. 332-333.

- [2] Hench LL. Biomaterials: a forecast for the future. *Biomaterials*. 1998;19:1419-1423.
- [3] Clemson Advisory Board for Biomaterials Definition of the word biomaterial The 6th Annual International Biomaterial Symposium 1974. p. 20-24.
- [4] Wesolowski SA, Dennis C. *Fundamentals of Vascular Grafting*. New York: McGraw-Hill publication, 1963.
- [5] Paul R. Alkaline aqueous electrolyte cell for biomedical application. *J Electrochem Soc* 1980;127(8):1667-1678.
- [6] Browning E. *Toxicity of Industrial Metals*. 2nd ed. Butterworths. London, 1969.
- [7] 島村 昭治, 未來?拓?先端材料, 工業調査?, 1989; pp. 186-190.
- [8] Hierholzer S, Hierholzer G, Sauer KH, Paterson RS. Increased corrosion of stainless steel implants in infected plated fractures. *Arch Orthop Trauma Surg* 1984;102(3):198-200.
- [9] 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* 1983;4(3):175-180.
- [10] Chang CK, Wu JS, Mao DL, Ding CX. Mechanical and histological evaluations of hydroxyapatite-coated and noncoated Ti6Al4V implants in tibia bone. *J Biomed Mater Res* 2001;56(1):17-23.
- [11] Heughebaert M, LeGeros RZ, Gineste M. Physicochemical characterization of deposits associated with HA ceramics implanted in nonosseous sites. *J Biomed Mater Res* 1988;22(3):257-268.
- [12] Ripamonti U. Osteoinduction in porous hydroxyapatite implanted in heterotopic sites of different animal models. *Biomaterials* 1996;17(1):31-35.
- [13] Magan A, Ripamonti U. Geometry of porous hydroxyapatite implants influences osteogenesis in baboons (*Papio ursinus*). *J Craniofac Surg* 1996;7(1):71-78.
- [14] Goh JCH. Biomechanics and advances in total joint replacement design. *Proc the 3rd World Congress of Biomechanics (WCB ' 98)* 1998;4:182-347.
- [15] Schmalzried TP, Callaghan JJ. Current concepts review: wear in total hip and knee replacements. *J Bone Joint Surg B* 1999;81:115-136.
- [16] Hall SJ. *Basic Biomechanics: the biomechanics of human bone growth and development*. Mosby-Year Book: St Louis. 1995;4:86-109.
- [17] Chen WP, Liu PH, Liao JD. Modular Finite Element Mesh Generation and Contact Stress Analysis of Total Hip Replacement. *Chinese J Mechanics* 1998;14: 51-60.
- [18] 王盈錦, 林峰輝, 胡孝光 等編著, 生物醫學材料, 國立編譯館, 1992.
- [19] Hayasahi K. Biodegradation of implant materials. *JSME Int J* 1987;30:(268) 1517-1525.
- [20] Chiba A, Sakakura S, Kobayashi K, Kusayanagi K. Dissolution amounts of nickel, chromium and iron from SUS 304, 316 and 444 stainless steels in sodium chloride solutions. *J Mater Sci* 1997;32:1995-2000.
- [21] [23]Noort RVan. Titanium: the implant of today. *J Mater Sci Mater Med* 1987;22: 3801-3811.
- [22] Williams DF. *Biocompatibility of Clinical implant materials*. v2. CRC press. Inc. Boca Raton. Florida, 1981. p. 112.
- [23] Branemark PI, Hansson BO, Adell R, Breine U, Lindstrom J, Hallen O, Ohman A. Osseointegrated implants in the treatment of the edentulous jaw. Experience from a 10-year period. *Scand J Plast Reconstr Surg Suppl* 1977;16:1-132.
- [24] Branemark KP, Hansson B, Adell R. Intraosseous anchorage dental prostheses: I experimental studies. *Scand J Plast Reconstr Surg Suppl* 1977;16:1-4.
- [25] Kokubo T, Nakamura T, Miyaji F. *Bioceramics 9: Proceedings of the 9th International Symposium on Ceramics in Medicine*. Otsu Japart, 1996. p.11.
- [26] Kathy W. The use of titanium for medical application in USA. *Mater Sci and Eng A* 1996;123:134-137.
- [27] Abkowitz S. *The emergence of the titanium industry and the development of the Ti-6Al-4V alloy: collections and recollections*. TMS. Warrendale. PA: USA, 2000. p. 42.
- [28] Moffat DL, Larbalestier DC. The competition between Martensite and Omega in Quenched Ti-Nb Alloys. *Metall Trans A* 1988;19(7):1677-1686.
- [29] Williams JC. High performance materials development in the 21st century trends and direction. *Mater Sci for vols* 2004;449-452:7-12.
- [30] Covington LC, Schutz RW. Corrosion resistance of titanium. *Metals Handbook*. 9th. ASM publications. Ohio, 3:413-415, 1979.
- [31] Donachie MJ. *Titanium and titanium alloys source book*. Metals Park. OH: The American Society for Metals. 1982. p.10-19.
- [32] 賴耿陽, 金屬鈦, 復漢出版社, 1990, p.1-60.
- [33] Brobst DA, Pratt WP. United states mineral resources: U.S. geological survey professional paper. No: 820, 1973. p. 662.
- [34] Donachie jr MJ. *Titanium atechanical guide*. ASM International. Metal Park: Oh44073, 1988. p.14.
- [35] Ogden HR. *Rare Metals Handbook*. in: Clifford AH editors, Rinhdd Publishing Corporation. Chapman & Hall Ltd. London. 1961.p.559-579.
- [36] Collings EW. *The physical metallurgy of titanium alloys*. in: Gegel HL editors. ASM Series in Metal Processing. Edward Arnold publications. Cleveland. Metals Park:OH, 1984. p.66-478.
- [37] Burgers WG. On the process of transition of the cubic-body-centered modification into the hexagonal-close-packed modification of zirconium. *Physica* 1934;1:561-586.

- [38] 丹尼·爾漢克爾, 工程材料.美商麥格羅·希爾出版社, 2002, p. 161-163.
- [39] Kahles JF, Field M, Eylon D, Froes FH. Machining of titanium alloys. *J Met* 1985;37(4):27-35.
- [40] Blenkinsop PA. High temperature titanium alloys. IMI Titanium Limited. Birmingham. England, 1986. p.189-198.
- [41] Machado AR, Wallbank J. Machining of titanium and its alloys - a review. *Proc Inst Mech Eng B* 1990;204(1):53-60.
- [42] Borradaile JB, Jeal RH. Mechanical properties of titanium alloys. Warrendale: Metallurgical society of AIME, 1980. p.1-3.
- [43] 金重勳, 工程材料, 復文出版社, 1996, p. 389.
- [44] Leyens C, Peters M. Titanium and Titanium Alloys: Fundamentals and Applications. John Wiley & Son Inc, 2003.
- [45] Murray JL. Phase Diagrams of Binary Titanium Alloys. ASM International. Metal Park:OH, 1987. p.68-340.
- [46] Margolin H, Rozenberg L. Titanium '80 Science and Technology. Proceeding of the 4th International Conference on Titanium. 1980.
- [47] Lee CM, Ju CP, Chern Lin JH. Structure-property relationship of cast Ti-Nb alloys. *J Oral Rehabil* 2002;29:314-322.
- [48] Hall GS, Seagle SR, Bomberger HB. Improvement in High Temperature Tensile and Creep Properties of Titanium Alloy. *Titan Sci and Tec* 1973;4:2141-2150.
- [49] Bania PJ, Hall JA. Titanium Science and Technology. Deutsche Gesellschaft fur Metallkunde. Oberursel. Germany, 1985.
- [50] Louzguine DV, Kato H, Inoue A. High strength and ductile binary Ti-Fe composite alloy. *J Alloy Comp* 2004;384(1-2):L1-L3.
- [51] Louzguine DV, Kato H, Inoue A. High-strength hypereutectic Ti-Fe-Co bulk alloy with good ductility. *Philos mag lett* 2004;84(6):359-364.
- [52] Louzguine DV, Louzguina LV, Kato H. Investigation of Ti-Fe-Co bulk alloys with high strength and enhanced ductility. *Acta Mater* 2005;53:2009-2017.
- [53] 機械工程手冊編輯委員會, 金屬材料, 五南圖書出版, 台北, 台灣p.647.
- [54] Long M, Rack HJ. Titanium alloys in total joint replacement-a materials science perspective. *Biomaterials* 1998;19:1621-1639.
- [55] Taylor JC, Hondrum SO, Prasad A, Brodersen CA. Effects of joint configuration for the arc welding of cast Ti-6Al-4V alloy rods in argon. *J Prosthet Dent* 1998;79(3):291-297.
- [56] Berg E, Wagner WC, Davik G., Dootz ER. Mechanical properties of laser-welded cast and wrought titanium. *J Prosthet Dent* 1995;74(3):250-257.
- [57] Yoshinari M, Ozeki K, Sumii T. Properties of hydroxyapatite-coated Ti-6Al-4V alloy produced by the ion-plating method. *Bull Tokyo Dent Coll* 1991;32:147 – 156.
- [58] Nakajima H, Okabe T. Titanium in dentistry: development and research in the USA. *Dent Mater J* 1996;15:77-90.
- [59] Niinomi M. Mechanical properties of biomedical titanium alloys. *Mater Sci Eng A* 1998;243:231-236.
- [60] Wang K. The use of titanium for medical applications in the USA. *Mater Sci Engng A* 1996;213:134-137.
- [61] Steinemann SG, Perren SM. Titanium alloys as metallic biomaterials. in: Lutjering G, Zwicker U, Bunk W, editors. Titanium Science and Technology DGM 1985. p.1327-1334.
- [62] Laing PG, Ferguson Jr AB, Hodge ES. Tissue reaction in rabbit muscle exposed to metallic implants. *J Biomed Mater Res* 1967;1:135-149.
- [63] Buly RL, Huo MH, Salvati E. Titanium wear debris in failed cemented total hip arthroplasty. An analysis of 71 cases. *J Arthroplasty* 1992;7-3:315-323.
- [64] Zwicker R, Buehler K, Mueller R. Mechanical properties and tissue reactions of a titanium alloy for implant material. Titanium '80: Science and technology In: Kimura H, Izumi O, editors. Proceedings of the Fourth International Conference on Titanium. Kyoto. Japan. The Met. Soc. AIME. 1980. p.505-514.
- [65] Semlitsch M, Staub F, Weber H. Titanium-aluminium-niobium alloy, development for biocompatible, high strength surgical implants. *Biomed Tech* 1985;30:334-339.
- [66] Okazaki Y, Ito Y, Kyo K, Tateishi T. Corrosion resistance and corrosion fatigue strength of new titanium alloys for medical implants without V and Al. *Mat Sci Engng A* 1996;213:138-147.
- [67] Song Y, Xu DS, Yang R, Li D, Wu WT, Guo ZX. Theoretical study of the effects of alloying elements on the strength and modulus of α -type bio-titanium alloys. *Mater Sci Eng A* 1999;260:269-274.
- [68] Gibeling JC, Shelton DR, Malik CL. Application of fracture mechanics to the study of crack propagation in bone. In: Rack H, Lesuer D, Taleff E, editors. Edited Structural Biomaterials for the 21st Century, TMS. Warrendale. Pennsylvania:U.S.A., 2001. p. 239-254.
- [69] Wang K, Gustavson L, Dumbleton J. Low modulus, high strength, biocompatible titanium alloy for medical implants. In: Titanium '92 Science and Technology. Warrendale: The Minerals, Metals & Materials Society. 1993;2697-2704.
- [70] Wang KK, Gustavson LJ, Dumbleton JH. Microstructure and properties of a new beta titanium alloy, Ti-12Mo-6Zr-2Fe developed for surgical implants. In: Brown SA, Lemons JE, editors. Medical applications of titanium and its alloys: the material and biological issues. ASTM STP vol. 1272. ASTM. West Conshohocken, 1996. p. 49-60.
- [71] Robare EW, Bugle CM, Davidson JA, Daigle KP. Development of processing methods for Ti-13Nb-13Zr. In: Weiss I, Srinivasan R, Bania PJ, Eylon D, Semiatin SL, editors. Advances in the Technology of Titanium Alloy Processing. The Minerals. Metals and Materials Society, 1997. p.283-291.
- [72] Davidson JA, Mishra AK, Kovacs P, Poggie RA. New surface-hardened, low-modulus, corrosion-resistant Ti-13Nb-13Zr alloy for total hip

arthroplasty. *Biomed Mater Eng* 1994;4(3):231-243.

[73] Okazaki Y, Rao S, Ito Y, Tateishi T. Corrosion resistance, mechanical properties, corrosion fatigue strength and cytocompatibility of new Ti alloys without Al and V. 1998;19(13):1197-1215.

[74] Ito A, Okazaki Y, Tateishi T, Ito Y. In vitro biocompatibility, mechanical properties, and corrosion resistance of Ti-Zr-Nb-Ta-Pd and Ti-Sn-Nb-Ta-Pd alloys. *J Biomed Mater Res* 1995;29(7):893-899.

[75] Niinomi M. Fatigue performance and cyto-toxicity of low rigidity titanium alloy, Ti-29Nb-13Ta-4.6Zr. *Biomaterials* 2003;24(16):2673-2683.

[76] Lavos-Valereto C, Wolyneć S, Deboni MCZ, König Jr B. In vitro and in vivo biocompatibility testing of Ti-6Al-7Nb alloy with and without plasma-sprayed. *J Biomed Mater Res* 2001;58(6): 727-733.

[77] Been J, Faller K. Using Ti-5111 for marine fastener applications. *J O M* 1999;51:21-24.

[78] Gorynin IV. Titanium alloys for marine application. *Mater Sci Eng A* 1999;263:112-116.

[79] Kim SW, Oh S, You CK, Ahn MW, Kim KH, Kang IK, Lee JH, Kim S. Preliminary radiological in vivo study of calcium metaphosphate coated Ti-alloy implants. *Key Eng Mater* 2004;254-256:881-886.

[80] Ratner BD. A perspective on titanium biocompatibility. In: Brunette DM, Tengvall P, Textor M, Thomsen P, Editors, *Titanium in medicine*. Springer-Verlag. Berlin. Heidelberg, 2001. p.1-12.

[81] Shira C, Froes FH. Titanium golf clubs. *MRS. Bulletin*. 1998;23(3):42-46.

[82] Sjogren G, Andersson M, Bergman M. Laser welding of titanium in dentistry. *Acta Odontol Scand* 1988;46:247-253.

[83] Berg E, Davik G, Hegdahl T, Gjerdet NR. Hardness, strength, and ductility of prefabricated titanium rods used in the manufacture of spark erosion crowns. *J Prosthet Dent* 1996;75:419-425.

[84] 金聖泰, 小田豐, 住井俊夫, 齒科鑄造評價研究, 齒科學報, 1994;94:845-857.

[85] Sunnerkrantz PA, Syverud M, Hero H. Effect of casting atmosphere on the quality of Ti-crowns. *Scand J Dent Res* 1990;98:268-272.

[86] Zinelis S. Effect of pressure of helium, argon, krypton, and xenon on the porosity, microstructure, and mechanical properties of commercially pure titanium castings. *J Prosthet Dent* 2000;84(5):575-582.

[87] Miyakawa O, Watanabe K, Okawa S, Nakano S, Kobayashi M, Shiokawa N. Layered structure of cast titanium surface. *Dent Mater J* 1989;8(2):175-185.

[88] Takahashi J, Kimura H, Lautenschlager EP, Chern Lin JH, Moser JB, Greener EH. Casting pure titanium into commercial phosphate-bonded SiO₂ investment molds. *J Dent Res* 1990;69:1800-1805.

[89] Oda Y, Kudoh Y, Kawada E, Yoshinari M, Hasegawa K. Surface reaction between titanium castings and investments. *Bull Tokyo Dent Coll* 1996;37(3):129-136.

[90] Wang RR, Welsch GE, Castro-Cedeno M. Interfacial reactions of cast titanium with mold materials. *Int J Prosthodont* 1998;11(1):33-43.

[91] Ida K, Togaya T, Tsutsumi S, Takeuchi M. Effect of magnesia investments in the dental casting of pure titanium or titanium alloys. *Dent Mater J* 1982;1(1):8-21.

[92] 佟天夫, 熔模鑄造工藝, 機械工業出版社, 1991, p. 335-42.

[93] Molchanova EK. Phase Diagrams of Titanium Alloys. Israel Program for Scientific Translations. Jerusalem, 1965. p.154.

[94] Kuroda D, Niinomi M, Morinaga M, Kato Y, Yashiro T. Design and mechanical properties of new type titanium alloys for implant materials. *Mat Sci Eng A* 1998;243:244-249.

[95] Morinaga M, Yukawa N, Maya T. Theoretical design of titanium alloys. In: Lacombe P, editors. *Sixth World Conference of Titanium*. France. Societe Francaise de Metallurgie. 1988. p.1601-1606.

[96] 劉瑛, 鄧波, 應用d 電子合金設計理論優化GH907 合金組織及持久性能, 材料工程, 1997;7:23-29.

[97] Mackenzie JK, Bowles JS. The crystallography of martensite transformations. *Acta Metall* 1954;2:138.

[98] Ankem S, Seagle SR. Heat treatment of Metastable Beta Titanium Alloys. Beta Titanium Alloys in the 1980 ' s. in: Boyer RR, Rosenberg HW, editors. *The Metallurgical society of AIME*. 1984.

[99] Mantani Y, Tajima M. Phase transformation of quenched " martensite by aging in Ti-Nb alloys. *Mater Sci Eng A* 2006;438-440:315-319.

[100] Kobayashi S, Nakai K, Ohmori Y. Analysis of phase transformation in a Ti-10 mass% Zr alloy by hot stage optical microscopy. *Mater Trans* 2001;42(11):2398-2405.

[101] Ohmori Y, Ogo T, Nakai K, Kobayashi S. Effects of -phase on to , " transformations in a metastable titanium alloy. *Mater Sci Eng A* 2001;312:182-188.

[102] Beneteau A, Weisbeckera P, Geandierb G, Aeby-Gautiera E, Appolairea B. Austenitization and precipitate dissolution in high nitrogen steels: an in situ high temperature X-ray synchrotron diffraction analysis using the Rietveld method. *Mater Sci Eng A* 2005;393(1-2):63-70.

[103] Bowen AW. Omega Phase Formation in Metastable Beta-Titanium Alloys. *Beta Titanium Alloys in the 1980's* 1983;2:85-103.

[104] Yamada K, Ogawa A, Ouchi C, Eylon D. Effect of Al on omega phase transformation behavior in Ti-8 V-5 Fe-(1-3) Al alloy. *Mater Trans* 1996;37(4):855-859.

[105] Sikka SK, Vohra YK, Chidambaram R. Omega phase in materials. *Prog Mater Sci* 1982;27:245-310.

[106] Ahmed TA, Long M, Silverstri J, Ruiz C, Rack HJ. A new low modulus biocompatible titanium alloy. *Titanium 95': Sci. Technol*, 1996.

p.1760-1767.

- [107] 李夫舍茨, 金屬與合金的物理性能, 北京:冶金工業出版社, 1959.
- [108] Saito T, Furuta T, Hwang JH, Kuramoto S, Nishino K. Multifunctional Alloys Obtained via a Dislocation-Free Plastic Deformation Mechanism. *Science* 2004;300:464-467.
- [109] Brown ARG, Clark D, Eastabrook J. The Titanium-Niobium System. *Nature* 1964;201:914-915.
- [110] Song Y, Yang R, Li D, Hu Z, Guo Z. Calculation of bulk modulus of titanium alloys by first principles electronic structure theory. *J Computer-Aided Materials Design* 1999;6:355-362.
- [111] Silver FH. *Biomaterials, Medical Devices and Tissue Engineering: An Integrated Approach*. Boston: Chapman & Hall Press:London, 1994. p.15.
- [112] Steinemann SG. Surgical implant and alloy for use in making an implant. US Patent No. 4040129. 1977.
- [113] Kawhara K. Cytotoxicity of implantable metals and alloys. *Bull Jpn Inst Met* 1992;31:1033-1039.
- [114] 岡崎義光, 生体材料??????合金開?, 輕金屬, 1999;49(12):613-620.
- [115] 桜井 弘, 金屬?人体???必要?, 講談社?一????, 1996.
- [116] 寺岡久之, 森井??, 小林 純, ?養?食糧, 34:221, 1981.
- [117] 陳威凱, 牙科用鈦-鋁合金之微結構及性質研究, 大葉大學, 2007.
- [118] 姜宗佑, 生醫用鈦-鋁二元合金之結構及性質探討, 大葉大學, 2007.
- [119] Vander Voort G F. *Metallography principles and practice*. McGraw-Hill: U.S.A. 1984. p.449.
- [120] Hilliard JE. Estimating grain size by the intercept method. *Met Prog* 1964;84:99-102.
- [121] Guha A. *Metals handbook*. 9th ed. v8. In: Boy HE, Gall TL, editors. American Society for Metals Metals Park.1985. p.133-136.
- [122] Ho WF, Ju CP, Chern Lin JH. Structure and properties of cast binary Ti-Mo alloys. *Biomaterials* 1999;20:2115-2122.
- [123] Ohkubo C, Watanabe I, Ford JP, Nakajima H, Hosoi T, Okabe T. The machinability of cast titanium and Ti-6Al-4V alloy. *Biomaterials* 2000;21(4):421-428.
- [124] Takahashi M, Kikuchi M, Okuno O. Mechanical properties and grindability of experimental Ti-Au alloys. *Dent Mater J* 2004;23(2):203-210.
- [125] Ohkubo C, Hosoi T, Ford JP, Watanabe I. Effect of surface reaction layer on grindability of cast titanium alloys. *Dent Mater* 2006;22(3):268-274.
- [126] Kikuchi M, Takahashi M, Sato H, Okuno O, Nunn ME, Okabe T. Grindability of cast Ti-Hf alloys. *J Biomed Mater Res B Appl Biomater* 2006;77(1):34-38.
- [127] Margolin H, Nielsen JP. Titanium Metallurgy. in: *Modern Materials. Advances in Development and Application*. In: Hausner HH, editors. Vol 2, New York:Academic Press, 1960. p.225-325.
- [128] Collings EW. *Materials Properties Handbook: Titanium Alloys*. In: Boyer R, Welsch G, Collings EW, editors. ASM International. Materials Park:OH, 1994. p.1053.
- [129] Kobayashi E, Matsumoto S, Doi H, Yoneyama T, Hamanaka H. Mechanical properties of the binary titanium-zirconium alloys and their potential for biomedical materials. *J Biomed Mater Res* 1995;29:943-950.
- [130] Takahashi M, Kikuchi M, Takada Y. Grindability and microstructures of experimental Ti-Zr alloys. *J Dent Mater* 2006;25(5):327.
- [131] Bagariaskii IA, Nosova GI, Tagunova TV. Factors in the formation of metastable phase in titanium-base alloys. *Sov Phys Dokl (Engl Transl)* 1959;30:1014-1018.
- [132] Combe EC. *Notes on dental materials*, Churchill Livingstone. New York, 1977. p.64.
- [133] Davis R, Flower HM, West DRF. Martensitic transformations in Ti-Mo alloys. *J mater sci* 2004;14(3):712-722.
- [134] Williams JC. *Titanium Science and Technology; Proceeding, Metallurgical Society of AIME*, Plenum Press:New York, 1973. p.1433.
- [135] 簡仁德, 楊子毅, 張柳春, 材料科學與工程, 學銘圖書有限公司, 1996, p. 255-260.
- [136] Bobynd JD, Mortimer ES, Glassman AH, Engh CA, Miller J, Brooks C. Producing and avoiding stress shielding: laboratory and clinical observation of noncemented total hip arthroplasty. *Clin Orthop* 1992;274:79-96.
- [137] Ammen CW. *The Metalcaster 's Bible*. McGraw Hill PA U.S.A. 1980.
- [138] Kikuchi M, Takahashi M, Okabe T, Okuno O. Grindability of dental cast Ti-Ag and Ti-Cu alloys. *Dent Mater J* 2003;22(2):191-205.
- [139] Takeyama H, Murata R. Temperature dependence of tool wear. *J Jpn Soc Preci Eng* 1961;27(1):33-38. (in Japanese) [140] Narutaki N, Murakoshi A. Study on machining of titanium alloys. *Annals CIRP* 1983;32:1:65-69.
- [141] Chandler H.E. *Machining of reactive metals*. *Metals Handbook 9th ed., v16 Machining*. ASM Int. Metals Park: OH 1989. p. 844-846.
- [142] Kikuchi M, Takahashi M, Okuno O. Mechanical properties and grindability of dental cast Ti-Nb alloys. *Dent Mater J* 2003;22(3):328-42.
- [143] Porter LF, Rosenthal PC. Factors affecting fluidity of cast irons. *Trans AFS* 1952;60:725-739.
- [144] Cheng WW, Ju CP, Chern Lin JH. Structure castability and mechanical properties of commercially pure and alloyed titanium cast in graphite mould. *J Oral Rehabil* 2003;30:1-13.
- [145] Koike M, Itoh M, Okuno O, Kimura K, Takeda O, Okabe TH, Okabe T. Evaluation of Ti-Cr-Cu alloys for dental applications. *J Mater Eng Perform* 2005;14(6):778-783.

- [146] William DC. Materials science and engineering: an introduction. John Wiley & Sons New York, 2003.
- [147] Silcock JM. An x-ray examination of the β phase in TiV, TiMo and TiCr alloys. *Acta Metall* 1958;6:481-493.
- [148] Pack HJ, Kalish D, Fike KD. Stability of as-quenched beta- titanium alloys. *Mater Sci Eng* 1970;6:181-198.
- [149] Ohmori Y, Natsui H, Nakai K, Ohtsubo H. Effects of β phase formation on decomposition of α / β duplex phase structure in a metastable Ti alloy. *Mater Trans JIM* 1998;39(1):40-48.
- [150] Ageev NV, Karpinskii OG, Petrova LA. Stability of the β -solid solution of titanium-chromium alloys. *Zh Neorg Khim* 1976;6. (in Russian)
- [151] Saha RJ, Handy TK, Misra RDK, Jacob KT. On the evaluation of stability of rare earth oxides as face coats for investment casting of titanium. *Metall Trans B* 1990;21(3):559-566.
- [152] Frueh C, Poirier DR, Maguire MC. The effect of silica-containing binders on the titanium/face coat reaction. *Metall Mater Trans B* 1997;28:919-926.
- [153] Suzuki K, Nishikawa K, Watakabe S. Stability of yttria for titanium alloy precision casting mold. *Mater Trans JIM* 1997;38(1):54-62.
- [154] Saha RL, Misra RDK. Formation of low-melting eutectic at the metal-mould interface during titanium casting in zircon sand moulds. *J Mater Sci Lett* 1991;10:1318-1319.
- [155] Williams JC, Hickman BS, Marcus HK. The effect of omega phase on the mechanical properties of titanium alloys. *Metall Trans* 1971;2:1913-1919.
- [156] Kikuchi M, Takada Y, Kiyosue S, Yoda M, Woldu M, Cai Z, Okuno O, Okabe T. Mechanical properties and microstructures of cast Ti-Cu alloys. *Dent Mater* 2003;19:174-181.
- [157] William DC. Materials science and engineering: an integrated approach. John Wiley & Sons, New York, 2003. p. 255-256.
- [158] Lammie GA, Laird WRE. Osborne & Lammie 's partial dentures. London: Blackwell Scientific. 5th ed. 1986. p. 190-192.
- [159] Kikuchi M, Takada Y, Kiyosue S, Yoda M, Woldu M, Cai Z, Okuno O, Okabe T. Grindability of cast Ti-Cu alloys. *Dent Mater* 2003;19(5):375-381.