

牙科用鈦-鋯合金之微結構及性質研究

陳威凱、何文福；許學全

E-mail: 9608325@mail.dyu.edu.tw

摘要

本實驗目的針對一系列Ti-Zr合金，添加四種比例Zr元素於商業用純鈦(c.p. Ti)金屬中，探討Ti-Zr二元合金之結構、機械性質和研削性研究，期開發可應用於牙科鈦合金。並利用SEM之能量分散式元素分析儀(EDS)觀察彎曲測試後合金之金屬基材與陶瓷間鍵結界面，並且分析Ti-Zr合金與c.p. Ti間之熱膨脹係數。實驗結果顯示，所有Ti-Zr合金繞射峰皆符合Ti，並未出現相繞射峰。Ti-Zr合金系統的微硬度值，會隨著Zr元素的添加而增加，微硬度值範圍為266 HV (TZ1) 和350 HV (TZ4)之間。隨著Zr元素的添加，其彎曲強度、微硬度和彈性回復角皆呈現升高的趨勢，反觀彈性模數呈現降低趨勢，並且以TZ4的彈性回復角與c.p. Ti比較，可提高550%。每項金屬於研削性測試皆有主要的研削條件，以TZ4合金與c.p. Ti的低轉速條件比較，在研削量與研削比皆有提高。在500 m/min時，TZ4合金研削量是c.p. Ti的1.8倍，TZ4合金的研削比是c.p. Ti的1.6倍。由於TZ4合金有良好的機械性質、彈性回復能力及低轉速改進的研削性，故建議可將TZ4合金作為牙科加工性合金的潛力。所有Ti-Zr合金的主要鍵結強度範圍為15.3 MPa (TZ4)和25.1 MPa (TZ1)之間，以TZ1合金鍵結強度高於c.p. Ti，並為Ti-Zr二元合金系統最高鍵結強度。並且僅有TZ1合金鍵結強度高於三點彎曲測試的ISO 9693規範(25 MPa)。另一方面，觀察TZ3和TZ4合金經由燒結溫度並降溫的破斷試片表面。TZ4合金產生最大的彎曲現象，TZ1與c.p. Ti兩者無彎曲現象。而產生彎曲原因可能是合金與陶瓷經燒瓷後，兩者間熱膨脹不協調產生殘餘應力造成。所有Ti-Zr二元合金的熱膨脹係數的範圍為 $9.37 \times 10^{-6}/^{\circ}\text{C}$ (TZ4) 和 $9.88 \times 10^{-6}/^{\circ}\text{C}$ (TZ1)之間，皆低於c.p. Ti($10.12 \times 10^{-6}/^{\circ}\text{C}$)。彎曲的產生傾向於隨著Zr元素的添加，合金和陶瓷間的熱膨脹係數增大而變化。藉此以TZ1合金與Duceratin瓷粉間的熱膨脹係數數值的差異且低於其他Ti-Zr合金，作為彎曲測試的參考依據。

關鍵詞：鈦金屬；鈦合金；微結構與機械性質；瓷牙燒付；熱膨脹係數；研削性

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.....	ix 圖目錄.....
..... xiii 表目錄.....	xvi 第一章 前言 1.1 導言.....
..... 1 1.2 生醫材料的定義.....	2 1.3 生醫用金屬材料介紹.....
..... 3 1.4 生醫材料用於牙科領域.....	5 1.5 骨科植入材之性質.....
..... 6 1.6 植入材離子釋出的效應.....	7 第二章 鈦及鈦合金簡介 2.1 鈦的資源與應用.....
..... 9 2.2 鈦與鈦合金的基本性質.....	10 2.3 鈦合金之分類.....
..... 10 2.3.1 型鈦合金.....	10 2.3.2 + 型鈦合金.....
..... 11 2.3.3 型鈦合金.....	11 2.4 鈦合金與介金屬化合物.....
..... 14 2.5 氧化物與瓷的黏結.....	14 2.6 膨脹係數不同產生應力.....
..... 15 2.7 金屬強化機構.....	15 2.7.1 細化晶粒強化.....
..... 16 2.7.2 固溶強化.....	16 2.7.3 應變硬化.....
..... 17 2.8 研究目的.....	17 第三章 研究方法 3.1 實驗流程.....
..... 20 3.2 試料準備.....	20 3.2.1 純鈦.....
..... 20 3.2.2 鈦鋯合金.....	20 3.2.3 熔煉.....
..... 22 3.3 微結構分析.....	25 3.3.1 EDS 成分分析.....
..... 25 3.3.2 金相組織觀察.....	25 3.3.3 XRD 相分析.....
..... 25 3.4 機械性質測試.....	26 3.4.1 微硬度分析.....
..... 26 3.4.2 拉伸試驗.....	27 3.4.3 彎曲強度試驗.....
..... 28 3.5 瓷牙燒付.....	30 3.5.1 瓷粉之選用.....
..... 30 3.5.2 試片表面處理.....	30 3.5.3 瓷粉的堆築.....
..... 30 3.5.4 金屬與瓷牙鍵結強度.....	33 3.5.5 破斷面分析.....
..... 33 3.5.6 熱膨脹係數量測.....	34 3.6 研削性測試.....
..... 34 3.6.1 研削性測試試片準備.....	34 3.6.2 研削性測試系統設計並建立.....

..... 34	3.6.3 砂輪的選擇.....	35	3.6.4 研削荷重及砂輪轉速的選擇.....
..... 35	3.6.5 研削性評估方法.....	36	3.6.6 研削量(Grinding rate).....
... 36	3.6.7 研削比(Grinding ratio).....	37	第四章 結果與討論 4.1 微結構分析.....
..... 38	4.1.1 EDS 成分分析.....	38	4.1.2 XRD 繞射分析.....
..... 38	4.1.3 金相組織觀察.....	40	4.2 機械性質測試.....
..... 41	4.2.1 微硬度測試.....	41	4.2.2 拉伸試驗.....
..... 43	4.2.3 三點彎曲試驗.....	45	4.3 瓷牙燒付.....
..... 49	4.3.1 燒瓷後之試片觀察.....	49	4.3.2 鍵結強度測試.....
... 50	4.3.3 金屬-陶瓷破斷面觀察分析.....	52	4.3.4 金屬及陶瓷熱膨脹係數量測.....
4.4	研削性測試.....	70	4.4.1 計算c.p. Ti 與Ti-Zr 合金試片之密度.....
研削量及研削比分析.....	71	4.4.3 利用SEM 觀察研削切屑.....	73
金屬表面觀察.....	80	第五章 結論.....	84
.....	86	參考文獻.....	

參考文獻

- [1] Narushima T, " Titanium and its alloys as biomaterials, " J Jpn Inst Met, 55(11):561-565, 2005.
- [2] 鍾國雄, 牙科材料學, 合記圖書出版社, 民國82年。
- [3] Helmus MN and Tweden K, Materials selection, Encyclopedic Handbook of Biomaterials and Bioengineering. Part A: Materials, 1(1):27-59, 1995.
- [4] Hastings GW, " Biomedical engineering and materials for orthopaedic implants, " Journal of Physics E: Scientific Instruments, 13(6):599-607, 1980.
- [5] Kononen M and Kivilahti J, " Fusing of dental ceramics to titanium, " J Dent Res, 80(3):848-854, 2001.
- [6] Yilmaz H and Dincer C, " Comparison of the bond compatibility of titanium and an NiCr alloy to dental porcelain, " J Dent Rec, 27(3):215-222, 1999.
- [7] Akagi K, Okamoto Y, Matsuura T and Horibe T, " Properties of test metal ceramic titanium alloys, " J Prosthet Dent, 68(3):462-467, 1992.
- [8] Kimura H, Horng CJ, Okazaki M and Takahashi J, " Oxidation effects on porcelain-titanium interface reactions and bond strength, " J Dent Mater, 9(1):91-99, 1990.
- [9] Geurtsen W, " Biocompatibility of dental casting alloys, " Crit Rev Oral Biol Med, 13(1):71-84, 2002.
- [10] Giordano RA, " Dental ceramic restorative systems, " Compend Contin Educ Dent, 17(8):779-86, 1996.
- [11] Zitter H, " Corrosion behavior and biocompatibility of titanium alloys for implants, " Werkstoffe and Korrosion, 39(12): 574-582, 1988.
- [12] Anusavice KJ, " Phillips ' s Science of Dental Materials, " 10th ed., Philadelphia :W.B. Saunders, 1996.
- [13] Ida K, Togaya T, Tsutsumi S and Takeuchi M, " Effect of magnesia investments in the dental casting of pure titanium or titanium alloys, " J Dent Mater, 1:8-21, 1982.
- [14] Takahashi J, Kimura H, Lautenschlager EP, Chern JH and Moser JG, " Casting pure titanium into commercial phosphate bonded SiO₂ investment molds, " J Dent Res, 69:1800-1805, 1990.
- [15] Sunnerkrantz PA, Syverud M and Hero H, " Effect of casting atmosphere on the quality of Ti-crowns, " Scand J Dent Res, 98:268-272, 1990.
- [16] Park Y and Mori T, " An assessment of investments for titanium casting, " J Dent Res, 72:681, 1993.
- [17] Pang IC, Gilbert JL, Chai J and Lautenschlager EP, " Bonding characteristics of low-fusing porcelain bonded to pure titanium and palladium-copper alloy, " J Prosthet Dent, 73:17-25, 1995.
- [18] Wang RR, Welsch GE and Monteiro O, " Silicon nitride coating on titanium to enable titanium-ceramic bonding, " J Biomed Mater Res, 46:262-270, 1999.
- [19] Wang RR and Fung K, " Oxidation behavior of surface-modified titanium for titanium-ceramic restoration, " J Prothet Dent, 77:423-434, 1997.
- [20] Kononen M and Kivilahti J, " Bonding of low-fusing dental porcelain to commercially pure titanium, " J Biomed Mater Res, 28:1027-1035, 1994.
- [21] Gilbert JL, Covey DA and Lautenschlager EP, " Bond characteristics of porcelain fused to milled titanium, " J Dent Mater, 10:134-140, 1994.
- [22] Wang RR, Meyers E and Katz JL, " Scanning acoustic microscopy study of titanium - ceramic interface of dental restorations, " J Biomed Mater Res, 42:508-516,1998.
- [23] Smith D, Pilhar R and Murray C, " Preliminary studies of the surface characterization of dental implant materials, " Presented at the 11th Annual Meeting of the Society for Biomaterials. San Diego, 1985.

- [24] Hruska AR and Borelli P, "Quality criteria for pure titanium casting, laboratory soldering, intraoral welding, and a device to aid in making uncontaminated castings," *J Prosthet Dent*, 66:561-565, 1990.
- [25] Taira M and Moser JB, "Studies of Ti alloys for dental castings," *J Dent Mater*, 5:45-50, 1989.
- [26] Miyakawa O, Wantanabe K and Okawa S, "Layered structure of cast titanium surface," *J Dent Mater*, 8:175-185, 1989.
- [27] Miyakawa O, Wantanabe K and Okawa S, "Skin holes of titanium casting," *J Dent Mater*, 12:171-181, 1993.
- [28] King AW, Lautenschlager EP, Chai J and Gilbert J, "A comparison of the hardness of different types of titanium and conventional metal ceramics," *J Prosthet Dent*, 72:314-319, 1994.
- [29] King AW, Chai J and Lautenschlager EP, "The mechanical properties of milled and cast titanium for ceramic veneering," *J Int Prosthodont*, 7:532-537, 1994.
- [30] Wang RR, Welsch GE, Montero O and Brown IG, "Coating On titanium with chromium to enable titanium-porcelain bonding for dental restorations. In: Weiss IK, editor. *Advances in science and technology of titanium alloy processing*, Warrendal, Pennsylvania: The Minerals, Metals & Materials Society, 585-602, 1997.
- [31] Adachi M, Mackert JR, Parry EE and Fairhurst CW, "Oxide adherence and porcelain bonding to titanium and Ti-6Al-4V alloy," *J Dent Res*, 69(6):1230-1235, 1990.
- [32] Oshida Y, Fung LW and Isikbay SC, "Titanium-porcelain system," *Bio-Medical Materials & Engineering*, 7:13-34, 1997.
- [33] Wheeler KR, Karagianes MT and Sump KR, "Porous titanium alloy for Prosthesis attachment," in *Titanium Alloys in Surgical Implants*, STP 796, ASTM, 241-254, 1983.
- [34] Carlsson L, Rostlund T, Albrektsson B, Albrektsson T and Branemark P, "Osseointegration of titanium implants," *Acta Orthop Scand*, 57:285-289, 1986.
- [35] Cook SD, Kay JF, Thomas KA and Jarcho M, "Interface mechanics and histology of titanium and hydroxyapatite-coated titanium for dental implant applications," *Int J Oral Maxillofac Impl*, 2:15-22, 1987.
- [36] Jaffe WL and Scott DF, "Current concepts review: total hip arthroplasty with hydroxyapatite-coated prostheses," *J Bone Joint Surg*, 78(A):1918-1934, 1996.
- [37] Sharkness CM, Acosta SK, Moore Jr. RM, Hamburger S and Gross TP, "Metallic orthopedic implants and their possible association with cancer," *J. Long Term Effects Med. Implants*, 3(3) 237-249, 1993.
- [38] Liao JD, Wang MC and Yu CC, "Wear debris generated from a cup-on-ball hip wear simulator: Their morphologies and compositions," *Biomed. Eng. Appl. Basis Communications*, 11:129-138, 1999.
- [39] H. Kawahara, *J. Jpn. Inst. Met.*, 39(12):1033-1039, 1992.
- [40] Renner AM, "The versatile use of titanium in implant prosthodontics," *Quintessence Dent Technol*, 188-97, 2001.
- [41] Walter M, Reppel PD, Boning K and Freesmeyer WB, "Six-year followup of titanium and high-gold porcelain-fused-to-metal fixed partial dentures," *J Oral Rehabil*, 26:91-96, 1999.
- [42] Lautenschlager EP and Monaghan P, "Titanium and titanium alloys as dental materials," *J Int Dent*, 43:245-53, 1993.
- [43] Long M and Rack HJ, "Titanium alloys in total joint replacement - A materials science perspective," *Biomaterials*, 19(18):1621-1639, 1998.
- [44] Semlitsch M, Staub F and Weber H, *Biomed. Technik*, 30:334-339, 1995.
- [45] Zwicker U and Buhler K, "Titanium, 80, Science and Technology: Proceedings of the Fourth International Conference on Titanium," *Metallurgical Society of AIME*, 505-514, 1980.
- [46] 有賀伸一, 室田景久, 富田泰次, 六本木哲, 肥後矢吉, 大内千秋: *MB Orthop*, 8(10):1-8, 1995.
- [47] 新家光雄: *素形材*, 43:8-14, 2202.
- [48] Weiss I and Semiatin SL, "Thermomechanical processing of beta titanium alloys – an overview," *Mater Sci Engng A*, 243:46-65, 1998.
- [49] Ankem S and Greene CA, "Recent Developments in Microstructure/Property Relationships of Beta Titanium Alloys," *Materials Science and Engineering A263*, 127-131, 1999.
- [50] Wang K, "The use of titanium for medical applications in the USA," *Mater Sci Engng A*, 213:134-137, 1996.
- [51] Niinomi M, "Mechanical properties of biomedical titanium alloys," *Mater Sci Engng A*, 243:231-236, 1998.
- [52] Long M and Rack HJ, "Titanium alloys in total joint replacement-a materials science perspective," *Biomaterials*, 19:1621-1639, 1998.
- [53] Stefansson N, Weiss I, Hutt AJ and Allen PJ, *Titanium '95*, vol. 2 edit by Blenkinsop, P. A., Evans, W. J. and Flower, H. M., 980-987, The Institute of Materials, London, 1996.
- [54] Lin Z and Welsch GE, "Effects of oxygen and heat treatment on mechanical properties of alpha and beta titanium alloys," *Metal Trans A*, 19:527-542, 1998.
- [55] Ritchie D, Schaeffer HA and White D, "The presence of an iron oxide layer at the enamel/steel interface," *One-coat porcelain enamelling*, 599-604, 1983.
- [56] Dehoff PH and Anusavice KJ, "An analytical model to predict the effects of heating rate and applied load on glass transition temperatures of dental porcelain," *J Dent Res*, 65:643-647, 1986.
- [57] Togaya T, Suzuki M, Tsutsumi S and Ida K, "An application of pure titanium to the metal-porcelain system," *J Dent Mater*, 2:210-219,

1983.

[58] 簡仁德、楊子毅、張柳春，材料科學與工程，台北縣學銘圖書有限公司，第255-260頁，民國96年。

[59] Douglass DL, " The physical metallurgy of zirconium, " *At. Energy Rev.*, 3, 71-237, 1963.

[60] Kobayashi E, Matsumoto S, Doi H, Yoneyama T and Hamanaka H, " Mechanical properties of the binary titanium-zirconium alloys and their potential for biomedical materials, " *Journal of Biomedical Materials Research*, 29:943-950, 1995.

[61] Nakasuji K and Okada M, " New high strength titanium alloy Ti-10%Zr for spectacle frames, " *Materials Science and Engineering A*, 213:162-165, 1996.

[62] JL Murray, 1987.

[63] 何文福，鑄造鈦鋁合金之結構及性質研究，國立成功大學博士論文，1999。

[64] International Organization for Standardization. ISO 9693: 1999(E): Metal-ceramic dental restorative systems. Available at: <http://www.iso.ch/iso/en/prods-services/ISOstore/store.html>.

[65] Ohkubo C, Hosoi T, Ford JP and Watanabe I, " Effect of surface reaction layer on grindability of cast titanium alloys, " *Dental Materials*, 22(3):268-274 2006.

[66] Takahashi M, Kikuchi M and Takada Y, " Grindability and microstructures of experimental Ti-Zr alloys, " *齒科材料器械*, 25(5):327, 2006.

[67] Frueh C, Poirier DR and Maguire MC, " The Effect of Sicilica-Containing Binders on the Titanium/Face Coat Reaction, " *Metallurgical and Materials Transactions B*, 28B:919-926, 1997.

[68] Saha RL and Misra RDK, " Formation of Low-Melting Eutectic at the Metal-Mould Interface During Titanium Casting in Zircon Sand Moulds, " *Journal of Materials Science Letters*, 10:1318-1319, 1991.

[69] Suzuki K, Nishikawa K and Watakabe S, " Stability of Yttria for titanium Alloy Precision Casting Mold, " *Materials Transactions, JIM*, 38(1), 54-62, 1997.

[70] Saha RJ, Handy TK, Misra RDK. and Jacob KT, " On the Evaluation of Stability of Rare Earth Oxides as Face Coats for Investment Casting of Titanium " , *Metallurgical Transactions B*, 21B, 559-566, 1990.

[71] Takahashi J, Kimura H, Lautenschlager EP, Chern Lin JH, Moser JB and Greener EH, " Casting Pure Titanium into Commercial Phosphate-bonded SiO₂ Investment Molds, " *Journal of Dental Research*, 69(12):1800-1805, 1990.

[72] Ouchi C, Iizumi H and Mitao S, " Effects of Ultra-high Purification and Addition of Interstitial Elements on Properties of Pure Titanium and Titanium Alloy, " *Materials Science and Engineering*, A243, 186-195, 1998.

[73] Wang RR, Welsh GE and Castro-Cedeno M, " Interfacial Reactions of Cast Titanium with Mold Materials, " *The International Journal of prosthodontics*, 11(1):33-43, 1998.

[74] Victorin, L, El-Mahallawy N, Taha MA and Fredriksson H, " Metallographic Studies of Metal/Mould Reaction, " *Cast Metals*, 4(4):182-187, 1992.

[75] Combe EC, " Notes of dental materials " , 6th ed., Churchill Livingstone, Edinburgh, 64, 1992.

[76] Niinomi M., " Mechanical Properties of Biomedical Titanium Alloys, " *Materials Science and Engineering*, A243, 231-236, 1998.

[77] Wang K, " The Use of Titanium for Medical Applications in the U.S.A., " *Materials Science and Engineering*, A213, 134-137, 1996.

[78] Kuroda D, Niinomi M, Morinaga M, Kato Y and Yashiro T, " Design and Mechanical Properties of New Type Titanium Alloys for Implant materials, " *Materials Science and Engineering*, A243:244-249, 1998.

[79] Bobyn, JD, Mortimer ES, Glassman AH, Engh CA, Miller J and Brooks C, " Producing and Avoiding Stress Shielding: Laboratory and Clinical Observation of Noncemented Total Hip Arthroplasty, " *Clinical Orthop. Relat. Research*, 274:79-96, 1992.

[80] Yoda M, Konno T, Takada Y, Iijima K, Griggs J, Okuno O, Kimura K and Okabe T, " Bond strength of binary titanium alloys to porcelain, " *Biomed*, 22(12):1675-1681, 2001.

[81] Tuccillo JJ and Nielsen JP, " Shear stress measurements at a dental porcelain gold bond interface, " *J Dent Res*, 51:626 – 633, 1972.

[82] Al Hussaini I and Al Wazzan KA, " Effect of surface treatment on bond strength of low-fusing porcelain to commercially pure titanium, " *J Prosthet Dent*, 94(4):350-356, 2005.

[83] Garbelini WJ, Henriques GEP, Troia Jr. M, Mesquita MF and Dezan CC, " Evaluation of low-fusing ceramic system combined with titanium grades II and V by bending test and scanning electron microscopy, " *Journal of Applied Oral*, 11(4):354-360, 2003.

[84] Troia MG Jr, Henriques GE, Nobilo MA and Mesquita MF, " The effect of thermal cycling on the bond strength of low-fusing porcelain to commercially pure titanium and titanium-aluminium-vanadium alloy, " *J Dent Mater* 19(8):790-796, 2003.

[85] Al Hussaini I and Al Wazzan KA, " Effect of surface treatment on bond strength of low-fusing porcelain to commercially pure titanium, " *J Prosthet Dent*, 94(4):350-356, 2005.

[86] Adachi M, Mackert JR, Parry EE and Fairhurst CW, " Oxide Adherence and Porcelain Bonding to Titanium and Ti-6Al-4V Alloy, " *J Dent Res*, 69(6):1230-1235, 1990.

[87] Togaya T, Suzuki M, Tsutsumi S and Ida K, " An application of pure titanium to the metal porcelain system, " *J Dent Mater*, 2(2):210-219, 1983.