Effect of Machining Processes on the Microstructure and Electrochemical Corrosion Property of Bio-Titanium Alloy

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ABSTRACT

This study aimed at the effects of various manufacturing processes, including machining (cutting, milling and grinding), hot rolling and casting on the microstructures both bulk and superficies of the bio- medical grade Ti-6AI-4V ELI alloy. The experimental results indicate that after machining the microstructure of the bulk remains unchanged, while an oxide layer is evident at the surface, next to the outer-most layer, a very fine structure layer can be observed. Regarding the rolling process, at the rolling temperature of 900°C, the specimens show a slightly refined structure, whereas at 1000°C and 1100°C, they show a substantial coarse grain structure. The coarse structure of the 1000°C rolled specimens can be refined substantially by rerolling at temperatures lower than 957°C, which is the $\alpha+\beta\rightarrow\beta$ transformation temperature. Besides, the cast specimens normally exhibit a coarse structure in the bulk, with an α case at the surface. Finally, the corro- sion behaviors of the specimens obtained by various manufacturing processes show no signs of breakdown at potentials as high as 4000mv (SCE) and at relatively low critical anodic current densities, suggesting that these specimens should be far passive in human body en- vironments.

Keywords : Ti-6Al-4V ELI titanium alloy ; Polarization curve ; Corrosion-resistant ; Hank ’ s simulated body fluid ; Hot rolling

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REFERENCES

[1] Park J.B., Biomaterials, An Introduction, Plenum Press,New York, p 202, (1979) [2] Park J.B. and Lakes R.S., Biomaterials: An Introduction , Plenum Press, 2nded., New York, (1992) [3] Sherman W.D., Vanadium Steel Plates and Screws, Surg. Gynecol. Obstet. Vol.14, pp. 629-634. (1912) [4] Willams D.F. and Roaf R., Implants in Surgery, Chap. 1, W. B. Saunders Co., Philadelphia, (1973) [5] 呂厚山主編，人工關節外科學，科學出版社，民國87年 [6] Michaels and Block, Implants in Dentistry, W.B. Saunders Company, (1998) [7] 鍾國雄編著，牙科材料學，合記圖書出版社，民國86年 [8] Browning, Toxicity of Industrial Metal, 2nded., Butterworths , Lodon, (1969) [9] Frakes J.T., Brown S.D. and Kenner G.H., "Delayed Failure and Aging of Porous Alumina in Water and Physiological Msdium" , Am Soc. Bull. Vol.35, pp. 193-197, (1974) [10] Krainess F.E. and Knapp W.J., "Strength of a Dense Alumina Ceramic after Aging in Vitro", J. Biomed. Mater. Res. Vol.12, pp. 241-246, (1978). [11] Rateitschak K.H. and Wolf H.F., Color Atlas of Dental Medicine, Thieme Medical Publishers, pp. 11-24, (1995) [12] M.S. Block, J.N. Kent, and L.S. Guerra, Implants in Dentistry, W.B. Saunders Company.: pp. 45-62, (1997) [13] Park, J.B., Biomaterials, An Introduction. Plenum Press, New York. p 4, (1979) [14] 材料科學技術百科全書，中國大百科全書出版社，民國84年 [15] Ludwigson D.C., "Today’s Prosthetic Metals, are they Satisfactory for Surgical Use", J. Metals, pp. 226-229, (1964) [16] Barods D.I., Stainless Steels in Medical Devices : Handbook of Stainless Steels, Peckner D, and Bernstein I.M. (ed.), pp. 1-10, McGraw-Hill, New York, (1977) [17] Smith G., Cobalt-Nickel Base Alloys Containing Chromium and Molybdenum, U. S. Patent No. 3356542, December 6, (1967) [18] Devine T.M. and Wulff J., "Cast vs. Wrought Cobalt-

Chromium Surgical Implant Alloys", J. Biomed. Mater. Res. Vol.9, pp. 151-167, (1975) [19] Bothe R.T., Beaton L.E. and Davenport H.A., "Reaction of Bone to Multiple Metallic Implants", Surg. Gynecol. Obstet. Vol.71, pp. 598-602, (1940) [20] Leventhal G.S.J., Bone Joint Surg, Vol.33-A(2), p 473, (1951) [21] Beder O.E., Eade G. and Wash S. "An Investigation of Tissue Tolerance to Titanium Metal Implants in Dogs", Surgery, Vol.39, p 470, (1956) [22] 王正一著，醫學工程原理與應用，正中書局，民國85年 [23] 陳建任著，金屬材料再生醫產業的前瞻應用分析，金屬研究發展中 心，民國89年 [24] Sumner D.R. and Galante J.O., "Determinants of Stress Shielding: Designversus Materials Materials versus Interface", Clinical Orthopaedics and Related Research, v274, p202-212. (1992) [25] Engh C.A. and Bobyn J.D., "The Influence of Stem Size and Extent of Porous Coating on Femoral Bone Resorption After Primary Cemetnless Hip Arthroplasty", Clinical Ortho- paedics and Related Research, vol.231, pp. 7-28, (1988) [26] Cheal E., Spector M., and Haves W., "Role of Loads and Prosthesis Material Properties on the Mechanics of the Proximal Femur after Total Hip Arthoplasty". J. Orthop. Res. vol.10, pp. 405-422, (1992) [27] Bobyn J.D., Glassman A.H., Goto H., Krygier J., Miller J. and Brooks C.,“ The Effect of Stem Stiffness on Femoral Bone Resorption after Canineporous-Coated Total Hip Arthroplasty", Clin. Orthop. Relat. Res., vol.261, pp. 196-213, (1990) [28] Bobyn J.D., Mortimer E.S., Glassman A.H., Engh C.A., Miller J., and Brooks C., "Producing and Avoiding Stress Shielding: Laboratory and Clinical Observation of Non- cemented Total Hip Arthroplasty", Clin. Orthop. Relat. Res., ol274, pp. 79-96, (1992) [29] 柯文賢編著，腐蝕與其防治，全華科技圖書，民國87年 [30] Jone D.A., Principles and Prevention of Corrosion 2nd ed.,Pre- ntice Hall International, Inc., pp. 44-171, (1997) [31] 格里弟編著，電極動力學，徐氏基金會出版，民國85年 [32] 賴耿陽著，金屬鈦理論及應用，復漢出版社，民國82年 [33] E.A.鮑利索娃等著，陳石卿譯，鈦合金金相學，新華書店北京發行 所，民國75年 [34] Collings, Physical Metallurgy of Titanium Alloys, Batte- lle Memorial Institute, Columbus, Ohio, U.S.A., (1984) [35] Matthew J.D. Jr. (editor), Titanium Atechnical Guide, ASM International, Metal Park, Oh44073, p 14, (1988) [36] Mattew J. Donachie. Jr., Titanium, 1st ed., ASM Inter- national, Metal ,Park, (1989) [37] Weiss I., Froes F. H., Eylon D. and Welsch G.E., "Modifi- cation of Alpha Morphology in Ti-6AI-4V by Thermo- mechnical Processing", Metallurgical Transactions A, Vol. 17A, pp. 1935-1947, (1986) [38] Tian J., Liu X., Zhu G. and Su H., "Failure Case on Compressor Blades Practical Metallography" , Vol.31 (2) , pp. 98-102, (1994) [39] parr G.R., Gardner L. k., Toth R. W., "Titanium:the Mystery Metal of Implant Dentisty, Dental Materials Aspects", The journal of Prosthetic Dentist [40] Uhling H. H., Corrosion Handbook, John Willey and Song, pp. 23-26, (1951) [41] Kabanov B., Burstein R. and Frumkin A., Discussions Faraday Soc., 1,259, (1947) [42] Frankenthal R. and Electrochem J., Soc.,114,542, (1967) [43] Uhling H H.and Winston R. Revie "Corrosion and Corrosion Control" 3ed , pp. 69-71, (1991) [44] Pourbaix M., "Atlas of Electrochemical Equilibria in Aqueous Solu tions", Pergamon Press, Elmsford,N.Y., (1996) [45] 唐兆榮，鈦在水溶液之鈍化行為，國立成功大學碩士論文 [46] Bewer G. et. al., Metals J., Jan,37, (1982) [47] Uhling H H., "Passivity in Metal and Alloys", Corrsion science, Vol. 19, p 777, (1979) [48] ASTM, F136-98, (2000)