Titanium, Niobium, Zirconium, and Tantalum for Medical and Surgical Applications

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Foreword

This publication, *Titanium, Niobium, Zirconium, and Tantalum for Medical and Surgical Applications* includes peer reviewed papers presented at the ASTM F04 symposium by this same name in November of 2004. The symposium, held in Washington, DC, on November 9–10, 2005, focused on alloys whose primary constituents were one or more of these elements. The information included in the symposium was intended to provide an update on research results obtained since the last ASTM symposium on *Medical Applications of Titanium and Its Alloys* in 1994. The chairs of the symposium were Lyle D. Zardiackas from the University of Mississippi Medical Center, Howard Freese from Allvac, and Matthew Kraay from Case Western Reserve University and are likewise editors of this publication.

In light of the success of the previous symposium in 1994, the scope of this symposium was the presentation of information on the development of new alloys and processing techniques for medical applications, characterization of fundamental materials properties critical to their use for biomedical applications, and evaluation of biological and clinical performance.

The editors would like to express their appreciation to Dorothy Fitzpatrick for her tireless efforts in organizing the symposium, Maria Langiewicz and Don Marlowe for keeping us on track in publishing the papers and this text, and to Kathy Perrett for keeping the three of us organized and on time. Finally we would like to thank all of the ASTM staff for their efforts and the many reviewers of the individual papers for their time and expertise.

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Contents

Overview

ALLOY PROCESSING

Mechancial and Physical Properties of Titanium-12Molybdenum–6Zirconium-2Iron Beta Titanium Alloy—N. G. D. MURRAY, V. R. JABLOKOV, AND H. L. FREESE 3

Creation of Oxidized Zirconium Orthopaedic Implants—G. HUNTER, J. DICKINSON, B. HERB, AND R. GRAHAM 16

Metallurgical Attachment of a Porous Tantalum Foam to a Titanium Substrate for Orthopaedic Applications—D. J. MEDLIN, J. SCRAFTON, AND R. SHETTY 30

Influence of Oxygen Content on the Mechanical Properties of Titanium-35 Niobium-7Zirconium-5Tantalum Beta Titanium Alloy—V. R. JABLOKOV, N. G. D. MURRAY, H. J. RACK, AND H. L. FREESE. 40

Effect of Aging Treatments on the Tensile Properties of Ti-35Nb-7Zr-5Ta-(0.06–0.7) O Alloys—J. I. QAZI, V. TSAKIRIS, B. MARQUARDT, AND H. J. RACK 52

Beta Titanium Alloy Processed for High-Strength Orthopaedic Applications—B. MARQUARDT AND R. SHETTY 71

The Application of Ti-15Mo Beta Titanium Alloy in High-Strength Structural Orthopedic Applications—V. R. JABLOKOV, M. J. NUTT, M. E. RICHELSOPH, AND H. L. FREESE 83

ALLOY PROPERTIES

Mechanical Properties of Cast Ti-Fe-O-N Alloys—M. KOIKE, Q. GUO, M. BREZNER, H. FUJII, AND T. OKABE 103

Effect of Surface Reaction Layer on Three-Point Flexure Bond Strength of Resin Composite to Cast Ti and Ti-6Al-7Nb—I. WATANABE, J. LIU, A. SAIMOTO, J. GRIGGS, AND T. OKABE. 113

Corrosion Resistance, Mechanical Properties, Fatigue Properties, and Tissue Response of Ti-15Zr-4Nb-4Ta Alloy—Y. OKAZAKI AND E. GOTOH 120

Super Elastic Functional β Titanium Alloy with Low Young's Modulus for Biomedical Applications—M. NIINOMI, T. AKAHORI, Y. HATTORI, K. MORIKAW, T. KASUGA, H. FUKUI, A. SUZUKI, K. KYO, AND S. NIWA 135

Comparative Evaluations of Surface Characteristics of cp Titanium, Ti-6Al-4V and Ti-15Mo-2.8Nb-0.2Si (Timetal®21SRx)—D. W. PETERSEN, J. E. LEMONS, AND L. C. LUCAS 151

Comparison of Stress Corrosion Cracking Characteristics of Cp Ti, Ti-6Al-7Nb Ti-6Al-4V, and Ti-15Mo—R. S. WILLIAMSON, M. D. ROACH, AND L. D. ZARDIACKAS 166

Comparison of the Corrosion Fatigue Characteristics of CP Ti-Grade 4, Ti-6Al-4V ELI, Ti-6Al-7Nb, and Ti-15Mo—M. D. ROACH, R. S. WILLIAMSON, AND L. D. ZARDIACKAS 183

Comparison of Stress Corrosion Cracking and Corrosion Fatigue (Anodized and Non-Anodized Grade 4 CP Ti)—L. D. ZARDIACKAS, M. D. ROACH, AND R. S. WILLIAMSON 202

BIOLOGICAL AND CLINICAL EVALUATION

Corrosion of Modular Titanium-Alloy Stems in Cementless Hip Replacement—R. M. URBAN, J. L. GILBERT, AND J. J. JACOBS 215

Influence of Exposure Conditions on Bacterial Adhesion to Zirconium Alloys—E. A. YAMOKOSKI, B. W. BUCZYNSKI, N. STOJILOVIC, J. W. SEABOLT, L. M. BLOE, R. FOSTER, N. ZITO, M. M. KORY, R. P. STEINER, AND R. D. RAMSIER 225

A Methodology to Fabricate Titanium and Stainless Steel Wear Debris for Experimental Use: A Comparison of Size, Shape, and Chemistry—C. M. SPRECHER, J. KUNZE, B. BURIAN, N. VILLINGER, J. J. JACOBS, E. SCHNEIDER, AND M. A. WIMMER 239

Zirconium and Niobium Affect Human Osteoblasts, Fibroblasts and Lymphocytes in a Similar Manner to More Traditional Implant Alloy Metals—N. J. HALLAB, S. ANDERSON, M. CAICEDO, AND J. J. JACOBS 248

Indexes 260

Overview

The use of the reactive metals and their alloys for medical applications has continued to expand. Because of their unique properties, they have found use in a variety of biomedical applications from pace makers to hips. Since the time of the last ASTM symposium on medical applications of titanium, a great deal of research has been focused on the development, processing, properties and clinical performance of devices made from these alloys. As such, the symposium was divided into three sections 1) processing, 2) properties, and 3) biological and clinical performance.

Alloy Processing

The seven papers in this section include information on the formulation and processing of five important, new implantable metallic biomaterials:

- Ti-12Mo-6Zr-2Fe alloy ("TMZF")
- Zr-2.5Nb alloy ("Oxidized Zirconium", "Oxinium")
- Tantalum foam ("Trabecular Metal")
- Ti-35Nb-7Zr-5Ta alloy ("TiOsteum")
- Ti-15Mo alloy

The three titanium materials are metastable beta titanium alloys, manufactured and supplied in the mill annealed condition according to the guidelines of the ASTM F-04.12 "Metallurgical Materials" subcommittee. Five of these papers review the development and the processing of these beta titanium alloys, and the desired performance and properties of the alloy designers. Melting, thermomechanical processing, and finishing of semi-finished mill product forms can be quite different for these alloys than for the four α-phase CP titanium grades (CP-1, -2, -3, and -4), or for the three major α + β titanium alloys (Ti-6Al-4V, Ti-6Al-4V ELI, and Ti-6Al-7Nb). Although not discussed in detail in these papers, manufacturers of medical and surgical devices may experience initial difficulties as they establish cold forming and machining processes for these metastable β titanium alloys when they convert bar, rod, and wire products into finished device components. Several papers covered the influence of processing and chemical composition, particularly oxygen content, on the mechanical properties and microstructure of semi-finished mill products.

Papers by Murray et al. and Jablokov et al. look at chemical composition of ten different titanium grades and alloys. The Murray paper shows that Ti-12Mo-6Zr-2Fe alloy has a higher yield strength and better ductility, according to the published ASTM F 1813 standards, than the three major α + β titanium alloys (F 136, F 1295, and F 1472). Also, the F 1813 standard allows for a higher range of oxygen content, up to 0.28%, than those same three α + β alloys (0.13%, 0.20%, and 0.20% maximum respectively). The beta alloys generally have better ductility than α + β titanium alloys, while the increased interstitial oxygen content and greater alloy content (e.g., 12+6+2 vs. 6+4 and 6+7) generally result in greater yield strength. The Jablokov paper reports on the correlation of yield strength values that have been reported in mill certifications plotted versus oxygen content of many titanium grades and alloys. These surprisingly linear data fall into several clusters of titanium material types: the four CP titanium grades (α), three α + β titanium alloys, and three metastable beta titanium alloys. In the metallurgical literature, beta titanium alloys are characteristically reported to have a much broader range of interstitial oxygen solubility because of the physical metallurgy of the "bcc" crystalline structure. Qazi et al. report on aging studies for Ti-35Nb-7Zr-5Ta alloy with three oxygen contents, with some impressive fractography and electron microscopy analysis. Qazi concludes with the observation that increasing oxygen content in beta titanium alloys suppresses omega (ω) phase and promotes alpha (α) phase formation, finely dispersed, that results in a powerful alloy strengthening effect. Jablokov found that the ductility of Ti-35Nb-7Zr-5Ta is not negatively affected if strength is increased due to increasing oxygen content.

ASTM F 2066 specifies a single microstructure and condition for the Ti-15Mo beta titanium alloy: a wrought alloy with a "fully recrystallized beta phase structure" in the "beta annealed" condition. This unique binary alloy has moderate strength with high ductility when manufactured and supplied in this condition. Marquardt and Shetty, and Jablokov et al. suggest manufacturing and processing techniques that can significantly increase the strength and high cycle fatigue properties of the alloy, without a huge sacrifice in ductility. One processing method is an alpha/beta annealing process, and the other is a cold work reduction operation followed by an aging thermal treatment. The potential benefits from these processing techniques appear to warrant expansion of ASTM F 2066 standard beyond the current beta solution treated and quenched condition. In both studies, a broad range of microstructural conditions and associated mechanical properties are reported for the Ti-15Mo beta titanium alloy by altering rolling and/or drawing operations, and by selecting appropriate heat treatment procedures.

The Zr-2.5Nb alloy requires novel processing techniques by the alloy manufacturer and by the device manufacturer to achieve the uniform, extremely hard, and durable ceramic-like surface that is the key to this improved alloy for hard bearing designs. This is the first and, thus far, the only zirconium-base alloy that has been approved for clinical use for load-bearing articular components in orthopaedic applications. Hunter et al. describe the production processes for the manufacture of zirconium sponge (similar to that for making titanium sponge), alloy ingot, and semi-finished bar products. The special heat treatment process for converting ("transforming") a metal component's surface into a zirconium-oxide ceramic bearing is basically a gas-to-solid state diffusion process. This heat treatment creates a gradient between the zirconium alloy subsurface and the zirconium-oxide ceramic on the surface; a transition from metal to zirconium-oxide ceramic. The result is a stable, durable, low-friction bearing surface that has promising early clinical results for a low-wear couple with a UMHWPE counterface.

Medlin et al. report on the most interesting metallurgical advancement, this based on a porous "CP" tantalum foam product that can be attached to a metallic substrate, usually titanium, to fashion a "bimetallic" composite structure. Two methods are described to make a strong and durable bond between the two metallic components at the interface: a sintered powder process utilizing a sprayed titanium powder, and a diffusion bonding process. Data, sectioned photographs, and photomicrographs are presented that reveal a strong and quite durable bond between the two metal surfaces. Extensive mechanical and chemical testing has been carried out on a tantalum-titanium acetabular cup construct.

Session 2: Alloy Properties

Over the last three decades, the development of titanium and its alloys containing zirconium and niobium as well as the alloyed tantalum (small amounts of nitrogen, oxygen, and iron) for implant applications has continued to increase. Many of these alloys have unique properties such as a lower modulus of elasticity, better fatigue properties in a saline environment and enhanced biocompatibility. However, there continues to be gaps in available information and in our understanding not only of the properties but in the mechanisms of failure of many of these systems. The eight papers in this session covered bulk and surface properties of a number of different titanium alloys, which may be used for implants, as well as an evaluation of the fracture mechanisms.

The first two papers in this section were focused on dental applications of two new Japanese titanium alloys. The first paper by Okabe et al. compares the mechanical properties of castings of titanium with increased amounts of iron and nitrogen as compared to Grade 4 CP titanium. The evaluated mechanical properties, with the exception of elongation, were greater as compared to cast Grade 4 CP titanium. The second paper by Watanabe et al. focused on the effect of α-case on the flexural bond strength of dental composite to CP Ti and Ti-6Al-7Nb. As anticipated, the presence of α-case adversely affected the bond strengths of the composite to the α-case substrate.

The third and fourth papers reported results of the properties of two new titanium alloys. The corrosion, single cycle mechanical properties and fatigue, as well as biocompatibility of β-Ti-15Zr-4Nb-4Ta was the subject of this paper by Okazaki. Results of this study indicated that the alloy had promise for biomedical applications and that further research was justified. The paper by Niinomi et al. on β-Ti-29 Nb-13 Ta-4.6 Zr showed that under the conditions evaluated, this alloy has equal or greater tensile and fatigue properties compared to Ti-6Al-4V ELI. Additionally, the alloy showed super elastic behavior and good biocompatibility.

The last four papers in this session, determined and compared a variety of physical electrochemical and mechanical properties of four currently used titanium alloys with ASTM specifications. The first paper by Petersen et al. compared the substrate microstructure, surface oxide structure and thickness, and corrosion as a function of three surface treatments on CP titanium, Ti-6Al-4V, and Ti-15Mo-2.8Nb-0.2Si. Results showed no effect on substrate microstructure, no significant effect on oxide composition or thickness, and no variability in corrosion resistance as a function of surface treatment. The next two papers (Williamson et al. and Roach et al.) outlined the results of comparative studies on Grade 4 CP Ti, Ti-6Al-7Nb (α/β), Ti-6Al-4V ELI (α/β), and β-Ti-15Mo. The first paper compared the slow strain rate stress corrosion cracking (SCC) of these alloys with and without a notch. Results showed no differences in SCC in distilled water and Ringers solution in either smooth or notched samples and analysis of fracture surfaces showed no SCC morphology. The paper by Roach et al. compared tension-tension corrosion fatigue (CF) of these same alloys under the same conditions as the previous paper. The results of this research showed no effect of testing media on the fatigue of smooth or notched samples but a pronounced effect of the notch with a reduction in fatigue properties for all alloys evaluated. The final paper of the session (Zardiackas et al.) examined the effect of anodization on the CF and SCC of Grade 4 CP titanium with high oxygen content. Results showed no difference in any of the properties evaluated regardless of whether samples were anodized or not anodized.

Session 3: Biological and Clinical Evaluation

This session focused on the biological and clinical evaluation of titanium, niobium, zirconium, and tantalum used in the medical and surgical setting. Over the last two decades, contemporary hip replacements have universally incorporated at least some degree of modularity into their design. This most commonly involves the use of a Morse taper connection of the femoral head to the neck of the femoral stem; however, certain implants allow for independent fitting of the metaphyseal and diaphyseal areas of the femur with the use of connected modular segments. Although the advantages of modularity in hip replacement surgery are many, concern exists regarding the potential for fretting and crevice corrosion at these modular junctions. Paper #1 by Urban et al. reports the author's evaluation of 14 retrieved modular body (SROM) total hip stems removed at the time of revision surgery. Although corrosion of the modular junctions was frequently observed, particulate corrosion products were also found in the periprosthetic tissues. The results of this study demonstrate that in addition to the concerns about structural failure of the corroded modular tapers, particulate products of crevice corrosion in these devices can contribute to third-body articular surface wear and increased particulate burden in the periprosthetic tissues and resultant osteolysis.

Over the past 20 years, biologic fixation of joint replacement implants to the underlying bone has been shown to be a reliable alternative to cemented fixation with polymethylmethacrylate. Durable osseointegration can be achieved via bone ingrowth into porous surfaces consisting of sintered CoCr beads or diffusion bonded titanium fibermetal or via bone ongrowth on to plasma sprayed titanium or appropriate grit-blasted surfaces. Grit-blasted or corundumized surfaces have traditionally utilized bombardment of the substrate with aluminum oxide particles. This process results in these abrasive particles being embedded in the implant substrate with the potential for adverse effects on the implant interface (e.g., osteolysis) and increased third-body articular surface wear. Paper #3 entitled "Contamination-free, Grit blasted Titanium Surface" by Windler, Weber, and Rieder describes a new method of grit-blasting for implant surfaces, which uses iron particles, which unlike alumina, can be removed by chemical dissolution in nitric acid.

The problem of osteolysis has been a major focus of research in the area of joint replacement over the last 15 years. What we have commonly referred to as "cement disease" in the past, has now been clearly shown to in actuality be "particle disease." All particles, whether they are comprised of bone cement, corrosion products, or polyethylene, metal or even ceramic wear debris, can elicit an osteolytic response if present in sufficient numbers and of appropriate morphology (e.g., size, shape, and surface characteristic). The paper by Sprecher et al. describes a practical methodology to generate titanium and stainless steel wear debris particles for use in further study of the process of osteolysis and its treatment. The toxicity of soluble implant debris of zirconium and niobium containing alloys on human periprosthetic cell types was the subject of the research by Hallab et al. Implant alloys containing zirconium and niobium appear to induce a similar cellular response to other traditional alloys such as Ti-6Al-4V (ASTM F-138) and Co-Cr-Mo (ASTM F-75). This is reassuring considering the fact that these newer implant alloys are expected to be used with increased frequency in the future.

It is our hope that the information given in this text will serve as a resource for those working in this field and as reminder of the need to understand these materials, which will undoubtedly serve as the structural backbone for load bearing implants for decades to come. We must always be cognizant that we can never understand too much about the materials and devices that we place in our fellow man.

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