

Cobalt- Base Alloys for Biomedical Applications



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Foreword

This publication, *Cobalt-Base Alloys for Biomedical Applications*, contains 17 papers presented at the symposium of the same name, held on November 3 and 4, 1998, in Norfolk, Virginia. The symposium was sponsored by ASTM Committee F-4 on Medical and Surgical Materials and Devices. John A. Disegi from Synthes (USA), West Chester, Pennsylvania, Richard L. Kennedy from Allvac, Monroe, North Carolina, and Robert Pilliar of the University of Toronto, Toronto, Ontario, Canada presided as symposium chairmen and are editors of the resulting publication.

The scope of the symposium was intended to cover topics that have emerged in recent years such as alloy design, processing variables, corrosion/fretting resistance, abrasion and wear characterization, implant surface modification, biological response, and clinical performance. Although cobalt-base alloys are used extensively for a variety of dental, orthopaedic, neurological, and cardiovascular applications, the major portion of the publication is focused on orthopaedic applications.

The editors would like to express their appreciation for the help provided by two of the session chairmen: John Medley, Ph.D., from the University of Waterloo and Joshua Jacobs, M.D., from Rush Medical College.

We would also like to express our thanks to the ASTM staff that helped make the symposium and publication possible, most notably: D. Fitzpatrick for her help with symposium planning and E. Gambetta for the handling of manuscript submission and review. We are also indebted to the many reviewers for their prompt and careful reviews.

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Overview

Cast cobalt-base alloys were originally proposed for surgical implants over 60 years ago. Improvements in investment casting technology and a better metallurgical understanding of the cast Co-Cr-Mo system provided the technical justification to consider this alloy type for a variety of biomedical applications. Co-26Cr-6Mo investment castings performed reasonably well, but microstructural features and mechanical properties were not ideal for many surgical implant designs. Alloy processing considerations suggested that wrought versions of the cast grade material could provide metallurgical refinements such as better compositional uniformity, a finer grain size, higher tensile strength, increased ductility, and improved fatigue strength. Pioneering development programs were established between specialty alloy producers and implant device manufacturers to develop wrought cobalt-base implant alloys with enhanced metallurgical properties. The alloy development projects were successfully completed, and the first wrought low carbon Co-26Cr-6Mo composition was introduced in the 1980s for total joint prostheses. Wrought alloy versions were eventually used for orthopaedic, dental, neurological, and cardiovascular implant devices. These cobalt-base alloys provided a good combination of mechanical properties, corrosion resistance, and biocompatibility. As implant designs became more complex and the clinical applications were expanded, it became apparent that certain material features should be optimized. Some topics that have emerged in recent years include alloy design, processing variables, corrosion/fretting resistance, abrasion and wear characterization, implant surface modification, biological response, and clinical performance.

The symposium was organized to establish a forum for the presentation of new research and technical information related to the material issues that have been identified. The symposium and publication were divided into four major categories. This included: (1) Alloy Design and Processing (2) Mechanical Properties (3) Wear Characterization, and (4) Clinical Experience.

Alloy Design and Processing

Three papers were presented in this section which covered new alloy design schemes and innovative processing methods. The first paper by Tandon focused on the use of metal injection molding to provide near-net shapes. This work reviewed the processing parameters required to provide consolidated shapes with controlled properties. This work represented the first published study to examine this technology for Co-26Cr-6Mo alloy. Berry et al. provided important manufacturing information related to the production of a wrought high carbon analysis. Thermomechanical processing studies were aimed at optimizing the metallurgical structure in order to provide well-defined mechanical properties and improved wear resistance. The last paper in this section by the group at the National Institute of Standards and Technology investigated the potential of a new amorphous Co-20P alloy for orthopaedic applications. The surface characteristics of the electrodeposited film included excellent corrosion resistance, high hardness, and suggested future possibilities for exploiting this coating technology for cobalt-based implants.

Mechanical Properties

Six papers in this section emphasized the effect of microstructure modifications and processing variables on the mechanical properties of Co-Cr-Mo alloys. The paper by Becker and Bolton investi-

gated the use of powder metallurgy techniques to provide a material with controlled porosity. The presentation examined the influence of powder compaction pressures and sintering atmospheres. The use of this technology was considered ideal for the manufacture of shaped acetabular cups with unique properties. The work by Berlin et al. highlighted the importance of post processing on the mechanical properties of investment cast and wrought alloy versions. Post processing operations such as abrasive blasting had no effect on fatigue, but sintering of porous coatings and laser marking reduced the fatigue strength of investment cast and wrought alloys. The post sinter fatigue strength of low carbon wrought alloy was dramatically reduced and was lower than the hot isostatically pressed ASTM F 75 castings. The third paper in this section by Mishra et al. included extensive metallographic examination, tensile testing, and axial tension-tension fatigue testing to compare investment cast versus high-carbon-wrought compositions with porous coatings. They concluded that the decreased chemical segregation and finer grain size may have been responsible for the improved fatigue strength observed for the porous-coated wrought high-carbon analysis. The presentation by Wang et al. explained the use of a powder metallurgy process to improve the sintering behavior of a Co-Cr alloy. The as-sintered fatigue strength was increased by a factor of X2 because of oxide dispersion strengthening and retarded grain growth during sintering. The thermally stable alloy permits the use of higher forging temperatures and more complex hip stem designs. Lippard and Kennedy reviewed the manufacturing operations for the production of wrought bar product intended for a variety of biomedical applications. Important technical information was documented for primary melting, remelting, hot rolling, annealing, and cold-working processes utilized for commercially available Co-Cr-Mo compositions. The effects of thermomechanical processing on the microstructure and tensile properties was presented for wrought low-carbon and high-carbon ASTM F 1537 material. Rodriguez described fundamental research on the role of face-centered cubic (fcc) to hexagonal close packed (hcp) phase transformation during plastic deformation of Co-Cr-Mo compositions containing low- and high-carbon content. High-carbon content and slow cooling after thermal treatment inhibited the metastable fcc \Rightarrow hcp phase transformation. In contrast, a fast cooling rate after solution annealing and a controlled grain size range promoted phase transformation during deformation. The strain-induced phase transformation predominated when the carbon content was $<0.05\%$, while the size, morphology, and distribution of secondary carbide particles controlled the ductility and fracture behavior at higher carbon levels.

Wear Characterization

The first paper presented in this session by A. Wang et al. investigated the heads of Co-Cr-Mo hip implants using the scanning electron microscope. Surface examination of cast, wrought-low-carbon, and wrought-high-carbon heads before and after hip simulator testing indicated evidence of third-body wear. It was postulated that residual grinding stone material introduced during the implant manufacturing cycle might have been responsible for scratches observed on the articulating surfaces of 15 implants that were examined. The next paper by K. Wang et al. evaluated the wear characteristics of various Co-Cr alloy combinations when tested on a reciprocating wear machine. In this study, self-mated as-cast ASTM F 75 material demonstrated lower wear rates than as-cast plus heat-treated couples. The wear resistance of as-cast hip heads mated with as-cast acetabular cups was also shown to be superior to various combinations of wrought-low-carbon and wrought-high-carbon components. Hip simulator testing also confirmed that self-mated as-cast couples demonstrated wear trends that were comparable if not better than new generation wrought-high-carbon metal-on-metal components. St. John et al. investigated the wear properties of hip heads and cups

fabricated from high and low carbon-wrought Co-26Cr-6Mo alloy. Weight loss data generated in a hip simulator using EDTA stabilized bovine calf serum was statistically equivalent for sets of paired components manufactured from two types of ASTM F 1537 alloys. Killar and associates evaluated the effect of counterpart selection on the wear rate and surface morphology of ultra high molecular weight polyethylene (UHMWPE). Subsurface changes and wear rates of polymer cups in contact with implant quality ASTM F 138 stainless steel were more pronounced than with wrought Co-Cr-Mo alloy counterparts. Pellman presented an overview of the use of physical vapor deposition (PVD) coatings such as titanium nitride (TiN), zirconium nitride (ZrN), and diamond-like carbon (DLC) for medical devices. Wear, corrosion, and biocompatibility information was documented for these PVD films. Orthopaedic and dental applications were highlighted in addition to next generation coatings that are currently under development. Flores-Valdes et al. investigated a quaternary AlSi-FeMn intermetallic coating to improve the corrosion resistance and wear rate of cast Co-Cr-Mo alloy. A series of coatings were formed by reacting elemental powders in the temperature range of 873 to 1123 K. Continuous films deposited on cast F 75 material exhibited high hardness (1000 HV) and good interfacial adhesion.

Clinical Experience

Campbell et al. described the cellular response observed for clinically retrieved metal-on-metal hip components with CoCrMo bearing surfaces. CoCr particles that originated from the wear-in phase were responsible for tissue darkening (metallosis) reactions and included macrophages filled with black metallic particles in the nanometer size range. The wear debris was not associated with granuloma formation or necrotic tissue, but the authors stated that the long-term biological effects of in vivo wear products are not well defined. Hallab et al. analyzed serum protein fractions from patients with cobalt-base total joint arthroplasty components. The distribution of serum Cr and Co concentrations implied that specific metal-protein complexes were formed from the implant degradation products. The physiological and clinical significance of high metal serum content is unknown according to the researchers.

Significance and Future Work

Modified cast Co-Cr-Mo compositions with enhanced thermal properties and expanded capabilities to provide porous coatings with improved fatigue properties represent significant metallurgical advances. The ability to produce complex shapes based on powder metallurgy methods is a major advantage for medical device manufacturers. The influence of grain size, secondary phases, and interstitial levels on mechanical properties has been better defined for wrought low- and high-carbon alloys. Fundamental research into cobalt-based phase transformations has provided the opportunity to improve the thermomechanical processing response. Numerous studies have evaluated the effect of surface modifications that influence wear resistance, and test protocols have been established to characterize tribological properties. Clinical researchers have a better appreciation of the mechanisms responsible for osteolysis and other unfavorable cellular reactions associated with the generation of implant wear debris.

Additional studies are needed to fully understand how alloy-processing variables can be fine tuned to control important material attributes. Future challenges include the need to standardize wear testing methods in order to compare results generated by different research groups. The use of wear-resistant implant coatings must be carefully evaluated from the standpoint of third-body wear phenomena. Sophisticated analytical examination of retrieved implant devices and periopro-

thetic tissue should remain a high priority to expand our understanding of the material and design factors that effect clinical performance.

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