

# Characterization AND Performance OF Calcium Phosphate Coatings FOR Implants

HOROWITZ/PARR, EDITORS



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*Emanuel Horowitz and Jack E. Parr, Editors*

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## Foreword

This publication, *Characterization and Performance of Calcium Phosphate Coatings for Implants*, contains papers presented at the symposium of the same name, held in Miami, FL on 17 Nov. 1992. The symposium was sponsored by ASTM Committee F-4 on Medical and Surgical Materials and Devices. Emanuel Horowitz of Johns Hopkins University in Silver Spring, MD and Jack E. Parr of Zimmer, Inc. in Warsaw, IN presided as symposium chairmen and are editors of the resulting publication.

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# Overview

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The symposium on the Characterization and Performance of Calcium Phosphate Coatings for Implants was sponsored by the ASTM Committee F-4 on Medical and Surgical Materials and Devices in response to the elevated interest and activity dealing with calcium phosphate-type coatings for surgical and dental implants. This publication provides the reader with a useful perspective of the preparation, characterization, and application of calcium phosphate coatings for implants, as seen in the year 1992.

Like the proverbial alchemist in search of the philosopher's stone, modern day biomaterials scientists and engineers have been looking for the ideal material to coat their implants. Such a material would elicit no adverse physiological response and under optimum conditions would contribute to enhanced biocompatibility and long-term reliable performance in service. Calcium phosphate-type materials, including hydroxylapatite, attracted the attention of many people working in biomaterials research and development, industrial production of implants, as well as surgical and oral implantologists. This was because, for example, the chemical composition of hydroxylapatite was similar to that of the inorganic component of natural bone and teeth and the numerous reports of enhanced biocompatibility of medical and dental implants coated with this type of material. Within Committee F-4, there has been a surge of activity within the Ceramics Section leading to the establishment of new task forces that are working on the development and promulgation of standards for calcium phosphate-type ceramics. Some of the limitations of some of these materials are recognized (e.g., brittleness, solubility) but research is underway in many laboratories aimed at improving their mechanical and chemical performance characteristics.

In the opening paper of this publication, T. D. Driskell reviews the early history of calcium phosphate ceramics and reports that the first successful coating using this material occurred in 1972. He briefly describes his efforts and those of others on plasma flame sprayed hydroxylapatite coatings. A. J. Tofe et al. emphasize that the characteristics of the HA powder significantly influence the quality of the final coating. Thus, control of the properties of the starting material and the plasma spray conditions determine the degree of crystallinity and the HA coating implant bond strength. The synthesis, x-ray diffraction, infrared spectroscopy, scanning electron microscopy, particle size distribution, and the surface area analysis of the starting HA powder are discussed. Some important aspects of the quality control and characterization of HA raw materials and coatings are covered in the paper by K. W. Flohr. He points out that large variations in the chemical composition, impurities, and crystallinity of the "as received" HA powders were found. Such differences in HA powders, even in separate lots from the same supplier, give rise to final coatings that have different properties.

Using prepared standard samples of hydroxylapatite containing known amounts of crystalline and amorphous HA, J. S. Flach and co-workers describe a rapid and inexpensive x-ray diffraction method for measuring crystallinity in hydroxylapatite coatings. The x-ray diffraction analyses were conducted at  $2 - \theta$  between 25 and 40°, and from the obtained diffractograms, the area of the crystalline peaks for the standard samples was determined. The ratio of the crystalline area of a given standard to the crystalline area of the 100% crystalline standard  $\times 100$  was used to calculate the relative crystalline peak area. The actual crystallinity of the specimens was determined from a calibration curve plotting crystallinity (%) versus relative crystalline peak area (%). J. P. Legeros et al. report an x-ray diffraction method for calcium-phosphate coatings that does not require standard samples but depends on data from the files of the Joint Committee for Powder Diffraction Standards

(JCPDS). The authors claim that some other diffraction methods do not take into account the effects of line broadening and convolutions on the accuracy of the crystallinity measurement. The method described in the paper is said to be capable of yielding the percentage of each crystalline and non-crystalline phase in the coating. A second paper by the Legeros group authored by R. Z. Legeros et al. discusses the variations in the composition and crystallinity of hydroxylapatite materials. The analytical methods used in this study included x-ray diffraction, infrared spectroscopy, scanning electron microscopy, and chemical analyses. Commercial and non-commercial calcium phosphates and related biological materials were investigated with regard to chemical composition and crystallinity. The dissolution properties of ceramic and non-ceramic calcium phosphates were measured. This study, like the one reported earlier by Flohr, demonstrates that calcium phosphate-type powders and coatings exhibit variability in composition and crystallinity. The authors state that this variability may affect resorption in-vivo.

In their paper on nondestructive characterization of hydroxylapatite coated dental implants by the XRD method, L. Keller and P. Rey-Fessler explain that "perfect" crystalline and "imperfect" crystalline HA are found in the crystalline fraction of plasma-sprayed HA coatings. Thus, different degrees of crystallinity can be obtained depending on the method of analysis used in the determination. Furthermore, the destructive method of preparing specimens for x-ray diffraction analysis may affect the degree of crystallinity and sacrifice other important information. The authors describe the methodology and the modified x-ray diffractometer that was adapted for characterizing plasma-sprayed HA coatings on 3 to 4-mm diameter dental implants.

P. S. Prevey and R. J. Rothwell report a quantitative, nondestructive x-ray diffraction method using an external standard to characterize the crystallinity and weight fraction of the contaminant phases of plasma-sprayed HA coatings. A detailed explanation is given for the theoretical development of the external standard methodology after which the experimental measurement method is described. An assessment of the accuracy and reproducibility of the method is given. The characterization of composite hydroxylapatite coatings for both medical and dental implants is described by V. Sahay et al. A porous metallic coating is first plasma sprayed on to the implant substrate. Then an HA-type coating is plasma sprayed on top of the previously deposited layer to form a strongly interlocked and interdigitated composite structure. The chemical, physical, and mechanical properties of the implant coatings are reported. In-vivo evaluation of the composite porous coating, based on implantation of coated implants in the tibia of dogs is presented in terms of histological findings. The clinical evaluation of composite porous-coated total hip implants is also discussed. M. S. Tung and P. Sung remind us that the bioresponse of implant materials "depends critically upon the properties of the material." In their paper on calcium phosphate-type reference materials, they stress the need for an HA standard reference material to be used in the analysis, characterization, and standardization of hydroxylapatite implant materials. The methods of HA synthesis and preparation of HA are discussed. The results of chemical analysis, x-ray diffraction, infrared spectroscopy, thermal analysis, solubility measurements, and particle size distribution measurements are reported.

In a study of the plasma sprayed induced compositional and phase changes in calcium phosphate ceramic coatings, S. R. Radin and P. Ducheyne report on the in-vitro dissolution rates of these coatings in a calcium- and phosphate-free buffer solution at physiological pH. The authors investigated monophasic calcium-phosphate powders, biophasic powders, and multiphasic commercial plasma-sprayed coatings. Of the materials studied, they claim that hydroxylapatite is the only thermodynamically stable compound at physiological pH. Their data indicate that the material transformations that occur during the plasma spray process leads to increased coating dissolution. Data are provided on the dissolution rates of plasma-sprayed coatings, monophasic and biophasic powders. The paper by K. A. Gross and C. C. Berndt deals with the structural changes of plasma-



sprayed HA coatings subjected to in-vitro testing. HA powder was prepared and then plasma sprayed on to stainless steel substrates. Both as sprayed amorphous and heat-treated crystalline coatings were immersed in Ringer's solution for various period of time. The changes in the different HA coatings during immersion are discussed, and a model is proposed to explain the changes in the microstructure of the coatings. P. Ducheyne and S. R. Radin report the results of their investigation of different single-phase calcium-phosphate ceramics immersed in simulated physiological solution similar in electrolyte composition to human plasma. Hydroxylapatites with different crystallinity and chemical perfection,  $\alpha$ -TCP,  $\beta$ -TCP, and TTCP were used in the study. Calcium and phosphate concentrations in the solutions were measured as a function of immersion time. The authors provide data on the chemical surface transformations that occur in vitro. In the paper on hydroxylapatite coatings, J. F. Kay states that such coatings enhance bone adaptation, eliminate fibrous tissue seams, promote stronger bone implant bonding, decrease healing time, and inhibit corrosion of the metallic substrate. For non-precision implants where ideal bone contact is not attained, the HA coating is claimed to overcome the lack of direct implant-bone contact and foster bony proliferation and osseointegration. Kay asserts that the variable performance of HA coatings in vivo can be traced to the non-uniform properties of different coatings resulting from differences in their methods of preparation. HA coated and uncoated canine orthopedic devices were implanted in dogs for up to 52 weeks and data are reported on the interfacial bone-implant strength. HA-coated metallic implants gave consistently higher values than the non-HA coated implants. Tofe et al. address the nature of dissolution and resorption of dense and microporous hydroxylapatite. Scanning electron microscopy, x-ray diffraction, and infrared spectroscopy were used to characterize commercially available HA. They found, using human fibroblasts, that microporous surfaces facilitate cell-mediated resorption. T. Hanawa et al. provide an interesting perspective of the precipitation of calcium phosphate on calcium-ion-implanted titanium in neutral electrolyte solution similar to that of extracellular fluid. The surface of the calcium-ion-implanted titanium and titanium specimens were characterized before and after immersion in the electrolyte. They found that the precipitation of calcium and phosphate is greatly accelerated on calcium-ion-implanted titanium. A mechanism for this reaction is proposed.

Of special interest to manufacturers of calcium phosphate-type coated implants, medical and oral implantologists, and biomaterials scientists and engineers is the position of the Food and Drug Administration on these types of devices. T. J. Callahan et al. discuss the FDA's guidelines on the characterization of calcium-phosphate coatings on dental and orthopedic implants. The paper provides useful information on FDA submissions on calcium-phosphate coatings for orthopedic and endosseous dental implants. A list of relevant standards, methods and publications (Appendix A), as well as data on some chemical, physical, and mechanical characteristics of the calcium-phosphate powder and coatings (Appendix B) is presented. The last paper of this publication deals with ASTM Standards for bioceramics and information on retrieval and analysis. J. E. Lemons supports the need for the development of standards to compare and evaluate bioactive particulates and coatings and to facilitate the correlation of clinical data. Lemons discusses the early history of calcium-phosphate materials and points out that some of these investigations led to the preparation and promulgation of ASTM F-4 Standards (e.g., Beta-Tricalcium Phosphate for Surgical Implantation, ASTM F 1088). Within ASTM F-4, eight relatively new task forces concerned with calcium-phosphate powders and coatings are actively engaged in developing new standards or revising and updating existing standards. A detailed discussion is provided on device retrieval analyses conducted in the author's laboratory.

One final comment is considered pertinent. It may be unlikely that we will ever discover the ideal calcium phosphate-type ceramic or other implant material. Yet, if the implant material on hand

improves the medical condition and quality of life of the patient, we may have to use it until something better is developed.

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