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Standard Specification for Calcium Phosphate Coatings for Implantable Materials[1]

This standard is issued under the fixed designation F 1609; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This specification covers the material requirements for calcium phosphate coatings for surgical implant applications.

1.2 In particulate and monolithic form, the calcium phosphate materials system has been well-characterized regarding biological

[1] This specification is under the jurisdiction of ASTM Committee F04 on Medical and Surgical Materials and Devices and is the direct responsibility of Subcommittee F04.13 on Ceramic Materials.

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response **(1,2)**[2] and laboratory characterization **(2–4)**. Several publications **(5–10)** have documented the *in vitro* and *in vivo* properties of selected calcium phosphate coating systems.

1.3 This specification includes hydroxylapatite coatings, tricalcium phosphate coatings, or combinations thereof, with or without intentional minor additions (10 % or less, as opposed to trace elements) of other ceramic or metallics,[3] and applied by methods including, but not limited to, the following: (*1*) mechanical capture, (*2*) plasma spray deposition, (*3*) dipping/sintering, (*4*) electrophoretic deposition, (*5*) porcelainizing, and (*6*) sputtering.

1.4 Substrates may include smooth, porous, textured, and other implantable topographical forms.

1.5 This specification excludes organic coatings that may contain calcium and phosphate ionic species.

2. Referenced Documents

2.1 *ASTM Standards:*

C 313 Test Method for Adherence of Porcelain Enamel and Ceramic Coatings to Sheet Metal[4]

C 501 Test Method for Relative Resistance to Wear of Unglazed Ceramic Tile by the Taber Abraser[5]

C 633 Test Method for Adhesion or Cohesive Strength of Flame-Sprayed Coatings[6]

C 674 Test Methods for Flexural Properties of Ceramic Whiteware Materials[5]

C 949 Test Method for Porosity in Vitreous Whitewares by Dye Penetration[5]

[2] The boldface numbers in parentheses refer to the list of references at the end of this specification.

[3] For referenced ASTM standards, visit

[3] The Joint Committee on Powdered Diffraction has established a Powder Diffraction File. The committee operates on an international basis and cooperates closely with the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book Data Commission of ASTM Standards* volume information, refer to the standard's Document Summary page International Union of Crystallinity and ASTM. Hydroxylapatite data can be found on the ASTM website. file card No. 9-432; beta tricalcium phosphate data can be found on file card No. 9-169.

Discontinued 1991—See 1990

[4] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards,* Vol 15.02. volume information, refer to the standard's Document Summary page on the ASTM website.

E 376 Practice for Measuring Coating Thickness by Magnetic-Field or Eddy-Current (Electromagnetic) Test Methods[5]
F 1044 Test Method for Shear Testing of ~~Porous Metal~~ Calcium Phosphate Coatings and Metallic Coatings[6]
F 1088 Specification for Beta-Tricalcium Phosphate for Surgical Implantation[6]
F 1147 Test Method for Tension Testing of ~~Porous Metal~~ Calcium Phosphate Coatings and Metallic Coatings[6]
F ~~1185 Specification~~ 1160 Test Method for Shear and Bending Fatigue Testing of Calcium Phosphate and Metallis Medical and Composite Calcium Phosphate Metallic Coatings[6]
F 1185 Specification for Composition of Ceramic Hydroxylapatite for Surgical Implants[6]
F 1854 Shear and Bending Fatigue Testing of Calcium Phosphate and Metallis Medical and Composite Calcium Phosphate Metallic Coatings[6]
F 1926 Test Method for Evaluation of the Environmental Stability of Calcium Phosphate Coatings[6]
F 2024 Practice for X-Ray Diffraction Determination of Phase Content of Plasma-Sprayed Hydroxylapatite Coatings[6]

2.2 *Pharmacopeia Convention Documents:*[7]

National Formulary XVI, Tribasic Calcium Phosphate

United States Pharmacopeia:

U.S. Pharmacopeia XXI, Chemical Tests CaP (191), Lead <251>, Mercury <261>, Arsenic < 211>, and Heavy Metals <231> Method (1)

2.3 *Other Documents:*

U.S. Geological Survey Method, Cadmium[8]

U.S. Code of Federal Regulations Title 21− (CFR 21), Part 820–Quality System Regulation[9]

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[5] *Annual Book of ASTM Standards*, Vol ~~15.02.~~ 03.03.

[6] *Annual Book of ASTM Standards*, Vol ~~02.05.~~ 13.01.

~~*Annual Book of ASTM Standards*, Vol 03.03.~~

[7] Available from U.S. Pharmacopeia Convention, Inc., 12601 Twinbrook Parkway, Rockville, MD 20852.

~~*Annual Book*~~

[8] Crock, J. G., Felichte, F. E., and Briggs, P. H., "Determination of ~~ASTM~~ Elements in National Bureau of Standards Geological Reference Materials SRM 278 Obsidian and SRM 688 Basalt by Inductively Coupled Argon Plasma—Atomic Emission Spectrometry," *Geostandards Newsletter*, Vol 7, 1983, pp. 335–340~~1~~.

[9] Available from ~~U.S. Pharmacopeia Convention, Inc., 12601 Twinbrook Parkway, Rockville, MD 20852.~~ Standardization Documents Order Desk, Bldg. 4 Section D, 700 Robbins Ave., Philadelphia, PA 19111-5098, Attn: NPODS.

X-Ray Diffraction Analyses[10 3]

3. Terminology

3.1 *Definitions:*

3.1.1 *amorphous calcium phosphate*—a non-crystalline calcium phosphate.

3.1.2 *beta tricalcium phosphate*—a calcium phosphate substance of empirical chemical formula, $Ca_3(PO_4)_2$ (see Specification F 1088).

3.1.23 *calcium phosphate*—any one of a number of inorganic chemical compounds containing calcium and phosphate ions as its principal constituents.

3.1.34 *coating*—a layer of mechanically or chemically attached material covering a substrate material.

3.1.45 *hydroxylapatite*—A—a calcium phosphate crystalline compound of empirical chemical formula, $Ca_5(PO_4)_3OH$ (see Specification F 1185).

4. Chemical or Crystallographic Requirements, or Both

4.1 *Chemical*:

4.1.1 Elemental analysis for calcium and phosphorous and intentional additions (other than trace elements) will be consistent with the expected stoichiometry of the specific calcium phosphate compound(s).

4.1.2 *Trace Element Analysis for Hydroxylapatite and Beta Tricalcium Phosphate*—The concentration of trace elements in the coating shall be limited as follows:

Element	ppm, max
As	3
Cd	5
Hg	5
Pb	30
total heavy metals (as lead)	50

For reference purposes, the *U.S. Pharmacopeia XXI* and *U.S. Geological Survey Method, Cadmium*, shall be used.

4.1.3 The analysis of other trace elements may be required, based on the conditions, apparatus, or environments specific to the coating application technique used.

4.1.4 The analysis of intentional additional elements or compounds such as fluorine, manganese, magnesium, carbonate, etc. and so forth must be specified for calcium phosphate coatings.

4.1.5 Calcium to Phosphorus ratio (Ca/P) shall be performed on both the powder and coating forms using a suitable method.

4.2 *Crystallographic Characterization* :

4.2.1 This involves the degree of crystallinity, determined as a weight percent of the total substance.

4.2.2 This involves the identification of crystalline species

4.2.1 Crystallographic characterization shall be in accordance with Practice F 2024.

4.2.2 Testing shall include quantitative phase analysis and their weight percentages, expressed as a percent of the total substance.

4.2.3 This involves the identification of amorphous calcium phosphate content.

4.2.3 FTIR (Fourier Transform Infrared Spectroscopy) shall be performed to identify functional groups by infrared analysis. groups.

4.3 *Environmental Stability*—The characterization of environmental—Environmental stability testing shall be consistent performed in accordance with prior referenced methods using solutions best representing Test Method F 1926 to access the potential in-service device environments. relative dissolution behavior of the material.

5. Physical Characterization

5.1 *Coverage of Substrate*:

5.1.1 Microscopic examination of the surface will be made at 10× magnification; flaws, "bare" areas, "pinholes," cracking, foreign debris, unmelts, chips, delamination and coating borders, etc. the appearance at the coating/substrate interface, and so forth will be reported for those observed at 10× magnification.

5.1.2 Visible impurities shall be reported if observed at 10× magnification. reported.

5.2 *Thickness*—The thickness will be measured from cross sections and will be reported as the mean and range of thickness. in accordance with Test Method F 1854. If distinct layers are noted, each layer exist, they should be so characterized. reported.

5.2.1 Alternatively, a magnetic field or eddy current technique may be used if it has been shown to be equivalent to Test Method F 1854.

5.3 *Porosity*—The microporosity and macroporosity characterization shall be determined in accordance with Test Method F 1854.

5.4 *Color*—The—A macroscopic examination of color should be performed to guarantee a uniform and consistent appearance, in consideration of the specific process, substrate material and geometry, and coating thickness.

5.5 *Surface Topography*—tThe surface topography shall be measured using equipment designed to determine surface roughness dimensions as microinches or micrometres. roughness. Characterization of the surface topography of the underlying substrate may

be required, if applicable, for the specific coating method. Scanning electron microscopy shall be used to ~~establish~~ provide a visual representation of the coating surface ~~and cross-section morphology.~~ characteristics.

5.6 ~~*Other Characterizations*—Other characterizations may be required or applicable, depending on~~Density—Density of both the ~~end-use application. Standard test methods should~~ powder and coated forms shall be ~~used in all cases, where available, or acceptable alternatives developed. An additional ASTM test that may apply is Test Methods C 674.~~ performed using a suitable method.

6. Mechanical Characterization

6.1 The following mechanical characterizations may be applicable to a coating, depending on the substrate material or geometry, coating thickness or location, ~~and coating methods(s),~~ or ~~some combination thereof.~~ coating method(s). Characterization reports shall contain sufficient information regarding the test techniques, procedures, and standards used and details such as specimen orientation and proportional depth of thickness in order to represent the analysis accurately.

6.1.1 The tensile bond strength of the coating to the substrate shall be ~~measured~~ determined using ~~a non-penetrating adhesive such as FM-1000 Adhesive Film. The measurement technique shall follow the general procedure of~~ Test ~~Methods C 633 and F 1147. The tensile test shall be considered invalid if any portion of the metal substrate is exposed to the surface before testing, allowing direct bonding of the adhesive to the metal.~~

~~6.1.2 Shear~~ Method F 1147.

6.1.2 The shear strength ~~determinations~~ shall be ~~consistent with~~ determined using Test Method ~~F 1044, or a demonstrated equivalent technique, as long as the adhesive is demonstrated to be non-penetrating and the test technique allows for the coating to be placed in a pure shear condition, minimizing "peeling stress" modes.~~ F 1044.

6.1.3 The fatigue strength shall be determined ~~on an applicable full-scale device and as a materials system~~ using ~~appropriate testing methods applicable to the various service conditions.~~

~~6.1.4 Abrasion resistance shall be determined using a comparative model such as~~ Test Method ~~C 501, or a demonstrated equivalent, with two standards of comparison, one more abrasive and one less abrasive. A function-related installation abrasion test, specific to~~ F 1160. Both the ~~device~~ coating/substrate interface, and ~~its associated instrumentation, may additionally~~ the effect on the substrate should be ~~required.~~

~~6.1.5 Other mechanical evaluations~~ evaluated. The effect of ~~calcium phosphate coatings shall be made, depending~~ the coating on ~~service environments, installation techniques, or other load considerations.~~ the resulting fatigue strength of an actual device should also be considered.

7. Test Specimen Fabrication

7.1 All test specimens for coating characterizations shall be prepared from ~~indicative~~ coating lots and samples from the same production feedstock lots and prepared on the same ~~equipment, representative of~~ equipment used to apply the coating ~~as applied~~ to ~~the~~ actual devices.

7.2 For device characterization, all test specimens should be subjected to the same processing and sterilization as the finished device, if applicable.

~~8. Quality Program Requirements~~

~~8.1 The manufacture of~~Contact with Calcium Phosphate Coatings

8.1 In general, extra precautions should be taken when handling calcium phosphate coatings.

8.1.1 Contact with the coatings ~~will conform~~ should be limited to ~~good manufacturing practices (21 CFR 820).~~ soft, biocompatible polymers.

8.1.2 The only liquids to come in contact with the coating shall be distilled water, acetone, and isopropyl alcohol.

8.1.2.1 pH is critical, and should measure 7.0 or higher in any liquid that comes in contact with the coating.

8.1.3 Powder-free latex gloves shall be the only glove material for handling coatings.

9. Quality Program Requirements

9.1 The manufacture of calcium phosphate coatings will conform to the applicable FDA and ISO quality standards.

10. Keywords

910.1 bone implant; calcium phosphate; coating; dental implant materials; hydroxylapatite; mechanical tests; orthopedic medical devices; physical characterizations; tricalcium phosphate

APPENDIX

(Nonmandatory Information)

X1. RATIONALE

X1.1 Ceramic hydroxylapatite and beta-tricalcium phosphate are commercially available in many forms as synthetic bone grafting materials. Specifications F 1088 and F 1185 have been established for these substances as particulates. For most implant materials, the biological performance is critically dependent on the material's properties, including chemical and mechanical properties and physical form. These properties must be well-characterized and consistent in order to achieve reproducible clinical results and reliable biocompatibility. This specification ~~provides~~ shall cover biocompatible grades of calcium phosphate coatings only.

X1.2 Powder X-ray diffraction analysis provides differentiation between crystalline forms of these various calcium phosphate crystalline species, one or more of which will be a major phase in coatings covered by this specification, while others may occur as second or minor phases. It is anticipated that a separate performance standard may be necessary for each separate coating as designated by the major crystalline phase. The physical and mechanical property assessments are not specific to any one type of coating for this reason, but rather they are listed generically as guidelines for analysis. Minor or significant modifications to these procedures may have to be made to result in useful characterization data for the maintenance of individual coating consistency. The sources of general test methods for these coatings are listed in Section 2.

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