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### COATED IMPLANT AND METHOD OF MAKING THE SAME

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#### Abstract

An orthopaedic knee implant includes a femoral component having a substrate and a coating disposed on the surface of the substrate. A method for making a femoral component of an orthopaedic knee implant is also disclosed.

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## Background/Summary

[0001] This application is a continuation application of U.S. patent application Ser. No. 17/179,827, filed Feb. 19, 2021, which claims priority to U.S. Provisional Application 62/978,534, filed Feb. 19, 2020, U.S. Provisional Application 62/978,537, filed Feb. 19, 2020, and U.S. Provisional Application 63/010,300, filed Apr. 15, 2020, the entirety of each of the above-identified applications is hereby incorporated by reference. CROSS REFERENCE TO RELATED APPLICATIONS [0002] Cross reference is made to pending International Application Serial No. PCT/IB2021/051431 titled “COATED IMPLANT AND METHOD OF MAKING THE SAME” and International Application Serial No. PCT/IB2021/051430 titled “COATED IMPLANT AND METHOD OF MAKING THE SAME,” each of which is hereby incorporated by reference.

### TECHNICAL FIELD

[0003] The present disclosure relates generally to an implantable orthopaedic prosthesis, and more particularly to a femoral component of an implantable orthopaedic prosthesis.

### BACKGROUND

[0004] Joint arthroplasty is a well-known surgical procedure by which a diseased and/or damaged natural joint is replaced by a prosthetic joint. A typical knee prosthesis includes a patella prosthetic component, a tibial tray, a femoral component, and a tibial bearing positioned between the tibial tray and the femoral component. Femoral components are designed to be attached to a surgically-prepared distal end of a patient's femur. Tibial trays are designed to be attached to a surgically-prepared proximal end of a patient's tibia.

[0005] The femoral component and the tibial tray can be made of biocompatible materials such as metal alloys of cobalt-chrome. The tibial bearing component disposed between the femoral component and the tibial tray can be formed from a plastic material like polyethylene. However, cobalt alloys tend to be expensive, and accordingly, a need exists for a component made from a non-cobalt metal material and a method of manufacturing the same. For example, a need exists for a femoral component of a knee prosthesis out of a non-cobalt metal material and a method for manufacturing the same.

### SUMMARY

[0006] According to an aspect of the disclosure, an orthopaedic implant includes a femoral component. The femoral component may be configured to be coupled to the distal end of a patient's femur. The femoral component includes a substrate that comprises a titanium alloy. Illustratively, the substrate has a condylar surface that is curved in a sagittal plane and a bone-facing surface positioned opposite the condylar surface. An articular layer (also referred to as a “coating”) is disposed on the condylar surface. The coating comprises a first layer (also referred to as a “bonding layer” or “inner layer”) comprising niobium, zirconium, titanium, tantalum, platinum, molybdenum, or combinations thereof. The coating also comprises a second layer (also referred to as an “intermediate layer”) comprising a number of alternating sublayers. The coating further comprises a third layer (also referred to as an “outer layer”) comprising zirconium oxide, niobium oxide, zirconium oxynitride, niobium oxynitride, titanium, or a combination thereof. The first layer extends between and interconnects the second layer and the condylar surface. The second layer extends between and interconnects the first layer and the third layer. The third layer forms an outer articular surface of the femoral component.

[0007] In some embodiments, the second layer may comprise at least eight sublayers of alternating zirconium nitride and niobium nitride sublayers. In some embodiments, each zirconium nitride

sublayer of the alternating sublayers may have a thickness of about 0.5 nm to about 200 nm. In some embodiments, the second layer may have a thickness of about 3  $\mu\text{m}$  to about 6  $\mu\text{m}$ .

[0008] In some embodiments, the third layer may comprise at least about 90% monoclinic oxidized zirconium. In some embodiments, the third layer may have a thickness of about 100 nm to about 5  $\mu\text{m}$ .

[0009] In some embodiments, at least one sublayer of the second layer may comprise at least about 95% zirconium nitride.

[0010] In some embodiments, at least one sublayer of the second layer may have a thickness of about 5 nm to about 500 nm. In some embodiments, at least one sublayer of the second layer may comprise at least about 95% niobium nitride.

[0011] In some embodiments, the first layer may comprise at least about 90% zirconium. In some embodiments, the first layer may have a thickness of about 50 nm to about 1  $\mu\text{m}$ .

[0012] Illustratively, the femoral component may include a bone-engaging layer disposed on the bone-facing surface. In some embodiments, the bone-engaging layer may be porous.

[0013] In some embodiments, the second layer may comprise an inner sublayer and an outer sublayer. In some embodiments, the inner sublayer and the outer sublayer may have the same composition. In some embodiments, the second layer may comprise an intermediate sublayer having a composition different from the inner sublayer, the outer sublayer, or both.

[0014] In some embodiments, the third layer may be titanium zirconium nitride. Additionally, in some embodiments, the atomic percent of zirconium in the third layer may be 50 At % to 80 At %. In some embodiments, the atomic percent of zirconium in the third layer may be 30 At % to 85 At %.

[0015] In some embodiments, the number of alternating sublayers include a number of titanium zirconium nitride sublayers and a number of metallic layers. In some embodiments, the atomic percent of zirconium in the plurality of alternating sublayers is 30 At % to 85 At %. Additionally, in some embodiments, the atomic percent of zirconium-titanium alloy in the plurality of alternating sublayers is 30 At % to 85 At %.

[0016] According to another aspect, a process for forming a femoral component of an orthopaedic knee implant includes depositing a first layer comprising niobium, zirconium, titanium, tantalum, platinum, molybdenum, or combinations thereof, on a condylar surface of a substrate. The substrate comprises titanium. The condylar surface is curved in a sagittal plane. In some embodiments, the process includes depositing a second layer that comprises a number of alternating sublayers.

[0017] In some embodiments, the process may include oxidizing a portion of the second layer to form a third layer comprising oxidized zirconium.

[0018] In some embodiments, the alternating sublayers may comprise a sublayer of zirconium nitride and a sublayer of niobium. In some embodiments, depositing the number of alternating sublayers to form the second layer may comprise (a) creating a sublayer of zirconium nitride on the first layer, (b) creating a sublayer of niobium on the sublayer of zirconium nitride, and (c) repeating steps (a) and (b) to form the second layer.

[0019] In some embodiments, the process may include depositing a third layer on an outer surface of the second layer. In some embodiments, the third layer may comprise zirconium oxide, niobium oxide, zirconium oxynitride, niobium oxynitride, or a combination thereof.

[0020] Additional Embodiments are also contemplated.

[0021] Clause 1. An orthopaedic knee implant comprising: a femoral component configured to be coupled to a distal end of a patient's femur, the femoral component comprising (i) a substrate comprising a titanium alloy having (a) a condylar surface that is curved in a sagittal plane and (b) a bone-facing surface positioned opposite the condylar surface; and (ii) a coating disposed on the condylar surface, the coating comprising (a) a first layer comprising niobium, zirconium, titanium, tantalum, platinum, molybdenum, or combinations thereof, (b) a second layer comprising a number of alternating sublayers, and (c) a third layer comprising (i) a tetragonal zirconium oxide layer and

(ii) a monoclinic zirconium oxide layer, wherein (i) the first layer extends between and interconnects the second layer and the condylar surface, (ii) the second layer extends between and interconnects the first layer and the third layer, and (iii) the third layer forms an outer surface of the coating.

[0022] Clause 2. The orthopaedic knee implant of clause 1, wherein the second layer further comprises a sublayer comprising zirconium.

[0023] Clause 3. The orthopaedic knee implant of clause 2, wherein each of the zirconium sublayers comprises at least about 70% tetragonal zirconium.

[0024] Clause 4. The orthopaedic knee implant of any one of clauses 1-3, wherein the second layer comprises a first zirconium nitride sublayer and at least nine alternating sublayers of niobium nitride sublayers, zirconium sublayers, and zirconium nitride sublayers.

[0025] Clause 5. The orthopaedic knee implant of any one of clauses 1-4, wherein the tetragonal zirconium oxide layer extends between and interconnects the monoclinic zirconium oxide layer and the second layer.

[0026] Clause 6. The orthopaedic knee implant of any one of clauses 1-5, wherein the third layer has a thickness of about 2  $\mu\text{m}$  to about 5  $\mu\text{m}$ .

[0027] Clause 7. The orthopaedic knee implant of any one of clauses 1-6, wherein the tetragonal zirconium oxide layer has a thickness of about 200 nm to about 3  $\mu\text{m}$ .

[0028] Clause 8. The orthopaedic knee implant of any one of clause 1-7, wherein the monoclinic zirconium oxide layer has a thickness of about 200 nm to about 3  $\mu\text{m}$ .

[0029] Clause 9. The orthopaedic knee implant of any one of clauses 1-8, wherein the second layer has a thickness of about 3  $\mu\text{m}$  to about 6  $\mu\text{m}$ .

[0030] Clause 10. The orthopaedic knee implant of any one of clauses 1-9, wherein the second layer comprises zirconium nitride sublayers each having a thickness of about 10 nm to about 200 nm.

[0031] Clause 11. The orthopaedic knee implant of any one of clauses 4-10, wherein each zirconium nitride sublayer comprises at least about 95% zirconium nitride.

[0032] Clause 12. The orthopaedic knee implant of any one of clauses 1-11, wherein the second layer comprises niobium nitride sublayers each having a thickness of about 10 nm to about 200 nm.

[0033] Clause 13. The orthopaedic knee implant of any one of clause 4-12, wherein each niobium nitride sublayer comprises at least about 95% niobium nitride.

[0034] Clause 14. The orthopaedic knee implant of any one of clauses 1-13, wherein the second layer comprises zirconium sublayers each having a thickness of about 10 nm to about 200 nm.

[0035] Clause 15. The orthopaedic knee implant of any one of clauses 4-14, wherein each zirconium sublayer comprises at least about 95% zirconium.

[0036] Clause 16. The orthopaedic knee implant of any one of clauses 1-14, wherein the first layer comprises at least about 90% zirconium.

[0037] Clause 17. The orthopaedic knee implant of any one of clauses 1-16, wherein the first layer has a thickness of about 50 nm to about 1  $\mu\text{m}$ , or about 1  $\mu\text{m}$  to about 3  $\mu\text{m}$ .

[0038] Clause 18. The orthopaedic knee implant of any one of clauses 1-17, wherein the femoral component comprises a bone-engaging layer disposed on the bone-facing surface.

[0039] Clause 19. The orthopaedic knee implant of clause 18, wherein the bone-engaging layer is porous.

[0040] Clause 20. A process for forming a femoral component of an orthopaedic knee implant, the process comprising: i) depositing a first layer comprising zirconium on a condylar surface of a titanium substrate, wherein the condylar surface is curved in a sagittal plane; ii) depositing a number of alternating sublayers to form a second layer; and iii) depositing a third sublayer comprising zirconium nitride onto the second layer.

[0041] Clause 21. The process of clause 20, wherein the second depositing step comprises depositing a zirconium sublayer.

[0042] Clause 22. An orthopaedic knee implant comprising: a femoral component configured to be coupled to a distal end of a patient's femur, the femoral component comprising (i) a substrate comprising a titanium alloy having (a) a condylar surface that is curved in a sagittal plane and (b) a bone-facing surface positioned opposite the condylar surface; and (ii) a coating disposed on the condylar surface, the coating comprising (a) a first layer comprising niobium, zirconium, titanium, tantalum, platinum, molybdenum, alloys thereof, or combinations thereof, (b) a second layer comprising a number of alternating sublayers, and (c) a third layer comprising oxidized zirconium, wherein (i) the first layer extends between and interconnects the second layer and the condylar surface, (ii) the second layer extends between and interconnects the first layer and the third layer, and (iii) the third layer forms an outer surface of the coating.

[0043] Clause 23. The implant of clause 22, wherein the second layer comprises at least eight alternating sublayers of zirconium nitride and niobium nitride.

[0044] Clause 24. The implant of clause 23, wherein each zirconium nitride sublayer of the alternating sublayers has a thickness of about 5 nm to about 200 nm.

[0045] Clause 25. The implant of any one of clause 22-24, wherein the second layer has a thickness of about 3  $\mu\text{m}$  to about 6  $\mu\text{m}$ .

[0046] Clause 26. The implant of any one clauses 22-25, wherein the third layer comprises at least about 90% monoclinic oxidized zirconium.

[0047] Clause 27. The implant of any one of clauses 22-26, wherein the third layer has a thickness of about 100 nm to about 5  $\mu\text{m}$ .

[0048] Clause 28. The implant of any one of clauses 22-27, wherein at least one sublayer of the second layer comprises at least about 95% zirconium nitride.

[0049] Clause 29. The implant of any one of clauses 22-28, wherein at least one sublayer of the second layer has a thickness of about 5 nm to about 500 nm.

[0050] Clause 30. The implant of any one of clauses 22-29, wherein at least one sublayer of the second layer comprises at least about 95% niobium nitride.

[0051] Clause 31. The implant of any one of clauses 22-30, wherein the first layer comprises at least about 90% zirconium.

[0052] Clause 32. The implant of any one of clauses 22-31, wherein the first layer has a thickness of about 50 nm to about 1  $\mu\text{m}$ .

[0053] Clause 33. The implant of any one of clauses 22-32, wherein the femoral component comprises a bone-engaging layer disposed on the bone-facing surface.

[0054] Clause 34. The implant of clause 33, wherein the bone-engaging layer is porous.

[0055] Clause 35. The implant of any one of clauses 22-34, wherein the second layer comprises an inner sublayer and an outer sublayer.

[0056] Clause 36. The implant of clause 35, wherein the inner sublayer and the outer sublayer have the same composition.

[0057] Clause 37. The implant of any one of clauses 35-36, wherein the second layer comprises an intermediate sublayer having a composition different from the inner sublayer, the outer sublayer, or both.

[0058] Clause 38. A process for forming a femoral component of an orthopaedic knee implant, the process comprising: depositing a first layer comprising niobium, zirconium, titanium, tantalum, platinum, molybdenum, an alloy thereof, or combinations thereof on a condylar surface of a substrate comprising titanium, wherein the condylar surface is curved in a sagittal plane; and depositing a second layer comprising a number of alternating sublayers.

[0059] Clause 39. The process of clause 38, comprising oxidizing a portion of the second layer to form a third layer.

[0060] Clause 40. The process of any one of clauses 38-39, wherein the alternating sublayers comprise a sublayer of zirconium nitride and a sublayer of niobium nitride.

[0061] Clause 41. The process of any one of clauses 38-40, comprising depositing a third layer on

an outer surface of the second layer.

[0062] Clause 42. The process of clause 41, wherein the third layer comprises zirconium nitride, titanium zirconium nitride, zirconium oxide, niobium oxide, zirconium oxynitride, niobium oxynitride, or a combination thereof.

[0063] Clause 43. An orthopaedic knee implant comprising: a femoral component configured to be coupled to a distal end of a patient's femur, the femoral component comprising (i) a substrate comprising a titanium alloy having (a) a condylar surface that is curved in a sagittal plane and (b) a bone-facing surface positioned opposite the condylar surface; and (ii) a coating disposed on the condylar surface, the coating comprising (a) a first layer comprising niobium, zirconium, titanium, tantalum, platinum, molybdenum, alloys thereof, or combinations thereof, (b) a second layer comprising a number of alternating sublayers grouped together in bilayers or trilayers, and (c) a third layer comprising oxidized zirconium, wherein (i) the first layer extends between and interconnects the second layer and the condylar surface, (ii) the second layer extends between and interconnects the first layer and the third layer, and (iii) the third layer forms an outer surface of the coating.

[0064] Clause 44. The implant of clause 43, wherein the second layer comprises at least 12 bilayers and wherein each sublayer within a bilayer has a similar thickness.

[0065] Clause 45. The implant of clause 44, wherein each sublayer has a thickness of about 5 nm to about 200 nm.

[0066] Clause 46. The implant of any one of clause 43-45, wherein the second layer has a thickness of about 3  $\mu\text{m}$  to about 8  $\mu\text{m}$ .

[0067] Clause 47. The implant of any one of clauses 43-46, wherein the third layer comprises at least about 90% monoclinic oxidized zirconium.

[0068] Clause 48. The implant of any one of clauses 43-47, wherein the third layer has a thickness of about 100 nm to about 5  $\mu\text{m}$ .

[0069] Clause 49. The implant of clause 43, wherein the second layer comprises at least 8 trilayers and wherein each sublayer within a trilayer has a similar thickness.

[0070] Clause 50. The implant of clause 49, wherein each sublayer has a thickness of about 5 nm to about 500 nm.

[0071] Clause 51. The implant of clause 43, wherein the second layer comprises at least 12 bilayers and wherein each sublayer within a bilayer has a different thickness, and wherein all bilayers have a uniform thickness.

[0072] Clause 52. The implant of clause 43, wherein the second layer comprises at least 8 trilayers and wherein each sublayer within a trilayer has a different thickness, and wherein all trilayers have a uniform thickness.

[0073] Clause 53. The implant of any one of clauses 43-52, wherein the first layer has a thickness of about 50 nm to about 1  $\mu\text{m}$  or 100 nm to 2  $\mu\text{m}$ .

[0074] Clause 54. The implant of any one of clauses 43-53, wherein the femoral component comprises a bone-engaging layer disposed on the bone-facing surface.

[0075] Clause 55. The implant of clause 54, wherein the bone-engaging layer is porous.

[0076] Clause 56. The implant of clause 51, wherein each bilayer includes a first sublayer and a second sublayer, and the first sublayer has a thickness that decreases between 1% and 20% in each subsequent bilayer, and the second sublayer has a thickness that increases between 1% and 20% in each subsequent bilayer.

[0077] Clause 57. The implant of clause 56, wherein the first sublayer makes up at least 55% of the second layer.

[0078] Clause 58. The implant of any one of clauses 43-57, wherein the second layer comprises a metal sublayer selected from the group consisting of niobium, zirconium, titanium, tantalum, platinum, molybdenum, alloys thereof, and combinations thereof; a ceramic sublayer comprising niobium, zirconium, titanium, tantalum, molybdenum, platinum, or combinations thereof; and a

third layer selected from the group consisting of zirconium oxide, niobium oxide, zirconium oxynitride, niobium oxynitride, titanium nitride, titanium zirconium nitride, and combinations thereof.

[0079] Clause 59. The implant of clause 43, wherein the third layer comprises titanium zirconium nitride.

[0080] Clause 60. A process for forming a femoral component of an orthopaedic knee implant, the process comprising: depositing a first layer comprising niobium, zirconium, titanium, tantalum, platinum, molybdenum, or combinations thereof on a condylar surface of a substrate comprising titanium, wherein the condylar surface is curved in a sagittal plane; and depositing a number of alternating sublayers to form a second layer.

[0081] Clause 61. The process of clause 60, comprising oxidizing a portion of the second layer to form a third layer comprising oxidized zirconium.

[0082] Clause 62. The process of clause 61, wherein the alternating sublayers comprise a sublayer of zirconium nitride and a sublayer of niobium nitride.

[0083] Clause 63. The process of any one of clauses 60-62, comprising depositing a third layer on an outer surface of the second layer.

[0084] Clause 64. The process of clause 63, wherein the third layer comprises zirconium nitride, titanium zirconium nitride, zirconium oxide, niobium oxide, zirconium oxynitride, niobium oxynitride, or a combination thereof.

[0085] Clause 65. An orthopaedic knee implant comprising: a femoral component configured to be coupled to a distal end of a patient's femur, the femoral component comprising: (i) a substrate comprising a titanium alloy having (a) a condylar surface that is curved in a sagittal plane and (b) a bone-facing surface positioned opposite the condylar surface; and (ii) a coating disposed on the condylar surface, the coating comprising (a) a first layer comprising niobium, zirconium, titanium, tantalum, platinum, molybdenum, alloys thereof, or combinations thereof, (b) an outer ceramic third layer, and (c) a plurality of alternating sublayers positioned between and interconnecting the first layer and the outer ceramic third layer, wherein (i) the plurality of alternating sublayers are configured to resist crack propagation from the outer ceramic third layer, the plurality of alternating sublayers include a number of metallic sublayers and a number of ceramic sublayers that are harder than the metallic sublayers, and (ii) the outer ceramic third layer forms an outer articular surface of the femoral component and is shaped to contact a concave proximal surface of a tibial bearing.

[0086] Clause 66. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not clauses 49 or 52), and 65, wherein a first sublayer and a second sublayer form a bilayer comprising niobium and zirconium nitride, and the third layer comprises zirconium nitride.

[0087] Clause 67. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not clauses 49 or 52), and 65, wherein a first sublayer and a second sublayer form a bilayer comprising niobium and zirconium nitride, and the third layer comprises titanium zirconium nitride.

[0088] Clause 68. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not clauses 49 or 52), and 65, wherein a first sublayer and a second sublayer form a bilayer comprising zirconium nitride and zirconium, and the third layer comprises zirconium nitride.

[0089] Clause 69. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not clauses 49 or 52), and 65, wherein a first sublayer and a second sublayer form a bilayer comprising zirconium nitride and zirconium, and the third layer comprises titanium zirconium nitride.

[0090] Clause 70. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not clauses 49 or 52), and 65, wherein a first sublayer and a second sublayer form a bilayer comprising zirconium titanium and titanium zirconium nitride, and the third layer comprises titanium zirconium nitride.

[0091] Clause 71. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not clauses 49 or 52), and 65-70, wherein the third layer comprises zirconium nitride.

[0092] Clause 72. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not

clauses 49 or 52), and 65-70, wherein the third layer comprises titanium zirconium nitride.

[0093] Clause 73. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not clauses 49 or 52), and 65-70, wherein the intermediate layer includes a plurality of alternating titanium zirconium nitride sublayer and zirconium titanium alloy metal sublayer.

[0094] Clause 74. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not clauses 49 or 52), and 65-70, wherein the intermediate layer includes a plurality of alternating zirconium nitride sublayer and zirconium titanium alloy sublayer.

[0095] Clause 75. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59 (but not clauses 49 or 52), and 65-70, wherein the third layer comprises ceramic.

[0096] Clause 76. The orthopaedic knee implant of any one of clauses 1-19, 22-37, 43-59, and 65-75, wherein the plurality of alternating sublayers are grouped by bilayers or trilayers.

[0097] Clause 77. The orthopaedic knee implant of clause 76, wherein each bilayer or each trilayer have a uniform thickness to the other grouped sublayers in the intermediate layer, but the individual thickness of each sublayer within the grouping is varied.

[0098] Clause 78. The orthopaedic knee implant any one of clauses 1-19, 22-37, 43-59, and 65-77, wherein the third layer is titanium zirconium nitride.

[0099] Clause 79. The orthopaedic knee implant of clause 78, wherein the atomic percent of zirconium in the third layer is 50 At % to 80 At %.

[0100] Clause 80. The orthopaedic knee implant of clause 78, wherein the atomic percent of zirconium in the third layer is 30 At % to 85 At %.

[0101] Clause 81. The orthopaedic knee implant of clauses 1-19, 22-37, 43-59, and 65-80, wherein the plurality of alternating sublayers include a number of titanium zirconium nitride sublayers and a number of metallic layers.

[0102] Clause 82. The orthopaedic knee implant of clauses 81, wherein the atomic percent of zirconium in the plurality of alternating sublayers is 30 At % to 85 At %.

[0103] Clause 83. The orthopaedic knee implant of clauses 81, wherein the atomic percent of zirconium-titanium alloy in the plurality of alternating sublayers is 30 At % to 85 At %.

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## Description

### BRIEF DESCRIPTION

[0104] The detailed description particularly refers to the following figures, in which:

[0105] FIG. 1 is an exploded perspective view of an orthopaedic knee prosthesis, showing a femoral component, a tibial bearing, and a tibial tray;

[0106] FIG. 2 is a cross-sectional view of the femoral component and the tibial bearing of FIG. 1 along the sagittal plane, taken generally along line 2-2 of FIG. 1, as viewed in the direction of the arrows, note the porous-metal coating is not shown in cross section in FIG. 2 for clarity of description;

[0107] FIG. 3 is an enlarged cross-sectional view taken from FIG. 2 as indicated by the encircled area;

[0108] FIG. 4 is an illustrative diagrammatic view of a process for forming the coating of the femoral component of FIGS. 1-3;

[0109] FIG. 5 is an illustrative view of an embodiment of a femoral component including a substrate, a bonding layer, an intermediate layer, and an outer layer;

[0110] FIG. 6 is an illustrative view of an embodiment of a femoral component;

[0111] FIG. 7 is an illustrative view of an embodiment of a femoral component;

[0112] FIG. 8 is an illustrative view of an embodiment of a femoral component;

[0113] FIG. 9 is an illustrative view of an embodiment of a femoral component;

[0114] FIG. 10 is an illustrative view of an embodiment of a femoral component;



[0115] FIG. **11** is an illustrative view of an embodiment of a femoral component;  
[0116] FIG. **12** is an illustrative view of an embodiment of a femoral component;  
[0117] FIG. **13** is an illustrative view of an embodiment of a femoral component;  
[0118] FIG. **14** is an illustrative view of an embodiment of a femoral component;  
[0119] FIG. **15** is an illustrative view of an embodiment of a femoral component;  
[0120] FIG. **16** is an SEM image of a FIB cross-section of ML-nom;  
[0121] FIG. **17** is an SEM image of a FIB cross-section of MLG-nom;  
[0122] FIG. **18** is a graph showing the minimum load applied by a 20 micron tip to first chipping or delamination observed in the various coating samples;  
[0123] FIG. **19** is an SEM image of a FIB cross-section of ML-Nom;  
[0124] FIG. **20** is an SEM image of a FIB cross-section of Mono-10; and  
[0125] FIG. **21** is a graph showing the minimum load applied by a 200 micron tip to first chipping or delamination observed in various coating samples.

#### DETAILED DESCRIPTION

[0126] While the concepts of the present disclosure are susceptible to various modifications and alternative forms, specific exemplary embodiments thereof have been shown by way of example in the drawings and will herein be described in detail. It should be understood, however, that there is no intent to limit the concepts of the present disclosure to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

[0127] Terms representing anatomical references, such as anterior, posterior, medial, lateral, superior, inferior, etcetera, may be used throughout the specification in reference to the orthopaedic implants or orthopaedic prostheses described herein as well as in reference to the patient's natural anatomy. Such terms have well-understood meanings in both the study of anatomy and the field of orthopaedics. Use of such anatomical reference terms in the written description and claims is intended to be consistent with their well-understood meanings unless noted otherwise.

[0128] Referring now to FIG. **1**, in one embodiment, an orthopaedic knee prosthesis **10** includes a femoral component **12**, a tibial bearing **14**, and a tibial tray **16**. The femoral component **12** is configured to articulate with the tibial bearing **14**, which is configured to be coupled with the tibial tray **16**. In the illustrative embodiment of FIG. **1**, the tibial bearing **14** is embodied as a rotating or mobile tibial bearing and is configured to rotate relative to the tibial tray **16** during use. However, in other embodiments, the tibial bearing **14** may be embodied as a fixed tibial bearing, which may be limited or restricted from rotating relative to the tibial tray **16**.

[0129] The tibial tray **16** is configured to be secured to a surgically-prepared proximal end of a patient's tibia (not shown). The tibial tray **16** may be secured to the patient's tibia via use of bone cement or other attachment methods. The tibial tray **16** includes a platform **18** having a top surface **20** and a bottom surface **22**. Illustratively, the top surface **20** is generally planar. The tibial tray **16** also includes a stem **24** extending downwardly from the bottom surface **22** of the platform **18**. A cavity or bore **26** is defined in the top surface **20** of the platform **18** and extends downwardly into the stem **24**. The bore **26** is formed to receive a complimentary stem **36** of the tibial bearing **14** as discussed in more detail below.

[0130] As discussed above, the tibial bearing **14** is configured to be coupled with the tibial tray **16**. The tibial bearing **14** includes a platform **30** having an upper bearing surface **32** and a bottom bearing surface **34**. In the illustrative embodiment wherein the tibial bearing **14** is embodied as a rotating or mobile tibial bearing, the bearing **14** includes a stem **36** extending downwardly from the bottom surface **34** of the platform **30**. When the tibial bearing **14** is coupled to the tibial tray **16**, the stem **36** is received in the bore **26** of the tibial tray **16**. In use, the tibial bearing **14** is configured to rotate about an axis defined by the stem **36** relative to the tibial tray **16**. In embodiments wherein the tibial bearing **14** is embodied as a fixed tibial bearing, the bearing **14** may or may not include the stem **36** and/or may include other devices or features to secure the tibial bearing **14** to the tibial

tray **16** in a non-rotating configuration.

[0131] The upper bearing surface **32** of the tibial bearing **14** includes a medial bearing surface **42** and a lateral bearing surface **44**. The medial and lateral bearing surfaces **42**, **44** are configured to receive or otherwise contact corresponding medial and lateral condyles **52**, **54** of the femoral component **12** as discussed in more detail below. As such, each of the bearing surfaces **42**, **44** has a concave contour.

[0132] The femoral component **12** is configured to be coupled to a surgically-prepared surface of the distal end of a patient's femur (not shown). The femoral component **12** may be secured to the patient's femur via use of bone adhesive or other attachment methods. The femoral component **12** includes a pair of medial and lateral condyles **52**, **54**. The condyles **52**, **54** are spaced apart to define an intracondyle notch **56** therebetween. In use, the condyles **52**, **54** replace the natural condyles of the patient's femur and are configured to articulate on the corresponding bearing surfaces **42**, **44** of the platform **30** of the tibial bearing **14**.

[0133] The illustrative orthopaedic knee prosthesis **10** (sometime referred to as an “implant”) of FIG. **1** is embodied as a posterior cruciate-retaining knee prosthesis. That is, the femoral component **12** is embodied as a posterior cruciate-retaining knee prosthesis and the tibial bearing **14** is embodied as a posterior cruciate-retaining tibial bearing **14**. However, in other embodiments, the orthopaedic knee prosthesis **10** may be embodied as a posterior cruciate-sacrificing knee prosthesis.

[0134] Referring now to FIGS. **1** and **2**, the femoral component **12** is configured to articulate on the tibial bearing **14** during use. Each condyle **52**, **54** of the femoral component **12** includes an outer articular surface **50**, which is convexly curved in the sagittal plane and configured to face the respective bearing surface **42**, **44** of the tibial bearing **14**.

[0135] As shown in FIG. **2**, the femoral component **12** includes a substrate **60** and a coating **58**. Illustratively, the coating **58** is disposed on the substrate **60** and is configured to interact with the tibial bearing **14**. In some embodiments, the femoral component **12** includes a bone-engaging layer **62** located opposite the coating **58** to locate the substrate **60** therebetween. The bone-engaging layer **62** is configured to interact with a surgically prepared femur of a patient.

[0136] The substrate **60** comprises a condylar surface **66** and a bone-facing surface **64**, as shown in FIG. **2**. The condylar surface **66** is curved in a sagittal plane and is configured to locate the coating **58** on the substrate **60**. The bone-facing surface **64** is positioned opposite the condylar surface **66** and is arranged to face a surgically-prepared distal end of a patient's femur. In some embodiments, the bone-facing surface **64** contacts the surgically-prepared femur bone directly. In some embodiments, a bone-engaging layer **62** is coupled to the bone-facing surface **64** of the substrate **60**.

[0137] FIGS. **1** and **2** show a cementless embodiment of the femoral component **12** where the bone-engaging layer **62** is configured to be implanted in the absence of cement between the femoral component **12** and the surgically-prepared distal end of a patient's femur. In some embodiments, the bone-engaging layer **62** comprises titanium. It should be appreciated that the bone-engaging layer **62** could be a separately-applied coating such as Porocoat® Porous Coating, which is commercially available from DePuy Synthes of Warsaw, Indiana.

[0138] In some embodiments, the bone-engaging layer **62** can be defined by a porous three-dimensional structure formed by a plurality of interconnected struts. In one example, the plurality of interconnected struts form a plurality of geometric structures, which, in the illustrative embodiment, are rhombic trigonal trapezohedrons. It should be appreciated that such geometric structures may vary to fit the needs of a given design. Further, it should be appreciated that the bone-engaging layer **62** may be formed from any other alternative geometry suitable to fit the needs of a given design.

[0139] In some embodiments, the bone-engaging layer **62** is formed from a metal powder. Illustratively, the metal powder may include, but are not limited to, titanium, titanium alloys,

stainless steel, cobalt chrome alloys, tantalum, niobium, or a combination thereof. The bone-engaging layer **62** has a porosity suitable to facilitate bony ingrowth into the bone-engaging layer **62** of the femoral component **12** when implanted into the surgically-prepared surface of the distal end of a patient's femur.

[0140] In the illustrative embodiment described herein, the bone-engaging layer **62** is additively manufactured directly onto the bone-facing surface **64** of the femoral component **12**. In such an embodiment, the two structures—i.e., the femoral component **12** and bone-engaging layer **62**—may be manufactured contemporaneously during a common additive manufacturing process. For example, the two structures may be manufactured contemporaneously in a single 3D printing operation that yields a common, monolithic metallic component including both structures. Alternatively, the bone-engaging layer **62** could be manufactured as a separate component that is secured to the bone-facing surface **64** of the femoral component **12**.

[0141] In alternative embodiments, the femoral component **12** is configured to attach to the surgically-prepared distal end of a patient's femur using cement. In some embodiments, the femoral component **12** comprises a cement reservoir (not shown) disposed on the bone-facing surface **64**. In some embodiments, the bone adhesive is disposed on the bone-facing surface **64**. In some embodiments, the bone adhesive comprises bone cement. In some embodiments, the bone-facing surface **64** is configured to receive a bone adhesive.

[0142] In some embodiments, the substrate **60** is metallic. In some embodiments, the substrate **60** comprises a metal alloy. In some embodiments, the substrate **60** comprises a titanium alloy. In some embodiments, the substrate **60** comprises titanium and vanadium. In some embodiments, the substrate **60** comprises titanium, aluminum, and vanadium. In some embodiments, the substrate **60** comprises Ti-6Al-4V. In some embodiments, the substrate **60** consists essentially of Ti-6Al-4V.

[0143] Referring now to FIGS. **2** and **3**, the coating **58** is disposed on the condylar surface **66**. The coating **58** is located opposite the bone-facing surface **64** to locate the substrate **60** therebetween. The coating **58** is configured to interact with the bearing surfaces **42**, **44** and to articulate with the tibial bearing **14**.

[0144] The coating **58** has a number of layers **68**, **70**, **72**. The layers **68**, **70**, **72** may each be constructed with a material which possesses mechanical properties favorable for use in the construction of the coating **58** (e.g., enhanced wear resistance, resists chipping, resists delamination, tunable stiffness, ductile, corrosion resistance, and oxidation resistance).

[0145] In some embodiments, the coating **58** cooperates with the substrate **60** to minimize scratching of the outer articular surface **50** of the femoral component **12**. In some embodiments, the coating **58** cooperates with the substrate **60** to minimize cohesive chipping and delamination of the coating **58**. In some embodiments, the coating **58** cooperates with the substrate **60** to resist corrosion. In some embodiments, the coating **58** provides density and toughness. In some embodiments, the coating **58** cooperates with the substrate **60** to provide sufficient toughness to minimize or avoid fracturing.

[0146] Referring now to FIG. **3**, the coating **58** comprises an inner or bonding layer **68**, an intermediate layer **70**, and an outer layer **72**. The outer layer **72**, the intermediate layer **70**, or both the outer layer **72** and the intermediate layer **70** of the coating **58** is constructed with a material which possesses mechanical properties favorable for use in the construction of the coating **58**. For example, the intermediate layer **70** is constructed with materials that provide a stiffness and ductility that spread the load of a force, arrest cracking, and improve adhesion of the coating **58** to the substrate **60**. The bonding layer **68**, on the other hand, is constructed of a material which possesses mechanical properties favorable for use in securing the coating **58** to the substrate **60**.

[0147] It should be appreciated that, as used herein, the term “layer” is not intended to be limited to a “thickness” of material positioned proximate to another similarly dimensioned “thickness” of material, but rather is intended to include numerous structures, configurations, and constructions of material. For example, the term “layer” may include a portion, region, or other structure of material

which is positioned proximate to another portion, region, or structure of differing material. For example, although the interface between the intermediate layer **70** and the outer layer **72** is shown to be uniform in FIG. **3**, in some embodiments the interface is irregular such that the intermediate layer **70** and the outer layer **72** do not have a uniform thickness. In some embodiments, a “layer” is formed by modifying a surface or a portion of an existing layer. For example, in some embodiments, the outer layer **72** is formed from oxidizing an outer portion of the intermediate layer **70**. In alternative embodiments, a “layer” is formed by providing additional material to an existing surface. For example, in some embodiments, the bonding layer **68** is formed by depositing a material onto the condylar surface **66**.

[0148] As shown in FIG. **3**, the bonding layer **68** is disposed on the condylar surface **66**. The outer layer **72** is arranged to form the outer articular surface **50** of the coating **58** and hence the femoral component **12**. The intermediate layer **70** extends between and interconnects the bonding layer **68** and the outer layer **72**. In some embodiments, the coating **58** does not include an outer layer **72** (as shown in FIG. **11**) such that an exposed surface of the intermediate layer **70** may be further processed to form the outer articular surface **50**.

[0149] The bonding layer **68** extends between and interconnects the intermediate layer **70** and the condylar surface **66**. The inner layer **68** includes an inner surface **74** and an outer surface **76**. The inner surface **74** is located between the outer surface **76** and the condylar surface **66**. The outer surface **76** of the inner layer **68** is located between the inner surface **74** of the inner layer **68** and the intermediate layer **70**. In some embodiments, the inner layer **68** is configured to reduce delamination of the coating **58** from the femoral component **12**.

[0150] The bonding layer **68** may have a particular thickness as measured from the condylar surface **66**. In some embodiments, the bonding layer **68** may be present at a thickness in the nanoscale to the micron scale. In some embodiments, the bonding layer **68** has a thickness of about 0.5 nm to about 10 nm, about 0.5 nm to about 3 nm, or about 5 nm to about 10 nm. In some embodiments, the bonding layer **68** has a thickness of about 0.10  $\mu\text{m}$  to about 2  $\mu\text{m}$ . In some embodiments, the bonding layer **68** has a thickness of about 200 nm to about 1  $\mu\text{m}$ . In some embodiments, the bonding layer **68** has a thickness of at least about 0.10  $\mu\text{m}$ , at least about 0.20  $\mu\text{m}$ , at least about 0.30  $\mu\text{m}$ , at least about 0.5  $\mu\text{m}$ , at least about 1  $\mu\text{m}$ , at least about 1.5  $\mu\text{m}$ , or at least about 2  $\mu\text{m}$ . In some embodiments, the bonding layer **68** has a thickness of about 200 nm, about 220 nm, about 240 nm, about 260 nm, about 280 nm, about 300 nm, about 320 nm, about 340 nm, about 360 nm, about 38 nm, about 400 nm, about 420 nm, about 440 nm, about 460 nm, about 480 nm, about, or about 500 nm.

[0151] The bonding layer **68** may include metals, alloys, or other suitable material to provide mechanical properties favorable for use in securing the coating **58** to the substrate **60**. For example, the composition of the bonding layer **68** can be selected to minimize cohesive chipping of the coating **58** during manufacturing and in use. In illustrative embodiments, the bonding layer **68** comprises niobium, zirconium, titanium, tantalum, molybdenum, platinum, hafnium, combinations thereof, or any other suitable metal. In some embodiments, the bonding layer **68** comprises zirconium. In some embodiments, the bonding layer **68** comprises at least about 90% zirconium. In some embodiments, the bonding layer **68** comprises at least about 95% zirconium. In some embodiments, the bonding layer **68** comprises at least about 90% of niobium, titanium, tantalum, molybdenum, platinum, or combinations thereof. In some embodiments, the bonding layer **68** comprises at least about 95% niobium, zirconium, titanium, tantalum, molybdenum, platinum, hafnium, or combinations thereof.

[0152] As described above, the intermediate layer **70** extends between and interconnects the bonding layer **68** and the outer layer **72**. The intermediate layer **70** comprises an inner surface **78** and outer surface **80**. The inner surface **78** of the intermediate layer **70** is located between the inner layer **68** and the outer surface **80** of the intermediate layer **70**. The outer surface **80** of the intermediate layer **70** is located between the inner surface **78** of the intermediate layer **70** and the

outer layer **72**.

[0153] In some embodiments, the intermediate layer **70** has an overall thickness of about 3  $\mu\text{m}$  to about 7  $\mu\text{m}$ . In some embodiments, the intermediate layer **70** has an overall thickness of about 3  $\mu\text{m}$  to about 8  $\mu\text{m}$ . In some embodiments, the intermediate layer **70** has an overall thickness of about 5 nm to about 5  $\mu\text{m}$ . In some embodiments, the intermediate layer **70** has an overall thickness of about 1.5  $\mu\text{m}$  to about 2.0  $\mu\text{m}$ . In some embodiments, the intermediate layer **70** has an overall thickness of at least about 50 nm, at least about 100 nm, at least about 200 nm, at least about 0.5  $\mu\text{m}$ , at least about 1  $\mu\text{m}$ , at least about 2  $\mu\text{m}$ , at least about 3  $\mu\text{m}$ , or at least about 4  $\mu\text{m}$ . In some embodiments, the intermediate layer **70** has an overall thickness of about 3.2  $\mu\text{m}$ , about 3.5  $\mu\text{m}$ , about 4.0  $\mu\text{m}$ , about 4.2  $\mu\text{m}$ , about 4.3  $\mu\text{m}$ , about 4.5  $\mu\text{m}$ , about 5.0  $\mu\text{m}$ , about 5.3  $\mu\text{m}$ , about 5.5  $\mu\text{m}$ , about 6.0  $\mu\text{m}$ , about 6.3  $\mu\text{m}$ , about 6.4  $\mu\text{m}$ , or about 6.5  $\mu\text{m}$ .

[0154] The intermediate layer **70** can be formed of a plurality of sublayers. The order and composition of the sublayers **86**, **88**, **90** are configured to disperse the load and arrest cracking that may occur. In an illustrative embodiment, the intermediate layer **70** is formed of an inner sublayer **86**, an intermediate sublayer **88**, and an outer sublayer **90**. In some illustrative embodiments, some or all of the sublayers **86**, **88**, **90** repeat so that the intermediate layer **70** can include two or more of one of the sublayers.

[0155] The sublayers **86**, **88**, **90** can include metals, alloys, ceramics, or other suitable materials as described herein. Illustratively, the various combinations of sublayers **86**, **88**, or **90** provide fracture toughness and corrosion resistance. For example, each of the sublayers **86**, **88**, and **90** may comprise niobium, zirconium, titanium, tantalum, hafnium, molybdenum, platinum, combinations thereof, or any other suitable metal, including alloys thereof. Each of the sublayers **86**, **88**, and **90** may comprise a ceramic comprising niobium, zirconium, titanium, tantalum, molybdenum, platinum, combinations thereof, or any other suitable ceramic. Illustratively, a ceramic may comprise a metal and a nitride, a carbide, an oxide, or combinations thereof. For example, the ceramic may comprise zirconium nitride, titanium zirconium nitride, zirconium oxide, or niobium nitride.

[0156] In some embodiments, the number of alternating sublayers include a number of titanium zirconium nitride sublayers and a number of metallic layers. In some embodiments, the atomic percent of zirconium in the plurality of alternating sublayers is 30 At % to 85 At %. In some embodiments, the atomic percent of zirconium in the plurality of alternating sublayers is about 30 At %, about 35 At %, about 40 At %, about 45 At %, about 50 At %, about 55 At %, about 60 At %, about 65 At %, about 70 At %, about 75 At %, about 80 At %, or about 85 At %. Additionally, in some embodiments, the atomic percent of zirconium-titanium alloy in the plurality of alternating sublayers is 30 At % to 85 At %. In some embodiments, the atomic percent of zirconium-titanium alloy in the plurality of alternating sublayers is about 30 At %, about 35 At %, about 40 At %, about 45 At %, about 50 At %, about 55 At %, about 60 At %, about 65 At %, about 70 At %, about 75 At %, about 80 At %, or about 85 At %.

[0157] In illustrative embodiments, some of or all of the sublayers **86**, **88**, **90** may participate in a super lattice with adjacent layers or sublayers. In some embodiments, each of the sublayers **86**, **88**, **90** has a thickness of about 0.5 nm to about 10 nm, about 5 nm to about 10 nm, or about 0.5 nm to about 3 nm. In some embodiments, each of the sublayers **86**, **88**, **90** has a thickness of about 5 nm to about 500 nm.

[0158] The intermediate layer **70** may comprise two different sublayers, which may be superimposed alternately. Referring to FIG. 5 for example, the intermediate layer **70** may comprise an inner sublayer **86**, an intermediate sublayer **88**, and an outer sublayer **90**. The compositions of the inner sublayer **86**, the intermediate sublayer **88**, and the outer sublayer **90** may be the same or different. For example, the intermediate layer **70** may comprise a sequence of two sublayers, for example the inner sublayer **86** and the intermediate sublayer **88**, having the composition -A-B- or (-A-B-).sub.n where each of A and B are a different composition and n is at

least 1, at least 2, at least 4, or at least 10. In this embodiment, inner sublayer **86** is A and intermediate sublayer **88** is B. Where there is a repeat of two sublayers, such as A-B-A-B-A-B for example, each A-B may be referred to as a “bilayer.” Accordingly, a bilayer is a grouping of two sublayers. In some embodiments, the composition of layer A comprises zirconium nitride. In some embodiments, the composition of layer B comprises niobium nitride, tantalum nitride, hafnium nitride, niobium, tetragonal and/or monoclinic zirconium, tantalum, titanium, or hafnium. In some embodiments, the number of alternating sublayers is chosen so that the intermediate layer **70** reaches an overall thickness of, for example, up to about 2  $\mu\text{m}$ , up to about 4  $\mu\text{m}$ , up to about 6  $\mu\text{m}$ , or up to about 8  $\mu\text{m}$ .

[0159] Alternatively, the intermediate layer **70** may have a sequence of two repeating sublayers, for example an inner sublayer **86** and an intermediate sublayer **88**, and an outer sublayer **90**, as shown in FIGS. **3** and **5**. In some examples, the intermediate layer **70** includes a sequence A-(B-A).sub.n-C- including a repeating inner sublayer **86** and intermediate sublayer **88** where each of A and B are a different composition and n is at least 1, at least 2, at least 4, or at least 10, and where C is the outer sublayer **90** and has the same composition as one of the inner sublayer **86** or the intermediate sublayer **88**. In some embodiments, the composition of layer A comprises zirconium nitride. In some embodiments, the composition of layer B comprises niobium nitride, tantalum nitride, hafnium nitride, niobium, tetragonal and/or monoclinic zirconium, tantalum, titanium, or hafnium. In some embodiments, the outer sublayer **90** comprises zirconium nitride. In some embodiments, the intermediate layer **70** comprises a repeating sequence of i) a sublayer of zirconium nitride, ii) a sublayer of niobium, tetragonal and/or monoclinic zirconium, tantalum, titanium hafnium, niobium nitride, tantalum nitride, or hafnium nitride, and iii) capped by an outer sublayer **90** of zirconium nitride. In some embodiments, the number of alternating sublayers is chosen so that the intermediate layer **70** reaches a thickness of, for example, up to about 5  $\mu\text{m}$ .

[0160] Alternatively, the intermediate layer **70** may have a sequence of three repeating sublayers, for example, an inner sublayer **86**, an intermediate sublayer **88**, and an outer sublayer **90**. In some examples, the intermediate layer **70** includes a repeating sequence of the inner sublayer **86**, the intermediate sublayer **88**, and the outer sublayer **90**, having the composition -(A-B-C).sub.n- where each of A, B, and C are a different composition and n is at least 1, at least 2, at least 4, or at least 10. In this embodiment, inner sublayer **86** is A, intermediate sublayer **88** is B, and outer sublayer **90** is C. Where there is a repeat of three sublayers, such as A-B-C-A-B-C-A-B-C for example, each A-B-C may be referred to as a “trilayer.” Accordingly, a trilayer is a grouping of three sublayers. It should be noted that although the formula shows a sequence of A-B-C, any permutation on the order of the sublayers is contemplated, for example A-C-B, B-C-A, etc. It should be further noted that the intermediate layer **70** may comprise more than one sequence of sublayers, for example a sequence of -A-B-C-B-C-A- and the like. It should be further noted that the intermediate layer **70** may comprise more than one sequence of sublayers, for example a sequence of -A-B-A-B-A-B-A-C-A-C-A-C- and the like. It should be further noted that the intermediate layer **70** may comprise more than one sequence of sublayers, for example a sequence of -A-B-A-C-A-B-A-C-A-B-A-C- and the like. Referring to FIG. **13** for example, the intermediate layer **70** may comprise a first sequence of two sublayers having the composition -A-B- or (-A-B).sub.n where each of A and B are a different composition and n is at least 1, at least 2, at least 4, or at least 10 and a second sequence of two sublayers having the composition -A-C- or (-A-C).sub.n where each of A and C are a different composition and n is at least 1, at least 2, at least 4, or at least 10. Illustratively, any of composition A, B, or C can include niobium nitride, tantalum nitride, hafnium nitride, zirconium nitride, niobium, tetragonal and/or monoclinic zirconium, tantalum, titanium, or hafnium.

[0161] In some embodiments, the intermediate layer **70** comprises a zirconium nitride inner sublayer **86**, a niobium nitride intermediate sublayer **88**, and a zirconium nitride outer sublayer **90**. In some embodiments, the intermediate layer **70** comprises at least one zirconium nitride inner sublayer **86** and at least one niobium nitride intermediate sublayer **88**. In some embodiments, the

intermediate layer **70** comprises a number of alternating sublayers of zirconium nitride and niobium nitride. In some embodiments, the intermediate layer **70** comprises at least four alternating sublayers of the zirconium nitride inner sublayer **86** and the niobium nitride intermediate sublayer **88**. In illustrative embodiments, the zirconium nitride outer sublayer **90** is formed on the outermost niobium nitride intermediate sublayer **88**. It will be appreciated that although FIG. 3 shows a single sublayer of the zirconium nitride inner sublayer **86** and a single sublayer of the niobium nitride intermediate sublayer **88**, any number of alternating sublayers is contemplated.

[0162] In some embodiments, the inner sublayer **86** has a thickness of about 5 nm to about 500 nm. In some embodiments, the inner sublayer **86** has a thickness of at least about 0.05 nm, at least about 1 nm, at least about 5 nm, at least about 10 nm, at least about 50 nm, at least about 100 nm, at least about 150 nm, at least about 200 nm, at least about 250 nm, at least about 300 nm, at least about 350 nm, at least about 400 nm, at least about 450 nm, at least about 500 nm, or at least about 550 nm. In some embodiments, the inner sublayer **86** has a thickness of about 1 nm to about 200 nm or about 5 nm to about 100 nm. In some embodiments, the sublayer **86** has a thickness of about 30 nm, about 40 nm, about 50 nm, about 60 nm, about 70 nm, about 80 nm, about 90 nm, about 100 nm, about 110 nm, about 120 nm, about 130 nm, about 140 nm, about 150 nm, about 160 nm, about 170 nm, about 180 nm, about 190 nm, about 200 nm, about 210 nm, or about 220 nm. In some embodiments, the sublayer **86** has a thickness of about 65 nm, about 95 nm, about 115 nm, about 125 nm or about 205 nm.

[0163] In some embodiments, the inner sublayer **86** comprises at least about 90% zirconium nitride. In some embodiments, the inner sublayer **86** comprises at least about 95% zirconium nitride.

[0164] In some embodiments, the intermediate sublayer **88** has a thickness of about 5 nm to about 500 nm. In some embodiments, the intermediate sublayer **88** has a thickness of at least about 1 nm, at least about 5 nm, at least about 10 nm, at least about 50 nm, at least about 100 nm, at least about 150 nm, or at least about 200 nm, at least about 250 nm, at least about 300 nm, at least about 350 nm, at least about 400 nm, at least about 450 nm, at least about 500 nm, or at least about 550 nm. In some embodiments, the sublayer **88** has a thickness of about 30 nm, about 40 nm, about 50 nm, about 60 nm, about 70 nm, about 80 nm, about 90 nm, about 100 nm, about 110 nm, about 120 nm, about 130 nm, about 140 nm, about 150 nm, about 160 nm, about 170 nm, about 180 nm, about 190 nm, about 200 nm, about 210 nm, or about 220 nm. In some embodiments, the sublayer **88** has a thickness of about 65 nm, about 95 nm, about 115 nm, about 125 nm or about 205 nm.

[0165] In some embodiments, the intermediate sublayer **88** comprises at least about 90% niobium nitride, tantalum nitride, hafnium nitride, niobium, tetragonal and/or monoclinic zirconium, tantalum, titanium, or hafnium. In some embodiments, the intermediate sublayer **88** comprises at least about 95% niobium nitride, tantalum nitride, hafnium nitride, niobium, tetragonal and/or monoclinic zirconium, tantalum, titanium, or hafnium.

[0166] In some embodiments, the outer sublayer **90** has a thickness of about 1  $\mu\text{m}$  to about 5  $\mu\text{m}$ . In some embodiments, the outer sublayer **90** has a thickness of about 2  $\mu\text{m}$  to about 3  $\mu\text{m}$ . In some embodiments, the outer sublayer **90** has a thickness of at least about 0.5  $\mu\text{m}$ , at least about 1  $\mu\text{m}$ , at least about 1.5  $\mu\text{m}$ , at least about 2  $\mu\text{m}$ , at least about 2.5  $\mu\text{m}$ , at least about 3  $\mu\text{m}$ , at least about 3.5  $\mu\text{m}$ , at least about 4  $\mu\text{m}$ , at least about 4.5  $\mu\text{m}$ , at least about 5  $\mu\text{m}$ , or at least about 5.5  $\mu\text{m}$ . In some embodiments, the outer sublayer **90** forms the outer articular surface **50** of the femoral component **12** and coating **58**.

[0167] In some embodiments, the outer sublayer **90** comprises at least about 90% zirconium nitride. In some embodiments, the outer sublayer **90** comprises at least about 95% zirconium nitride.

[0168] In some illustrative embodiments, the outer layer **72** is configured to form the outer articular surface **50** of the coating **58** and hence the femoral component **12**. The outer layer **72** comprises an inner surface **82** and an outer surface **84**. The inner surface **82** of the outer layer **72** is located

between the intermediate layer **70** and the outer surface **84** of the outer layer **72**. The outer surface **84** of the outer layer **72** forms an outer surface **84** of the femoral component **12**. Illustratively, the outer surface **84** of the outer layer **72** forms the outer articular surface **50** of the femoral component **12** and is configured to interact and rotate about the tibial bearing **14**, as shown in FIG. 2.

[0169] In some examples, the outer layer **72** can be formed by depositing the outer layer **72** or by thermal growth through oxidation of a portion of the intermediate layer **70**. In some embodiments, the outer layer **72** has a thickness of at least about 0.2  $\mu\text{m}$ , at least about 0.5  $\mu\text{m}$ , at least about 1  $\mu\text{m}$ , at least about 2  $\mu\text{m}$ , at least about 3  $\mu\text{m}$ , at least about 4  $\mu\text{m}$ , at least about 5  $\mu\text{m}$ , or at least about 6  $\mu\text{m}$ . In some embodiments, the outer layer **72** has a thickness of at least about 50 nm, at least about 100 nm, at least about 150 nm, at least about 200 nm, or at least about 250 nm. When the outer layer **72** is deposited, the outer layer **72** can have a thickness of about 0.5  $\mu\text{m}$  to about 5  $\mu\text{m}$ . When the outer layer **72** is formed by oxidation, the outer layer **72** can have a thickness of about 100 nm to about 200 nm. In some embodiments, the outer layer **72** has a thickness of about 1000 nm, about 1500 nm, about 1800 nm, about 1900 nm, about 2000 nm, about 2400 nm, about 2500 nm, about 2800 nm, about 3000 nm, about 3100 nm, or about 3500 nm.

[0170] In an illustrative embodiment, the outer layer **72** is formed by oxidizing at least part of the intermediate layer **70**. For example, the outer surface **80** of the intermediate layer **70** can be oxidized to thermally grow the outer layer **72**. Illustratively, the thermal growing may occur by oxygen inserting into the lattice of portions, for example an outer portion, of the intermediate layer **70** to form an oxide. In some embodiments, the outer layer **72** comprises a ceramic. In illustrative embodiments, the ceramic of the outer layer **72** is an oxide of the composition of the intermediate layer **70**. In some embodiments, the outer layer **72** comprises an oxide of a niobium and zirconium alloy. In some embodiments, the outer layer **72** comprises zirconium oxide. In some embodiments, the outer layer **72** comprises niobium oxide. In some embodiments, the outer layer **72** comprises zirconium oxide and niobium oxide. In some embodiments, the outer layer **72** comprises monoclinic zirconium oxide. In some embodiments, the outer layer **72** comprises at least about 90% zirconium oxide. In some embodiments, the outer layer **72** comprises at least about 90% monoclinic zirconium oxide. In some embodiments, the outer layer **72** comprises monoclinic and/or tetragonal zirconium oxynitride. In some embodiments, the outer layer **72** comprises at least about 5% zirconium oxynitride. In some embodiments, the outer layer **72** comprises at least about 2% tetragonal zirconium oxide. In some embodiments, the outer layer **72** comprises at least about 2% cubic zirconium oxide. In some embodiments, the outer layer **72** comprises a ceramic that includes titanium. In one illustrative aspect, the outer layer **72** comprises titanium zirconium nitride. In some embodiments, the outer layer **72** comprises an oxidized metal and titanium.

[0171] In illustrative embodiments, the outer layer **72** is formed by depositing the outer layer **72**. In some illustrative embodiments, the outer layer **72** comprises deposited zirconium oxide. The deposited zirconium oxide of the outer layer **72** can be tetragonal zirconium oxide or monoclinic zirconium oxide. In an illustrative embodiment, when monoclinic zirconium oxide is deposited, a layer of tetragonal zirconium oxide will form between the monoclinic zirconium oxide and the intermediate layer **70**. In some illustrative embodiments, the outer layer **72** is formed by increasing the concentration of oxygen while depositing the outermost sublayer of the intermediate layer **70** such that the outer layer **72** is an oxide of the outermost sublayer of the intermediate layer **70**. For example, if the outermost sublayer (e.g., outer sublayer **90**) of the intermediate layer **70** is zirconium nitride, the outer layer **72** can be formed by increasing the oxygen concentration of the deposition to form oxidized zirconium nitride, sometimes called zirconium oxynitride. In some embodiments, the outer layer **72** may comprise zirconium oxynitride and niobium oxynitride.

[0172] In some embodiments, the third layer may be titanium zirconium nitride. Additionally, in some embodiments, the atomic percent of zirconium in the third layer may be 50 At % to 80 At %. In some embodiments, the atomic percent of zirconium in the third layer may be about 50 At %, about 55 At %, about 60 At %, about 65 At %, about 70 At %, about 75 At %, or about 80 At %. In



some embodiments, the atomic percent of zirconium in the third layer may be 30 At % to 85 At %. In some embodiments, the atomic percent of zirconium in the third layer may be about 30 At %, about 35 At %, about 40 At %, about 45 At %, about 50 At %, about 55 At %, about 60 At %, about 65 At %, about 70 At %, about 75 At %, about 80 At %, or about 85 At %.

[0173] In some embodiments, the bonding layer **68** comprises zirconium, the intermediate layer **70** comprises at least one zirconium nitride sublayer **86** and at least one niobium nitride sublayer **88**, and the outer layer **72** comprises oxidized zirconium.

[0174] Referring now to FIG. **4**, the femoral component **12** of an orthopaedic knee prosthesis **10** may be formed through a process **100**. In some embodiments, the process **100** comprises a first depositing step **110** of depositing the bonding layer **68**, a second depositing step **120** of depositing the intermediate layer **70**, and an oxidizing step **130**. In illustrative embodiments, the process **100** includes the steps of preparing the substrate **60** for the step of depositing **110**. In some embodiments, the process **100** includes finishing steps after the step of oxidizing **130** such as polishing.

[0175] Referring now to FIGS. **6-9**, shown are illustrative diagrammatic embodiments of a femoral component **12**. Illustratively, A denotes a sublayer and is shown in optionally repeating stack with a sublayer of zirconium nitride as shown in FIGS. **6-9**.

[0176] Referring now to FIGS. **10-15**, shown are illustrative diagrammatic embodiments of a femoral component **12**. In each example, A denotes a portion of the substrate **60**, B denotes a layer or sublayer comprising niobium, C denotes a layer or sublayer comprising zirconium nitride, one B and one C together form a bilayer, and D denotes a layer comprising niobium nitride. In some embodiments, the outer layer **72** of C denotes a layer comprising Ti-doped zirconium nitride. As shown illustratively in FIGS. **10-15**, the bonding layer **68** comprises niobium. In some embodiments, bonding layer **68** may comprise niobium, zirconium, titanium, tantalum, platinum, molybdenum, alloys thereof, or combinations thereof.

[0177] As shown in the embodiment of FIG. **10**, the intermediate layer **70** includes a number of alternating sublayers (C and B) such that  $n=24$  and the outer layer **72** is a single layer C. In the embodiment of FIG. **11**, the intermediate layer **70** is a single layer D. In this embodiment, single layer D may be further processed to form the outer articular surface **50** (e.g., oxidized). In the embodiment of FIG. **12**, the intermediate layer **70** includes a number of alternating sublayers (C and B) and (C and D) such that  $n=24$  and the outer layer **72** is a single layer C. In the embodiment of FIG. **13**, the intermediate layer **70** includes a number of alternating sublayers (C and D) and (B and C) such that  $n=24$  and the outer layer **72** is a single layer C. In the embodiment of FIG. **14**, the intermediate layer **70** includes a number of alternating sublayers (C-D-C-B) such that  $n=24$  and the outer layer **72** is a single layer C. In the embodiment of FIG. **15**, the intermediate layer **70** includes a number of alternating sublayers (C and D) such that  $n=24$  and the outer layer **72** is a single layer C.

[0178] The intermediate layer **70** can be a single layer, such as the layer comprising niobium nitride in FIG. **11**. Alternatively, the intermediate layer **70** can include repeating stacks of layers. In some embodiments, the intermediate layer **70** comprises a repeating stack of a sublayer comprising zirconium nitride and a sublayer comprising niobium, as illustratively shown in FIG. **10**. In some embodiments, the intermediate layer **70** comprises a first repeating stack of a sublayer **86** comprising zirconium nitride and a sublayer **88** comprising niobium and a second repeating stack of a sublayer **86** comprising zirconium nitride and a sublayer **88** comprising niobium nitride, as illustratively shown in FIGS. **12** and **13**. In some embodiments, the intermediate layer **70** comprises a repeating stack of a sublayer **86** comprising zirconium nitride, a sublayer **88** comprising niobium nitride, a sublayer **86** comprising zirconium nitride, and a sublayer **90** comprising niobium, as illustratively shown in FIG. **14**. In some embodiments, the intermediate layer **70** comprises a repeating stack of a sublayer **86** comprising zirconium nitride and a sublayer **88** comprising niobium nitride, as illustratively shown in FIG. **15**.

[0179] In the illustrative embodiments of FIGS. **10-15**, the bonding layer **68** has a thickness of about 0.5  $\mu\text{m}$  or about 5  $\mu\text{m}$ . Each sublayer **86** and **88**, except for the sublayer **90** furthest the substrate, of the intermediate layer **70** has a thickness of about 125 nm. Illustratively, each of the embodiments in FIGS. **10-15** includes an outer sublayer **90** of zirconium nitride having a thickness of about 3  $\mu\text{m}$ . This outer layer can optionally undergo further processing to form the outer layer **72**.

[0180] Alternatively, the intermediate layer **70** may comprise repeating sublayer sequences, wherein repeats have a uniform thickness throughout the span of the intermediate layer **70** but the individual sublayers' thicknesses vary. Referring to FIG. **17**, sublayers **86** and **88** are stacked in a repeating sequence with each repeat having a combined thickness that is uniform in the intermediate layer **70**, but each individual thickness of sublayer **86** or sublayer **88** is varied. For example, the percentage thickness of sublayer **86** may decrease incrementally and the percentage thickness of sublayer **88** may increase incrementally for each subsequent sequence. In one embodiment, a sublayer **86** may be 75% of the combined thickness and sublayer **88** may be 25% of the combined thickness of the first sequence. Then in the second sequence, sublayer **86** may comprise 70% and sublayer **88** may comprise 30%. Following that, the third sequence may comprise 65% sublayer **86** and 35% sublayer **88**. In this manner, sublayer **86** and sublayer **88** are graded stepwise over the span of the intermediate layer **70**. In some embodiments, sublayer **86**'s presence in a sequence is reduced by 5% in each subsequent sequences and sublayer **88**'s presence in a sequence is increased by 5% over the span of intermediate layer **70**. Accordingly, each sequence of sublayer **86** and sublayer **88** maintains a uniform thickness throughout the span of intermediate layer **70**. Further exemplary embodiments are provided in Tables 3, 4, and 5. In some embodiments, the amount present of sublayer **86** in a sequence reduces by about 2%, about 3%, about 4%, about 5%, about 6% about 7%, about 8%, about 9% about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20%, about 21%, about 22%, about 23%, about 24%, or about 25% in each subsequent sequence. Reciprocally, in some embodiments, the amount present of sublayer **88** increases about 2%, about 3%, about 4%, about 5%, about 6% about 7%, about 8%, about 9% about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20%, about 21%, about 22%, about 23%, about 24%, or about 25% in each subsequent sequence.

[0181] In some embodiments, the first depositing step **110** deposits a material and forms the bonding layer **68** on the condylar surface **66** of the substrate **60**. In some embodiments, the first depositing step **110** is performed by physical vapor deposition (PVD). In some embodiments, the first depositing step **110** is performed by a magnetron sputter system. In other embodiments, PVD may be performed using HiPIMS, IBAD, or other deposition systems.

[0182] In some embodiments, the second depositing step **120** forms the intermediate layer **70** on the outer surface **76** of the bonding layer **68**. In some embodiments, the second depositing step **120** is performed by PVD. In some embodiments, the step of depositing **120** is performed by a magnetron sputter system.

[0183] In some embodiments, the second depositing step **120** comprises depositing the inner sublayer **86**. Illustratively, the inner sublayer **86** is deposited onto the bonding layer **68** by the second depositing step **120**.

[0184] In some embodiments, the second depositing step **120** comprises depositing the intermediate sublayer **88** onto the inner sublayer **86**. In illustrative embodiments, the second step of depositing **120** includes repeating the steps of depositing the inner sublayer **86** and the intermediate sublayer **88** until a desired number of sublayers is achieved. Then, the outer sublayer **90** may be deposited on the outermost deposited sublayer (e.g., the inner sublayer **86** or the intermediate sublayer **88**).

[0185] In some embodiments, the second depositing step **120** comprises depositing the outer sublayer **90** onto the intermediate sublayer **88**. In illustrative embodiments, the second step of

depositing **120** includes repeating the steps of depositing the inner sublayer **86**, the intermediate sublayer **88**, and the outer sublayer **90** until a desired number of sublayers is achieved. Optionally, a final outer sublayer **90** is deposited on the outermost sublayer (e.g., the inner sublayer **86**, the intermediate sublayer **88**, or the outer sublayer **90**).

[0186] In some embodiments, the second depositing step **120** comprises depositing a zirconium nitride inner sublayer **86** onto the bonding layer **68**, depositing a niobium nitride intermediate sublayer **88** on the zirconium nitride inner sublayer **86**, and depositing a zirconium nitride outer sublayer **90** on the niobium nitride intermediate sublayer **88**.

[0187] In some embodiments, the second depositing step **120** is performed to produce a number of alternating sublayers of the zirconium nitride inner sublayer **86** and the niobium nitride intermediate sublayer **88**. In some embodiments, the steps of depositing the zirconium nitride inner sublayer **86** and the niobium nitride intermediate sublayer **88** are repeated until a desirable thickness is obtained. In some embodiments, the thickness is up to 6  $\mu\text{m}$ .

[0188] In some embodiments, the second depositing step **120** deposits an outer sublayer **90** of zirconium nitride for subsequent processing.

[0189] In some embodiments, the step of depositing **120** is performed by PVD. In some embodiments, the first depositing step **110** is performed by a magnetron sputter system. In other embodiments, PVD may be performed using HiPIMS, IBAD, or other deposition systems.

[0190] In some embodiments, the oxidizing step **130** oxidizes a portion of the intermediate layer **70** to form the outer layer **72**. In some embodiments, the oxidizing step **130** is performed as described in U.S. Pat. Nos. 6,447,550 and 5,324,009, the entirety of each of which is expressly incorporated herein by reference. In some embodiments, the oxidizing step **130** oxidizes at least a portion of the outer surface **80** of the intermediate layer **70**. In some embodiments, the oxidizing step **130** oxidizes at least a portion of the zirconium nitride outer sublayer **90** into oxidized zirconium thus forming the outer layer **72**. In some embodiments, the oxidizing step **130** oxidizes, partially or completely, the exposed surface of the zirconium nitride outer sublayer **90** into monoclinic oxidized zirconium. In some embodiments, the outer layer **72** comprises zirconium oxynitride. In some embodiments, the outer layer **72** comprises at least about 5% zirconium oxynitride.

[0191] In some embodiments, the oxidizing step **130** is performed by heating an environment comprising oxygen. In some embodiments, the environment is at a temperature of least 500° C. or about 540° C. In some embodiments, the environment is at a temperature of about 500° C. to about 600° C. In an illustrative embodiment, the environment comprises about 2.5% oxygen in argon. In some embodiments, the oxidizing step **130** is performed for about 5 hours.

[0192] In alternative embodiments, the process **100** comprises a step of depositing the outer layer **72** (not shown). The step of depositing the outer layer **72** is performed by PVD, which may be performed using a magnetron sputter system. In other embodiments, PVD may be performed using HiPIMS, IBAD, or other deposition systems. In some embodiments, the step of depositing the outer layer **72** deposits a layer of ceramic, for example zirconium oxide.

[0193] In some embodiments, the deposited zirconium oxide forming the outer layer **72** comprises tetragonal, monoclinic, or cubic zirconium oxide. In some embodiments, the deposited zirconium oxide forming the outer layer **72** comprises tetragonal, monoclinic, or cubic zirconium oxynitride.

[0194] In some embodiments, the coating **58** is configured to resist chipping when a force is applied. For example, the embodiment of FIG. **19**, shows the ability of a multi-layer coating **58** to resist chipping and arrest cracking when a force of about 9 N is applied. Cracking occurs when the tensile strength of the material fails and begins to fracture. As is illustrated in FIG. **19**, the niobium sublayer arrests the cracks that are forming in the zirconium nitride sublayers. Compare the toughness and ductility to FIG. **20**. As illustrated in FIG. **20**, a monolayer of zirconium nitride developed much longer cracks compared to the multilayer coating (i.e., Sample 5 discussed below) in FIG. **19**.

Examples

[0195] In the following Examples, a series of monolayer zirconium nitride (ZrN) coatings with a niobium (Nb) bonding layer were produced and tested. Additionally, various multilayer Nb/ZrN coatings of varying architecture and thickness were produced and tested. Table 1 provides information on each sample. Sample coatings 1-11 used a Nb bonding layer of about 140 nm to 400 nm to facilitate adhesion between the Ti-6Al-4V substrate and the coating. The coatings were prepared by deposition using either magnetron sputtering with enrichment of the plasma with ions produced by thermionic emission (Sample 5) from electrodes using the chamber walls as the anode (Plasma Enhanced Magnetron Sputtering), or via unbalanced magnetron sputtering to achieve the same objective of increasing the ionization rate of the plasma. The unbalanced magnetron deposition was performed on a Flexicoat 1200 platform. Deposition parameters were selected from a series of experimental runs performed prior to producing the test samples described below.

TABLE-US-00001

Coating	Type	Monolayer (M)	Total Sample
1	Mono	2 M Nb—ZrN 2 microns	2
2	Mono	5 M Nb—ZrN 5 microns	5
3	Mono	8 M Nb—ZrN 8 microns	8
4	Mono	10 M Nb—ZrN 10 microns	10
5	ML	nom ML Nb—[Nb/ZrN].sub.17—ZrN 9 microns	9
6	ML	+ 20 ML Nb—[Nb/ZrN].sub.17—ZrN 10.7 microns	10.7
7	ML	— 20 ML Nb—[Nb/ZrN].sub.17—ZrN 7 microns	7
8	ML	— 40 ML Nb—[Nb/ZrN].sub.17—ZrN 5.2 microns	5.2
9	MLG	— nom ML Nb—[Nb/ZrN].sub.17—ZrN 7 microns	7
10	MLG	+ 25 ML Nb—[Nb/ZrN].sub.17—ZrN 8.7 microns	8.7
11	MLG	— 25 ML Nb—[Nb/ZrN].sub.17—ZrN 5.5 microns	5.5
12	LCS	TiN M TiN 10 microns	10

[0196] Monolayer (Samples 1-4): Ti-Al6-V4 (“Ti-6-4”) coupons were polished to less than 40 nm roughness average (Ra) and were cleaned in preparation for thin film deposition. Four monolayer ZrN coatings with thicknesses ranging from 2 pins to 10 pins were produced by unbalanced magnetron sputtering in a Flexicoat 1200 coating platform. Coating thickness was verified by examination of cross sections produced by either mounting and cross sectioning or by Focused Ion Beam (FIB) followed by examination in a scanning electron microscope (SEM).

[0197] Multilayer (Samples 5-8): Ti-6-4 coupons were polished to less than 40 nm Ra and were cleaned in preparation for thin film deposition. A series of multilayer Nb/ZrN coatings were produced by unbalanced magnetron sputtering in a Flexicoat 1200 coating platform. Thickness of the various sublayers within the intermediate layer were determined by examination of cross sections produced by either mounting and cross sectioning or by FIB sectioning followed by examination in an SEM. All multilayered coatings (i.e., Samples 5-11) had 34 sublayers, or described below as 17 bilayers, of Nb/ZrN with Nb representing 55-60% of the bilayer thickness. Sample 5, designated ML-nom is a coating designed as having a potential nominal thickness with each Nb/ZrN bilayer having a thickness of about 300 nm, a ZrN outer layer thickness of about 2500 nm, and a Nb bonding layer thickness of about 400 nm. This coating is shown in cross-section in FIG. 16 with the layer thicknesses summarized in Table 2. Three additional multilayer (ML) coatings were produced by growing all layers by 20% (ML+20), shrinking all layers by 20% (ML-20), and shrinking all layers by 40% (ML-40) as compared to ML-nom (Sample 5). Samples 5-8 are summarized in Table 2.

TABLE-US-00002

Sample	Layer	bi-	sublayer	sublayer	layer	thickness	No. (nm)	layers	(nm)	(nm)	(nm)	(nm)	(nm)
5	2500	17	136	178	400	8238	6	3100	17	163.2	213.6	480	9985.6
7	1900	17	108.8	142.4	320	6490.4	8	1500	17	81.6	106.8	240	4702.8

[0198] Multilayer Graded (Samples 9-11): Finally, coatings with a graded stiffness were prepared in a series of 3 multilayer graded coatings with the same bilayer number (i.e., 17) of the non-graded structures described above, but with the % Nb in the first bilayer set to about 75% of the bilayer thickness and then reduced by 5% in subsequent bilayer's such that bilayer 17 contained about 33% Nb. A potential nominal graded coating with 2400 nm ZrN outer layer and total thickness of 8738

nm was produced and is identified as MLG-Nom (i.e., Sample 9) and is shown in FIB cross section in FIG. 17 and summarized in Table 3. All layers were increased by 25% (MLG+25) and reduced by 25% in MLG-25 with summary thicknesses shown in Tables 4 and 5.

TABLE-US-00003 TABLE 3 Thicknesses and parameters of the Multilayer Graded Coating MLG – Nom (Sample 9) Thickness of Coating Components Bilayer # within the Nb ZrN intermediate sublayer sublayer Bilayer layer (nm) (nm) thickness 1 188 63 251 2 179 73 251 3 170 82 251 4 161 90 251 5 153 98 251 6 145 106 251 7 138 113 251 8 131 120 251 9 125 126 251 10 118 133 251 11 113 139 251 12 107 144 251 13 102 150 251 14 97 155 251 15 92 160 251 16 87 164 251 17 83 168 251 Nb bonding layer (nm) 320 ZrN outer layer (nm) 2400 Total Coating thickness (nm) 6990

TABLE-US-00004 TABLE 4 Thickness and parameters of the Multilayer Graded Coating MLG + 25 (Sample 10) Thickness of Coating Components Bilayerlayer # within the Nb ZrN Bilayer intermediate sublayer sublayer thickness layer (nm) (nm) nm 1 235 79 314 2 223 91 314 3 212 102 314 4 201 113 314 5 191 123 314 6 182 132 314 7 173 141 314 8 164 150 314 9 156 158 314 10 148 166 314 11 141 173 314 12 134 180 314 13 127 187 314 14 121 193 314 15 115 199 314 16 109 205 314 17 103 211 314 Nb bonding layer (nm) 400 ZrN outer layer (nm) 3000 Total Coating thickness (nm) 8738

TABLE-US-00005 TABLE 5 Thickness and parameters of the Multilayer Graded Coating MLG – 25 (Sample 11) Thickness of Coating Components Bilayer # within the Nb ZrN Bilayer intermediate sublayer sublayer thickness layer (nm) (nm) nm) 1 141 47 188 2 134 54 188 3 127 61 188 4 121 68 188 5 115 74 188 6 109 79 188 7 104 85 188 8 98 90 188 9 94 95 188 10 89 100 188 11 84 104 188 12 80 108 188 13 76 112 188 14 72 116 188 15 69 120 188 16 65 123 188 17 62 126 188 Nb bonding layer (nm) 240 ZrN outer layer (nm) 1800 Total coating thickness (nm) 5243 [0199] Control (Sample 12): Samples 5-11 were compared to the monolayered coatings (Samples 1-4) and a commercially available coating to demonstrate the advantages and improvements in the described coatings.

[0200] Scratch testing. A scratch test was developed that reproduced scratches observed on Cobalt chromium (CoCr) femoral retrievals. A diamond tip with either a 20  $\mu$ m or 200  $\mu$ m radius, applied loads from 1-6 Newtons (N) or from 3-36 N, respectively, to reproduce the majority of scratches on retrievals and was applied to the Monolayer and Multilayer samples described above as well as the Commercial Comparator.

[0201] The results shown in FIG. 18 and FIG. 21 and tabulated in Table 6 and Table 7, respectively, show that the multilayer Nb/ZrN samples resisted chipping and delamination better than those produced with a monolayer of ZrN (Samples 2 and 4) and to a similar extent as the Commercial Comparator (Sample 12) of similar thickness. FIG. 19 shows a cross section of multilayer coating ML-Nom (Sample 5) after scratch testing, which shows how the ductile Nb layers arrest cracks that begin in the harder and more brittle ZrN layers.

TABLE-US-00006 TABLE 6 Results of Scratch Test (shown graphically in FIG. 18) on the various coating samples with increasing force. Sample Name 20  $\mu$ m Indenter (No.) 1N 3N 6N 9N Mono-2 (1) Chipping Delam Delam Delam Mono-5 (2) Chipping Delam Delam Mono-8 (3) Chipping Chipping Chipping Mono-10 (4) Chipping Chipping ML – nom (5) Chipping ML + 20 (6) ML – 20 (7) Chipping Delam ML – 40 (8) Delam Delam MLG – nom (9) Chipping Delam MLG + 25 (10) Chipping Chipping MLG – 25 (11) Chipping Chipping Chipping

TABLE-US-00007 TABLE 7 Results of Scratch Test (shown graphically in FIG. 21) on the various samples with increasing force. Sample Name 200  $\mu$ m Indenter (No.) 3N 6N 9N 18N 27N 36N Mono-2 (1) Chipping Delam Delam Mono-5 (2) Chipping Delam Mono-8 (3) Chipping Chipping Mono-10 (4) Chipping ML-nom (5) Chipping ML+20 (6) ML-20 (7) Delam ML-40 (8) Chipping Delam MLG-nom (9) Chipping MLG+25 (10) Chipping MLG-25 (11) Chipping Delam LCS TiN (12) Chipping Delam

[0202] While the disclosure has been illustrated and described in detail in the drawings and foregoing description, such an illustration and description is to be considered as exemplary and not

restrictive in character, it being understood that only illustrative embodiments have been shown and described and that all changes and modifications that come within the spirit of the disclosure are desired to be protected.

[0203] There are a plurality of advantages of the present disclosure arising from the various features of the method, apparatus, and system described herein. It will be noted that alternative embodiments of the method, apparatus, and system of the present disclosure may not include all of the features described yet still benefit from at least some of the advantages of such features. Those of ordinary skill in the art may readily devise their own implementations of the method, apparatus, and system that incorporate one or more of the features of the present invention and fall within the spirit and scope of the present disclosure as defined by the appended claims.

## Claims

**1.-20.** (canceled)

**21.** An orthopaedic knee implant comprising: a femoral component configured to be coupled to a distal end of a patient's femur, the femoral component comprising (i) a substrate comprising a titanium alloy having (a) a condylar surface that is curved in a sagittal plane and (b) a bone-facing surface positioned opposite the condylar surface; and (ii) a coating disposed on the condylar surface, the coating comprising (a) a bonding layer comprising niobium, zirconium, titanium, tantalum, platinum, molybdenum, an alloy thereof, or combinations thereof, (b) an outer ceramic layer, and characterized in that the coating comprises: (c) a plurality of alternating sublayers positioned between and interconnecting the bonding layer and the outer ceramic layer, wherein (i) the plurality of alternating sublayers are configured to resist crack propagation from the outer ceramic layer, the plurality of alternating sublayers include a number of metallic sublayers and a number of ceramic sublayers that are harder than the metallic sublayers, and (ii) the outer ceramic layer forms an outer articular surface of the femoral component and is shaped to contact a concave proximal surface of a tibial bearing.

**22.** The implant of claim 21, wherein the plurality of alternating sublayers comprises at least eight sublayers of alternating zirconium nitride and niobium nitride sublayers.

**23.** The implant of claim 22, wherein each zirconium nitride sublayer of the alternating sublayers has a thickness of about 5 nm to about 200 nm.

**24.** The implant of claim 23, wherein the plurality of alternating sublayers have a thickness of about 3  $\mu\text{m}$  to about 8  $\mu\text{m}$ .

**25.** The implant of claim 21, wherein the outer ceramic layer comprises at least about 90% monoclinic oxidized zirconium.

**26.** The implant of claim 25, wherein the outer ceramic layer has a thickness of about 100 nm to about 5  $\mu\text{m}$ .

**27.** The implant of claim 26, wherein at least one sublayer of the plurality of alternating sublayers comprises at least about 95% zirconium nitride.

**28.** The implant of claim 21, wherein at least one sublayer of the plurality of alternating sublayers has a thickness of about 5 nm to about 500 nm.

**29.** The implant of claim 28, wherein at least one sublayer of the plurality of alternating sublayers comprises at least about 95% niobium nitride.

**30.** The implant of claim 21, wherein the bonding layer comprises at least about 90% zirconium.

**31.** The implant of claim 30, wherein the bonding layer has a thickness of about 50 nm to about 2  $\mu\text{m}$ .

**32.** The implant of claim 21, wherein the femoral component comprises a bone-engaging layer disposed on the bone-facing surface.

**33.** The implant of claim 32, wherein the bone-engaging layer is porous.

**34.** The implant of claim 21, wherein the plurality of alternating sublayers comprises an inner

sublayer and an outer sublayer, optionally wherein the inner sublayer and the outer sublayer have the same composition.

**35.** The implant of claim 34, wherein the plurality of alternating sublayers comprises an intermediate sublayer having a composition different from the inner sublayer, the outer sublayer, or both.

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