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Wear resistant article and method of making

Abstract

A wear resistant article including a substrate and a bulk metallic glass coating including an alloy of a base metal, a transition metal, boron, and silicon, wherein the bulk metallic glass coating has a thickness of about 0.05 millimeter or greater and a functionally graded microstructure. A method of producing an article with a wear resistant coating by additively printing a bulk metallic glass coating onto at least a portion of the article.

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References Cited

U.S. PATENT DOCUMENTS

Patent No.	Issued Date	Patentee Name	U.S. Cl.	CPC
10214824	12/2018	Bogue et al.	N/A	N/A
10626883	12/2019	Mironets et al.	N/A	N/A
11014162	12/2020	Hofmann	N/A	N/A
11905578	12/2023	Hofmann et al.	N/A	N/A
2010/0006185	12/2009	Johnson	148/403	C22C 45/00
2011/0048587	12/2010	Vecchio	148/403	C21D 1/26
2011/0142678	12/2010	Santiago et al.	N/A	N/A
2011/0204700	12/2010	Blue et al.	N/A	N/A
2015/0314566	12/2014	Poole	428/614	C22C 45/00
2016/0251970	12/2015	Strock et al.	N/A	N/A
2018/0363477	12/2017	Hafner et al.	N/A	N/A
2019/0001440	12/2018	Zrodowski	N/A	B22F 10/36
2019/0301291	12/2018	Uihlein et al.	N/A	N/A
2020/0362879	12/2019	Mironets et al.	N/A	N/A
2020/0376809	12/2019	Vogli	N/A	B23K 20/24
2022/0212254	12/2021	Hofmann	N/A	B33Y 10/00
2023/0053703	12/2022	Cho et al.	N/A	N/A
2023/0056819	12/2022	Cho et al.	N/A	N/A

FOREIGN PATENT DOCUMENTS

Patent No.	Application Date	Country	CPC
2017179422	12/2016	JP	N/A
WO200694935	12/2005	WO	N/A

OTHER PUBLICATIONS

Deng et al., “The fabrication and property evaluation of Zr—Ti—B—Si thin film metallic glass materials”, 2014, Surface & Coatings Technology, vol. 259, pp. 115-122. (Year: 2014). cited by examiner

Basu et al., Bulk Metallic Glasses: A New Class of Engineering Materials, Sadhana, vol. 28, Parts 3 & 4, Jun./Aug. 2003, pp. 783-798. cited by applicant

Frazier, Metal Additive Manufacturing: A Review, Journal of Materials Engineering and Performance, vol. 23, No. 6, 2014, pp. 1917-1928. cited by applicant

Inoue, Bulk Glassy Alloys: Historical Development and Current Research, Advanced Materials and Materials Genome—Review, Engineering, vol. 1, Issue 2, 2015, pp. 185-191. cited by applicant

Mahbooba et al., Additive Manufacturing of an Iron-Based Bulk Metallic Glass Larger Than the Critical Casting Thickness, Applied Materials Today, vol. 11, 2018, pp. 264-269. cited by applicant

Shen et al., Evolution of Crystalline Phase During Laser Processing of Zr—Based Metallic Glass, Journal of Non-Crystalline Solids, vol. 481, 2018, pp. 299-305. cited by applicant

Sohrabi et al., Additive Manufacturing of Bulk Metallic Glasses—Process, Challenges and Properties: A Review, Metals, vol. 11, No. 8, 2021, 59 Pages. https://doi.org/10.3390/met11081279. cited by applicant
Suryanarayana et al., Chapter 3: Glass-Forming Ability of Alloys, Bulk Metallic Glasses, Second Edition, 2018, pp. 45-137. https://doi.org/10.1201/9781315153483. cited by applicant
Williams et al., Laser Processing of Bulk Metallic Glass: A Review, Journal of Materials Processing Technology, vol. 247, 2017, pp. 73-91. https://doi.org/10.1016/j.imatprotec.2017.03.034. cited by applicant
Wrobel et al., A Comprehensive Review of Additive Manufacturing in Construction of Electrical Machines, IEEE Transactions on Energy Conversion, vol. 35, No. 2, Jun. 2020, pp. 1054-1064. https://doi.org/10.1109/TEC.020.2964942. cited by applicant
Xia et al., Calculation of Crystallization Start Line for Zr.SUB.48.Cu.SUB.45.Al.SUB.7 .Bulk Metallic Glass at a High Heating and Cooling Rate, Journal of Alloys and Compounds, vol. 484, Issues 1-2, 2009, pp. 698-701. https://doi.org/10.1016/j.jallcom.2009.05.019. cited by applicant
Zhang et al., Additive Manufacturing of Functionally Graded Materials: A Review, Materials Science & Engineering: A, vol. 764, Sep. 2019, 138209. https://doi.org/10.1016/j.msea.2019.138209. cited by applicant

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Background/Summary

PRIORITY INFORMATION
(1) The present application claims priority to Indian Patent Application Number 202311001109 filed on Jan. 5, 2023.
FIELD
(2) The present disclosure relates to wear resistant articles and their methods of making via additively printing.
BACKGROUND
(3) The operating environment within a gas turbine engine is both thermally and chemically hostile. High temperature iron, nickel and cobalt-based superalloys have been developed for engine components. In addition, titanium alloys are also used for particular applications, such as the leading edges of composite fan blades. Components formed from such alloys often cannot withstand long service exposures if located in certain sections of a gas turbine engine, such as the turbine and/or combustor sections. Hot corrosion of gas turbine engine components generally occurs when sulfur compounds and/or dust attacks the components' surfaces. Sources of sulfur compounds include fuel and ingestion from environment. Dust predominately comes from environment ingestion. The presence of corrosive compounds and/or dust is responsible for corrosion of hot section components like compressors and/or disks.
(4) Current erosion and wear coatings are predominantly ceramic metal composites (cermets). However, cermet coatings have moderate strength and low ductility. Moreover, they are applied via line-of-sight processes, which are limited to non-complex, external surfaces. In addition, current metallic glass coatings are typically thin films. Therefore, improved anti-corrosion coatings are needed.

Description

BRIEF DESCRIPTION OF THE DRAWINGS

(1) A full and enabling disclosure of the present disclosure, including the best mode thereof, directed to one of ordinary skill in the art, is set forth in the specification, which makes reference to the appended figures, in which:

(2) FIG. **1** is a schematic, cross-sectional view of an exemplary gas turbine engine;

(3) FIG. **2** is an enlarged view of a portion of the exemplary gas turbine engine of FIG. **1**, showing a fan blade and a portion of a fan hub and shroud where a wear resistant coating may be located according to exemplary embodiments of the present disclosure;

(4) FIG. **3** is a cross-sectional view of a trailing edge of a blade where a wear resistant coating may be located according to exemplary embodiments of the present disclosure;

(5) FIG. **4** is a cross-sectional view of a leading edge of the blade where a wear resistant coating may be located according to exemplary embodiments of the present disclosure; and

(6) FIG. **5** is a cross-sectional representation of a wear resistant coating applied to a substrate component according to exemplary embodiments of the present disclosure.

DETAILED DESCRIPTION

(7) Reference will now be made in detail to present embodiments of the disclosure, one or more examples of which are illustrated in the accompanying drawings. The detailed description uses numerical and letter designations to refer to features in the drawings. Like or similar designations in the drawings and description have been used to refer to like or similar parts of the disclosure.

(8) The word “exemplary” is used herein to mean “serving as an example, instance, or illustration.” Any implementation described herein as “exemplary” is not necessarily to be construed as preferred or advantageous over other implementations. Additionally, unless specifically identified otherwise, all embodiments described herein should be considered exemplary.

(9) The singular forms “a”, “an”, and “the” include plural references unless the context clearly dictates otherwise.

(10) The term “at least one of” in the context of, e.g., “at least one of A, B, and C” refers to only A, only B, only C, or any combination of A, B, and C.

(11) In the present disclosure, when a layer is being described as “on” or “over” another layer or substrate, it is to be understood that the layers can either be directly contacting each other or have another layer or feature between the layers, unless expressly stated to the contrary. Thus, these terms are simply describing the relative position of the layers to each other and do not necessarily mean “on top of” since the relative position above or below depends upon the orientation of the device to the viewer.

(12) Chemical elements are discussed in the present disclosure using their common chemical abbreviation, such as commonly found on a periodic table of elements. For example, hydrogen is represented by its common chemical abbreviation H; helium is represented by its common chemical abbreviation He; and so forth.

(13) Wear resistant articles are generally provided, along with methods of their formation via additive manufacturing processes. The wear resistant article generally includes a substrate and a bulk metallic glass coating. The bulk metallic glass coating includes an alloy of a base metal, a transition metal, boron, and silicon. The bulk metallic glass coating has a thickness of 50 micrometers (μm) or greater and a functionally graded microstructure. In one embodiment, the method includes additively printing a bulk metallic glass coating onto at least a portion of the article. The bulk metallic glass coating incudes an alloy of a base metal, a transition metal, boron, and silicon. The bulk metallic glass coating has a thickness of 50 μm or greater.

(14) As noted above, iron, nickel and cobalt-based superalloys have been developed for engine components subjected to high temperatures. In addition, titanium alloys have been used for the

leading edges of composite fan blades. These alloys are subjected to foreign object damage (FOD) such as sand, dust, bird strikes, hail stones as well as erosion from moisture. To improve the wear-resistance and service-life of these engine components inexpensive bulk metallic glass alloy compositions including, for example, Ti-TM-B—Si, Fe-TM-B—Si, Ni/Co-TM-B—Si, Al-TM-B—Si (where “TM” refers to a transition metal or mixture of transition metals) may be additively printed on to surface thereof, such as on the leading edge thereof.

(15) Referring now to the drawings, wherein identical numerals indicate the same elements throughout the figures, FIG. **1** provides a schematic, cross-sectional view of a gas turbine engine **10** that includes a propulsion apparatus. While the illustrated example is a high-bypass turbofan engine, the principles of the present disclosure are also applicable to other types of engines, such as low-bypass turbofans, turbojets, turboprops, etc. The engine **10** has a longitudinal center line or axis **11**. As used herein, the terms “axial” and “longitudinal” both refer to a direction parallel to the center-line axis **11**, while “radial” refers to a direction perpendicular to the axial direction, and “tangential” or “circumferential” refers to a direction mutually perpendicular to the axial and radial directions. As used herein, the terms “forward” or “front” refer to a location relatively upstream in an air flow passing through or around a component, and the terms “aft” or “rear” refer to a location relatively downstream in an air flow passing through or around a component. The direction of this flow is shown by the arrow “F” in FIG. **1**. These directional terms are used merely for convenience in description and do not require a particular orientation of the structures described thereby.

(16) The engine **10** has a fan **12**, booster **16**, compressor **18**, combustor **20**, high pressure turbine or “HPT” **22**, and low-pressure turbine or “LPT” **24** arranged in serial flow relationship. In operation, pressurized air from the compressor **18** is mixed with fuel in the combustor **20** and ignited, thereby generating combustion gases. Some work is extracted from these gases by the high-pressure turbine **22** which drives the compressor **18** via an outer shaft **26**. The combustion gases then flow into the low-pressure turbine **24**, which drives the fan **12** and booster **16** via an inner shaft **28**.

(17) The fan **12** is one example of a propulsion apparatus. It will be understood that the principles described herein are applicable to other kinds of propulsion apparatus operable to produce propulsive thrust, such as ducted propellers or compressors. Instead of a gas turbine engine, the fan **12** or other propulsion apparatus could be driven by another type of prime mover such as: heat engines, motors (e.g. electric, hydraulic, or pneumatic), or combinations thereof (for example electric hybrid drivetrains). The propulsion apparatus may be driven directly by a prime mover, or through an intermediate geartrain.

(18) Referring to FIG. **2**, fan **12** includes a plurality of fan blades **30**. The fan blades **30** are mounted to a fan disk **32** (shown in FIG. **1**) that extends from a root **33** to a tip **34** and defines a length L. Additionally, each fan blade **30** includes a pressure side **35**, a suction side **36**, and reinforcement that includes a leading edge **38**, and a trailing edge **39**.

(19) As shown in FIG. **2**, the fan casing **40** includes an inner annular surface **50**. The inner annular surface **50** has a generally circular cross-section and defines an inner diameter of the inner casing **40**. The inner annular surface **50** is configured to channel the incoming air through the fan **12** (FIG. **1**) to ensure that the fan **12** (FIG. **1**) will compress the bulk of the air entering the engine **10**. By way of example and not limitation, the fan casing **40** can be made of the following: a metal, a composite material, and a combination thereof.

(20) The inner casing **40** includes a thin layer of shroud material **41** positioned adjacent to a blade tip path defined by the blades **30** of the fan **12**. The shroud material **41** is supported by a containment structure **43**. According to the illustrated embodiment, the containment structure **43** is generally solid and is not configured as a honeycomb structure or as other trench filler material such as that found in a conventional fan casing. Instead, the casing **40** consists essentially of a solid metal containment structure **43** and the shroud material **41**.

(21) A small radial gap **14** is present between the tips **34** of the fan blades **30** and the inner annular surface **50**. It is this clearance, i.e., the radial gap **14**, that is minimized in order to promote the

efficiency of the engine **10**.

(22) The airfoil body **31** is made from a composite material, defined herein as a material including two or more distinct materials combined into one structure, for example a matrix having reinforcing fibers embedded therein. One example of a composite system suitable for use in aerospace applications includes an epoxy matrix with carbon fiber reinforcement.

(23) In addition to the composite material, the fan blade **30** also incorporates at least one cladding element. In the specific example shown in FIG. **2**, the cladding elements comprise a leading edge guard **60** and a tip cap **62**.

(24) The leading edge guard **60** is attached to the body **31** to define the leading edge **38**. The leading edge guard **60** provides the fan blade **30** with additional impact resistance, erosion resistance, and improved resistance of the composite structure to delamination.

(25) As best seen in FIG. **4**, the leading edge guard **60** includes a tip portion **55**, i.e., a tip region, and a body portion **57**, i.e., a body region, that meet at a boundary **56**. The leading edge guard **60** further comprises a nose **64** with a pair of wings **66** extending aft therefrom. The wings **66** taper in thickness as they extend away from the nose **64**. Exterior surfaces of the nose **64** and the wings **66** collectively define an exterior surface of the leading edge guard **60**. The shape and dimensions of the exterior surfaces of the nose **64** and the wings **66** are selected to act as an aerodynamic extension of the airfoil body **31**. Stated another way, the exterior shape of the blade **30** is defined in part by the airfoil body **31** and in part by the leading edge guard **60**. The leading edge guard **60** may be attached to the airfoil body **31** with a known type of adhesive.

(26) The tip portion **55** and the body portion **57** define interior surfaces of the nose **64** and wings **66** that collectively define an interior surface **72** of the leading edge guard **60**. The shape and dimensions of the interior surface **72** are selected to closely fit the exterior of the airfoil body **31**.

(27) The body portion **57** of the leading edge guard **60** is made from a first material that may be a metal alloy of a composition providing desired strength and weight characteristics. Non-limiting examples of suitable metal alloys for construction of the leading edge guard **60** include titanium-based alloys and superalloys, nickel-based alloys and superalloys, and iron-based alloys and superalloys. The body portion **57** of the leading edge guard may also be made of a nonmetallic material.

(28) The tip portion **55** of the leading edge guard **60** is made from a second material that may be a metal alloy of a composition providing desired strength and weight characteristics. Non-limiting examples of suitable alloys for construction of the leading edge guard **60** include titanium-based alloys and superalloys, nickel-based alloys and superalloys, and iron-based alloys and superalloys. The leading edge guard **60** may also be made of a nonmetallic material.

(29) Referring now to FIGS. **2** and **3**, the tip cap **62** overlies portions of the pressure and suction sides **35**, **36** that are adjacent to the tip **34**. The tip cap **62** provides additional impact protection, as well as stiffens the airfoil body **31** along the tip **34** and the trailing edge **39**. The tip cap **62** includes a pair of side walls **76** and **78**. The exterior surfaces of the side walls **76** and **78** collectively define an exterior surface of the tip cap **62**. The shape and dimensions of the exterior surface are selected to act as an aerodynamic extension of the airfoil body **31**. Stated another way, the exterior shape of the blade **30** is defined in part by the airfoil body **31** and in part by the tip cap **62**. The tip cap **62** may be attached to the airfoil body **31** with a known type of adhesive.

(30) Interior surfaces of the side walls **76** and **78** collectively define an interior surface **74** of the tip cap **62**. The shape and dimensions of the interior surface **74** are selected to closely fit the exterior of the airfoil body **31**.

(31) Continuing to refer to FIG. **2**, the tip cap **62** includes a tip portion **82** and a trailing edge portion **83**. The two portions **82** and **83** roughly define an L-shape. An upper forward edge **84** of the tip cap **62** abuts the leading edge guard **60**.

(32) The tip cap **62** may be made from a metal alloy of a composition providing desired strength and weight characteristics. Non-limiting examples of suitable alloys for construction of the tip cap

62 include titanium-based alloys and superalloys, nickel-based alloys and superalloys, and iron-based alloys and superalloys.
(33) FIG. **5** depicts, in cross-section, the coating of the present disclosure deposited on an engine component to form a wear resistant article **105**. Wear resistant coating **110** is deposited on the surface **120** of a substrate **130** to define the wear resistant article **105**. The wear resistant article **105** may be any component used in a gas turbine engine, such as a turbine engine disks, blades, and/or retainers as described hereinabove. The surface **120** can be any surface of an engine component **105**. The substrate **130** may comprise a superalloy based on titanium, nickel, cobalt, iron or a combination thereof.
(34) As discussed above, the wear resistant article **105** of the present disclosure includes a bulk metallic glass coating **110** on a substrate. In certain embodiments, the substrate is made of titanium, aluminum, iron, nickel, cobalt, niobium, chromium, molybdenum, tantalum, tungsten, rhenium, or an alloy thereof (including superalloys thereof). In one embodiment, the substrate is made of titanium or an alloy thereof (including superalloys thereof). In an embodiment, the substrate is a leading edge of a fan blade of a jet engine.
(35) Bulk metallic glass is a solid metallic material with an amorphous (disordered) atomic structure, as compared to convention metal materials which have an ordered crystalline atomic structure. Unlike conventional glass materials, bulk metallic glasses are good electrical conductors. Bulk metallic glasses provide high strength (on the order of about 1 to 4 gigapascals) and good ductility (e.g., 1% to 5%). This combination provides strong coatings with resistance to fracture. In addition, bulk metallic glasses are generally corrosion resistant. Accordingly, the bulk metallic glass coating provides an advantageous combination of strength, long life, and wear resistance.
(36) In certain embodiments, the bulk metallic glass of the present disclosure is an alloy including a base metal (M), a transition metal (TM), boron (B), and silicon (Si)
(37) $M\text{ - TM - }B\text{ - Si}.$
In an embodiment, the base metal is titanium, aluminum, iron, nickel, or cobalt or a combination thereof. In an embodiment, the base metal is titanium.
(38) In certain embodiments, the transition metal may be any known transition metal(s). In one embodiment, the transition metal is vanadium, chromium, manganese, iron, cobalt, nickel, zirconium, niobium, molybdenum, ruthenium, rhodium, tungsten, hafnium, tantalum, tungsten, or rhenium, or a combination thereof. In certain embodiments, the transition metal is molybdenum, zirconium, palladium, or tungsten, or a combination thereof. In certain embodiments of the present disclosure, the transition metal is present in an amount of 0.1% to 15% by weight, or 0.5% to 10% by weight, or 1% to 5% by weight based on the total weight of the bulk metallic glass. Without wishing to be bound by any particular theory, it is believed that this amount of transition metal allows for the formation of particles of transition metal borides and/or silicides in the bulk metallic glass coating while still allowing for the ductile metal matrix to remain substantially continuous.
(39) In certain embodiments of the present disclosure, the boron is present in an amount of 1% to 5% by weight, or 1.5% to 4% by weight, or 2% to 3% by weight based on the total weight of the bulk metallic glass. In certain embodiments of the present disclosure, the silicon is present in an amount of 1% to 10% by weight, or 2% to 7.5% by weight, or 3 to 5% by weight based on the total weight of the bulk metallic glass coating. Without wishing to be bound by any particular theory, it is believed that this amount of boron and the silicon allows for the formation of particles of transition metal borides and/or silicides in the bulk metallic glass coating, which have very high hardness.
(40) In certain embodiments of the present disclosure, the borides and/or silicides particles are present in an amount of 0.5% to 20% by weight, or 1% to 10% by weight, or 2% to 5% by weight based on the total weight of the bulk metallic glass coating. Thus, in an embodiment, the bulk metallic glass coatings take the form of transition metal boride and/or silicide particles interspersed in a ductile metal matrix. The bulk metallic coatings may have a functionally graded

microstructure. As used herein, “functionally graded microstructure” means that the metallic glass coating has areas of hard particles trapped or suspended in a metal matrix continuous phase, which is more ductile. These alternating hard and ductile areas produce a material that, as discussed above, is both strong and wear resistant. Moreover, the surface may also be provided with a pattern in which some areas have great hardness and other have greater ductility to provide the same combination of strength and wear resistance. Such a pattern may be formed by controlling/varying the amount of transition metal borides and/or silicides supplied to particular areas (e.g., decreasing the amount of transition metal borides and/or silicides in certain areas while increasing the amount of transition metal borides and/or silicides in other areas). Such patterns may be formed by additive manufacturing technologies.
(41) Additive manufacturing technologies may generally be described as technologies for building objects point-by-point or layer-by-layer, typically in a vertical direction. Other methods of fabrication are contemplated and within the scope of the present disclosure. For example, although the discussion herein refers to the addition of material to form successive layers or point-by-point addition, the presently disclosed subject matter may be practiced with any additive manufacturing technology or other manufacturing technology, including layer-additive processes, layer-subtractive processes, or hybrid processes. Additive printing encompasses a variety of technologies for producing components in an additive, point-by-point fashion. In powder bed fusion, a focused energy beam is used to fuse powder particles together. The energy beam may be either an electron beam or laser. Laser powder bed fusion processes are referred to in the industry by many different names, the most common of which being selective laser sintering (SLS) and selective laser melting (SLM), depending on the nature of the powder fusion process. When the powder to be fused is metal, the terms direct metal laser sintering (DMLS) and direct metal laser melting (DMLM) are commonly used.
(42) The bulk metallic glass coating is described above in detail. In an embodiment of the present disclosure, a bulk metallic glass coating is additively printed onto at least a portion of an article. In general, a powder containing the base metal, the transition metal, boron, and silicon is deposited on the surface of the substrate and successive portions of the powder are then fused to form the bulk metallic glass coating.
(43) Metallic glasses are formed by rapidly cooling (e.g., at a rate higher than the critical cooling rate), which prevents ordered crystalline structures from forming during solidification. As used herein, the term “critical cooling rate” means that rate of cooling of the alloy that delineates between the formation of metallic glass and conventional crystalline metal. Thus, if the alloy is cooled at a rate greater that the critical cooling rate it will form a metallic glass. On the other hand, if the alloy is cooled at a rate less that the critical cooling rate it will form a conventional crystalline metal. This a localized effect and there may be areas of metallic glass adjacent to areas of convention crystalline metal dues to local cooling. Moreover, there may be areas of transition between the two structures which exhibit features of each.
(44) In an embodiment, the bulk metallic glass coating is subjected to further heat treatment, such as annealing, to produce particles of transition metal borides and/or silicides, which have very high hardness. In an embodiment, the heat treatment is the local heating of the bulk metallic glass coating to a temperature of 300° C. to 600° C. (such as 300° C. to 500° C.). In certain embodiments, the heat treatment can be carried out during initial manufacturing or may be carried out at a later time, for example, when the article has been assembled into an end product. In certain embodiments of the present disclosure, the boride and/or silicide particles are present in an amount of 0.5% to 20% by weight, or 1% to 10% by weight, or 2% to 5% by weight based on the total weight of the bulk metallic glass coating.
(45) In certain embodiments of the present disclosure the bulk metallic glass coating has a thickness of 50 μm to 20 millimeters, or 500 μm to 10 millimeters, or 1 millimeter to 5 millimeters.
(46) The additive printing processes employed in the embodiments of the method of the present

description also allow flexibility in producing the bulk metallic glass coatings. The point-by-point additive processes described herein allow for the deposition of coatings on the surface of substrates with complex geometries. Moreover, these processes allow for fine tuning the thickness of the coating across the surface of the substrate to provide, for example, greater thickness in some areas (e.g., for greater protection) and less thickness in other areas (e.g., for less bulk). Furthermore, the additive printing process makes it possible to use the bulk metallic glass coatings to repair defects or damage to the substrate by additively printing the bulk metallic glass coating only where needed to fill in the void left by the defect or damage. In certain embodiments, the additive printing may be used to produce a coating surface with a pattern of various hard and ductile areas.
(47) Further aspects are provided by the subject matter of the following clauses:
(48) A wear resistant article comprising: a substrate; and a bulk metallic glass coating comprising an alloy of a base metal, a transition metal, boron, and silicon, wherein the bulk metallic glass coating has a thickness of 50 μm or greater and a functionally graded microstructure.
(49) The wear resistant article of one or more of these clauses, the substrate comprising a metal selected from the group consisting of titanium, aluminum, iron, nickel, cobalt, niobium, chromium, molybdenum, tantalum, tungsten, rhenium, and alloys thereof.
(50) The wear resistant article of one or more of these clauses, the substrate comprising titanium or an alloy thereof.
(51) The wear resistant article of one or more of these clauses, wherein the substrate is a leading edge of a fan blade of a jet engine.
(52) The wear resistant article of one or more of these clauses, wherein the base metal is titanium and the transition metal is selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, nickel, zirconium, niobium, molybdenum, ruthenium, rhodium, tungsten, hafnium, tantalum, rhenium, and alloys thereof.
(53) The wear resistant article of one or more of these clauses, wherein the base metal is titanium and the transition metal is selected from the group consisting of molybdenum, zirconium, palladium, tungsten, and alloys thereof.
(54) The wear resistant article of one or more of these clauses, the bulk metallic glass coating comprising: 0.1% to 15% of the transition metal, 1 to 5% boron, and 1 to 10% silicon.
(55) The wear resistant article of one or more of these clauses, wherein the bulk metallic glass coating has a thickness between 50 μm and 20 millimeters.
(56) The wear resistant article of one or more of these clauses, wherein the bulk metallic glass coating has a thickness between 1 millimeter and 10 millimeters.
(57) The wear resistant article of one or more of these clauses, wherein the functionally graded microstructure comprises 0.5% to 20% by weight of hard particles dispersed within an amorphous matrix of the bulk metallic glass coating.
(58) The wear resistant article of one or more of these clauses, wherein the hard particles comprise borides, silicides, or a combination thereof.
(59) A method of producing an article with a wear resistant coating, the method comprising additively printing a bulk metallic glass coating onto at least a portion of the article, the bulk metallic glass coating comprising an alloy of a base metal, a transition metal, boron, and silicon, wherein the bulk metallic glass coating has a thickness of 50 μm or greater.
(60) The method of one or more of these clauses, wherein the portion of the article being coated comprises a metal selected from the groups consisting of titanium, aluminum, iron, nickel, cobalt, niobium, chromium, molybdenum, tantalum, tungsten, rhenium, and alloys thereof.
(61) The method of one or more of these clauses, wherein the portion of the article being coated comprises titanium or an alloy thereof.
(62) The method of one or more of these clauses, wherein the portion of the article being coated is a leading edge of a fan blade of a jet engine.
(63) The method of one or more of these clauses, wherein the base metal is titanium and the

transition metal is selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, nickel, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, and tungsten, and alloys thereof.
(64) The method of one or more of these clauses, wherein the base metal is titanium and the transition metal is selected from the group consisting of molybdenum, zirconium, palladium, and tungsten, and alloys thereof.
(65) The method of one or more of these clauses, the bulk metallic glass coating comprising: 0.1% to 15% of the transition metal, 1 to 5% boron, and 1 to 10% silicon.
(66) The method of one or more of these clauses, wherein the bulk metallic glass coating has a thickness between 50 μm and 20 millimeters.
(67) The method of one or more of these clauses, wherein the bulk metallic glass coating has a thickness between 1 millimeter and 10 millimeters.
(68) The method of one or more of these clauses, further comprising annealing the bulk metallic glass coating to form a functionally graded microstructure in the coating.
(69) The method of one or more of these clauses, wherein the functionally graded microstructure comprises 1% to 20% boride or silicide hard particles dispersed within an amorphous matrix of the bulk metallic glass coating.
(70) This written description uses examples to disclose the present disclosure, including the best mode, and also to enable any person skilled in the art to practice the disclosure, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the disclosure is defined by the claims, and may include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they include structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

Claims

1. A wear resistant article, comprising: a substrate; and a bulk metallic glass coating comprising an alloy of titanium that includes 0.1% to 15% by weight of a transition metal, 2% to 3% by weight boron, and 3% to 5% by weight silicon, wherein the bulk metallic glass coating has a thickness of 50 μm or greater and a functionally graded microstructure.
2. The wear resistant article of claim 1, wherein the substrate comprises a metal selected from the group consisting of titanium, aluminum, iron, nickel, cobalt, niobium, chromium, molybdenum, tantalum, tungsten, rhenium, and alloys thereof.
3. The wear resistant article of claim 1, wherein the substrate comprises titanium or an alloy thereof.
4. The wear resistant article of claim 1, wherein the substrate is a leading edge of a fan blade of a jet engine.
5. The wear resistant article of claim 1, wherein the transition metal is selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, nickel, zirconium, niobium, molybdenum, ruthenium, rhodium, tungsten, hafnium, tantalum, rhenium, and alloys thereof.
6. The wear resistant article of claim 1, wherein the transition metal is selected from the group consisting of molybdenum, zirconium, palladium, tungsten, and alloys thereof.
7. The wear resistant article of claim 1, wherein the bulk metallic glass coating has a thickness between 50 μm and 20 millimeters.
8. The wear resistant article of claim 1, wherein the bulk metallic glass coating has a thickness between 1 millimeter and 10 millimeters.
9. The wear resistant article of claim 1, wherein the functionally graded microstructure comprises 0.5% to 20% by weight of hard particles dispersed within an amorphous matrix of the bulk metallic

glass coating, wherein the hard particles comprise borides, silicides, or a combination thereof.
10. A method of producing an article with a wear resistant coating, the method comprising: additively printing a bulk metallic glass coating onto at least a portion of the article, wherein the bulk metallic glass coating comprises an alloy of titanium that includes 0.1% to 15% by weight of a transition metal, 2% to 3% by weight boron, and 3% to 5% by weight silicon, and wherein the bulk metallic glass coating has a thickness of 50 μm or greater and a functionally graded microstructure.
11. The method of producing the article with the wear resistant coating of claim 10, wherein the portion of the article being coated comprises a metal selected from the group consisting of titanium, aluminum, iron, nickel, cobalt, niobium, chromium, molybdenum, tantalum, tungsten, rhenium, and alloys thereof.
12. The method of producing the article with the wear resistant coating of claim 10, wherein the portion of the article being coated comprises titanium or an alloy thereof.
13. The method of producing the article with the wear resistant coating of claim 10, wherein the portion of the article being coated is a leading edge of a fan blade of a jet engine.
14. The method of producing the article with the wear resistant coating of claim 10, wherein the transition metal is selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, nickel, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, tungsten, and alloys thereof.
15. The method of producing the article with the wear resistant coating of claim 10, wherein the transition metal is selected from the group consisting of molybdenum, zirconium, palladium, tungsten, and alloys thereof.
16. The method of producing the article with the wear resistant coating of claim 10, wherein the bulk metallic glass coating has a thickness of 50 μm and 20 millimeters.
17. The method of producing the article with the wear resistant coating of claim 10, further comprising: annealing the bulk metallic glass coating to form the functionally graded microstructure in the coating.
18. The method of producing the article with the wear resistant coating of claim 17, wherein the functionally graded microstructure comprises 1% to 20% by weight boride or silicide hard particles dispersed within an amorphous matrix of the bulk metallic glass coating.