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FARMER et al.(10) **Pub. No.: US 2014/0147601 A1**(43) **Pub. Date: May 29, 2014**(54) **CAVITATION AND IMPINGEMENT
RESISTANT MATERIALS WITH
PHOTONICALLY ASSISTED COLD SPRAY****Publication Classification**(71) Applicant: **Lawrence Livermore National
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427/383.1; 427/554; 427/551(72) Inventors: **Joseph C. FARMER**, Tracy, CA (US);
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Livermore, CA (US)(57) **ABSTRACT**(21) Appl. No.: **13/964,323**(22) Filed: **Aug. 12, 2013**

Various methods are disclosed for coating or treating a substrate to enhance resistance of the substrate to at least one of cavitation and liquid impingement. One specific method may involve providing an amorphous metal composition which is able to be atomized. The amorphous metal composition may be applied as an atomized spray to a surface of the substrate via a high velocity spray operation to coat the surface. The coated surface may have at least one of a Vickers hardness number of at least about 1100 HVN, or a yield strength of at least about 700 MPa, or a thermal stability between about 600° C. and about 700° C., and is highly resistant to the effects of cavitation and/or liquid impingement.

Related U.S. Application Data

(60) Provisional application No. 61/729,954, filed on Nov. 26, 2012.

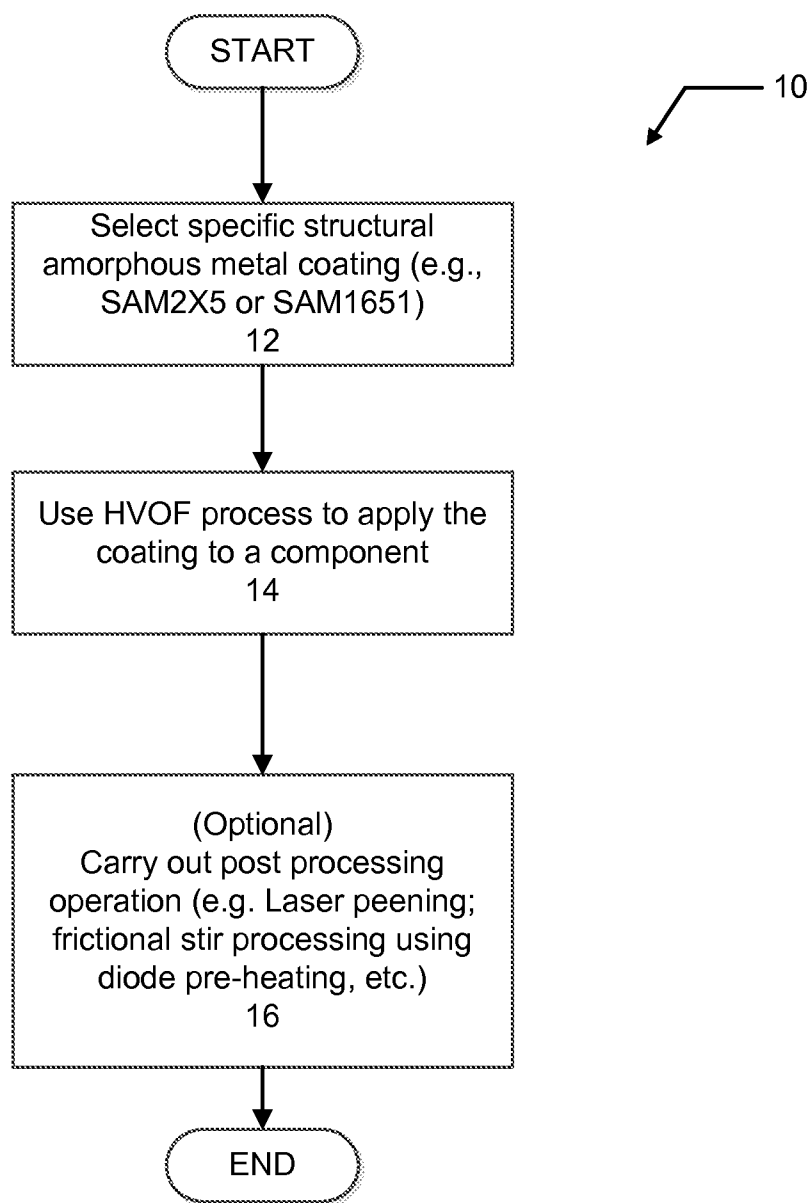
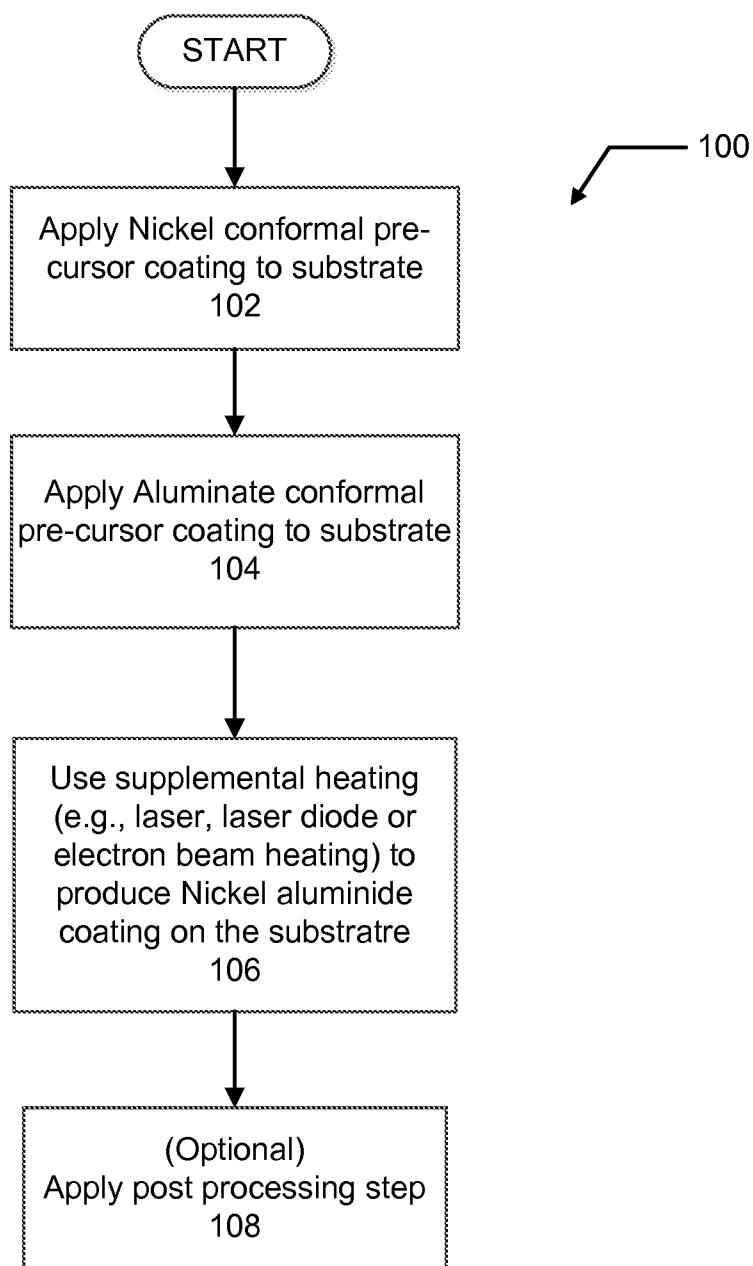
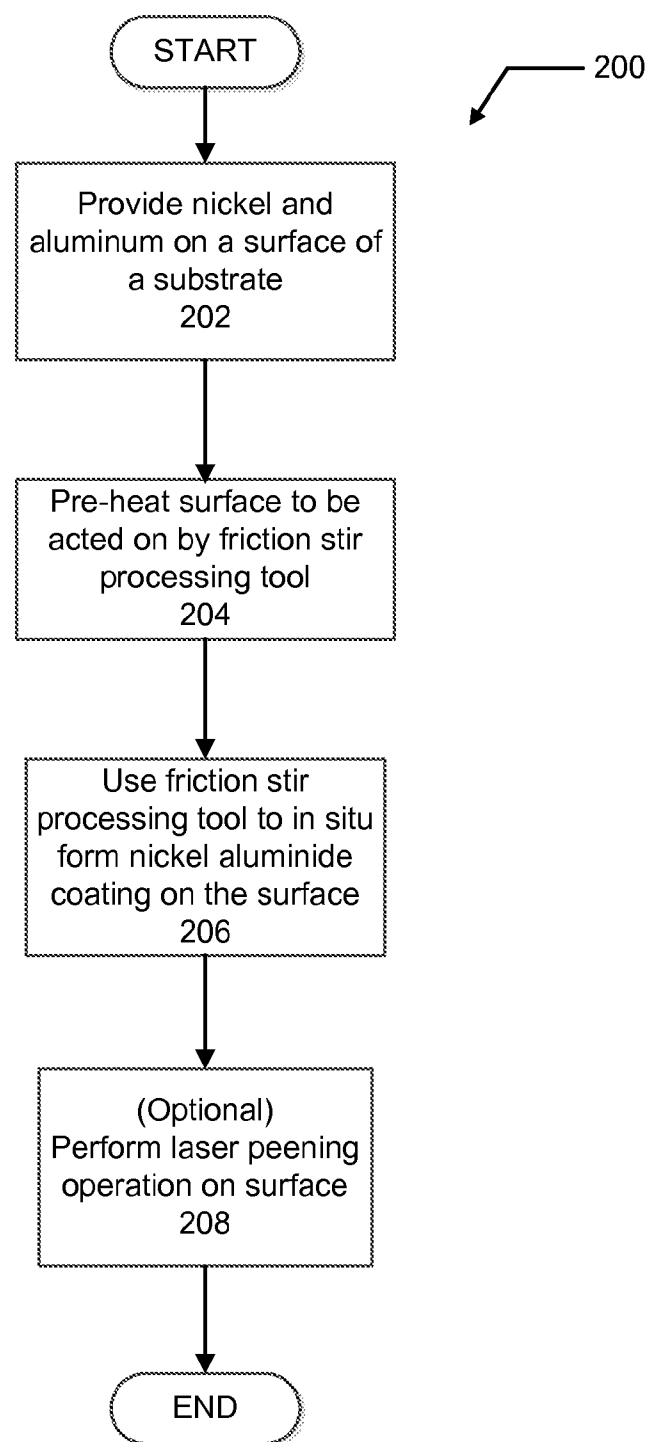
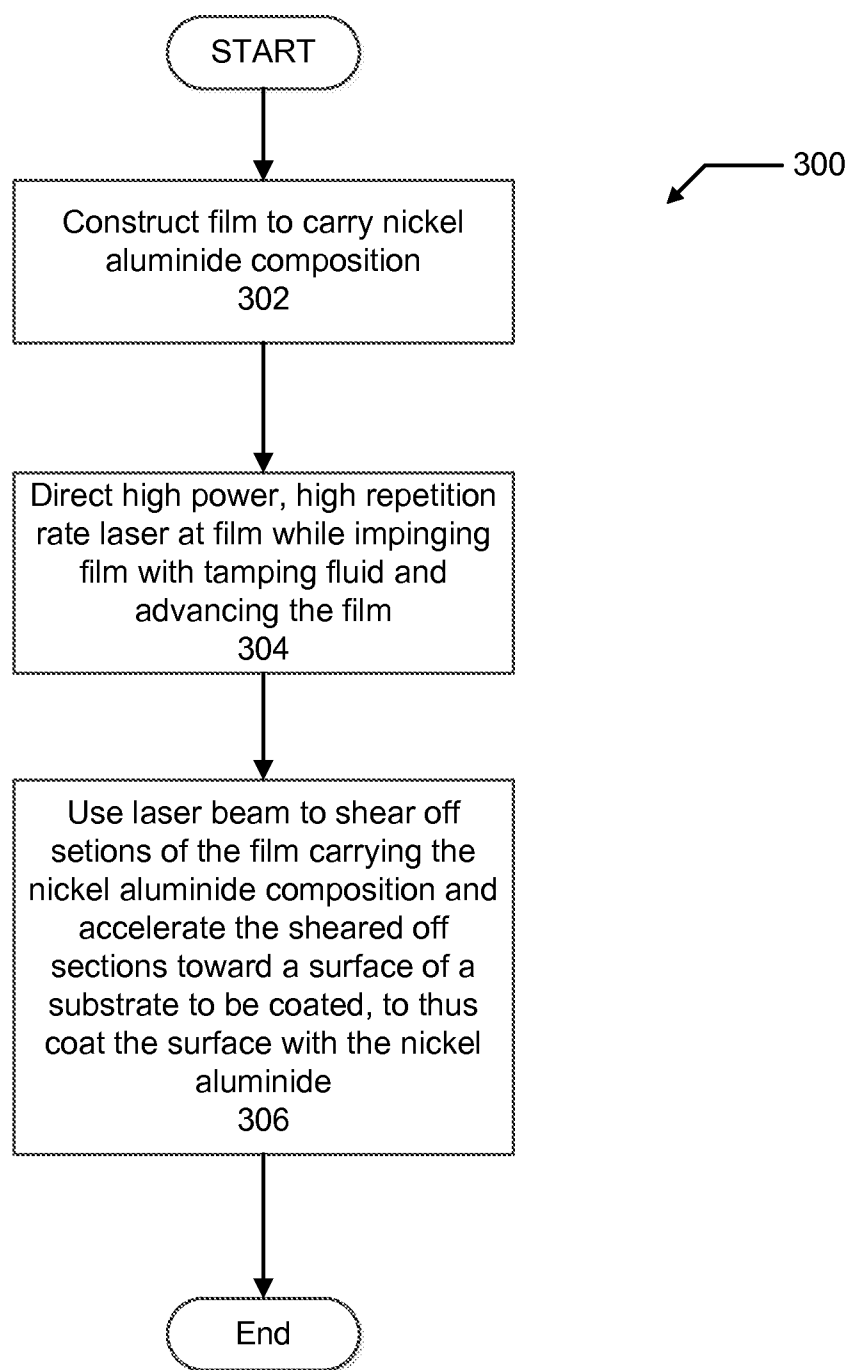


FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

CAVITATION AND IMPINGEMENT RESISTANT MATERIALS WITH PHOTONICALLY ASSISTED COLD SPRAY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 61/729,954, filed on Nov. 26, 2012, the entire disclosure of which is hereby incorporated by reference into the present application.

STATEMENT OF GOVERNMENT RIGHTS

[0002] The United States Government has rights in this invention pursuant to Contract No. DE-AC52-07NA27344 between the U.S. Department of Energy and Lawrence Livermore National Security, LLC, for the operation of Lawrence Livermore National Laboratory.

FIELD

[0003] The present disclosure relates to coatings and/or operations that may be carried out on a structure or component to improve its structural integrity and fatigue resistance, and more particularly to methods for treating a surface and/or applying coatings that are especially effective in resisting wear and structural damage to a component or structural element exposed to cavitation and liquid impingement.

BACKGROUND

[0004] The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

[0005] When a liquid enters a low-pressure region, gas-filled cavities can form in the liquid. When these bubbles travel in the flow to regions of higher pressure, the bubbles may collapse. In the industry this condition is known as "cavitation." Generally, through the action of asymmetric implosion instabilities, the collapsing bubbles may generate extremely high velocity jets that can impinge materials with dynamic pressures on the order of thousands of atmospheres. These pressures can cause substantial erosion and corrosion damage at the surface of control valves, pumps, impellers, propellers, dams, spillways and other engineered components. It is also recognized that the noise created by cavitation is a particular problem in applications where stealth is important. For example, cavitation is a particular challenge for military submarines, since it dramatically increases the chances of being detected by passive sonar.

[0006] Liquid impingement is another concern with various types of industrial devices and various types of equipment. Liquid impingement occurs when liquid droplets in high velocity streams of gas and steam impact solid surfaces in regions where there are abrupt changes in the direction of flow. Kinetic energy is transferred to the solid surfaces during impact, which can cause substantial erosion of the surface(s). Liquid impingement may be experienced by turbine blades in both fossil-fueled and nuclear power generators.

[0007] Accordingly, there is a significant need for materials and/or processes which are able to combat the effects of cavitation and liquid impingement on various types of structures and components and, in particular, components such as jet engines, gas turbines, steam turbines, propellers, and other similar components where exceptional service life, reliability and durability are required.

SUMMARY

[0008] In one aspect the present disclosure relates to a method of coating a substrate to enhance resistance of the substrate to at least one of cavitation and liquid impingement. The method may comprise providing an amorphous metal composition which can be atomized. The amorphous metal composition may be applied as an atomized spray to a surface of the substrate via a high velocity spray operation to coat the surface. The coated surface may have at least one of a Vickers hardness number of at least about 1100 HVN, a yield strength of at least about 700 MPa, or a thermal stability between about 600° C. and about 700° C.

[0009] In another aspect the present disclosure relates to a method of coating a substrate to enhance resistance of the substrate to at least one of cavitation and liquid impingement. The method may comprise providing an amorphous metal composition. The amorphous metal composition may be applied to a surface of the substrate via at least one of a cold spray process or a high velocity oxy fuel (HVOF) process to coat the surface. A post coating operation may be used to further heat the coated surface. The coated surface may have a yield strength of at least about 700 MPa. The method may optionally include a preliminary operation of substrate heating with diodes or another means to soften the substrate. The particulates deposited by the cold spray or HVOF process are expected to have even better penetration in the substrate, and the resulting coating is expected to have even better adhesion to the substrate.

[0010] In still another aspect the present disclosure relates to a method for coating a substrate to enhance resistance of the substrate to at least one of cavitation and liquid impingement. The method may comprise providing an amorphous metal composition on a portion of a film, with the film being positioned over, and in proximity to, the substrate. A tamping fluid may be applied to a surface portion of the film which is not facing the substrate. A laser pulse may be applied to the surface portion of the film which is not facing the substrate. The laser pulse may be of sufficient energy to shear off and accelerate a portion of the film which is carrying the amorphous metal composition onto the substrate at a high velocity to bond the amorphous metal composition to the substrate.

[0011] In still another aspect the present disclosure relates to a method for coating a substrate to enhance resistance of the substrate to at least one of cavitation and liquid impingement. The method may comprise providing an amorphous metal composition including nickel and aluminum on a surface of a substrate. A portion of the surface may then be preheated before being acted on by a friction stir processing tool. The friction stir processing tool may then be used to perform a friction stir operation on the nickel and aluminum to form, in situ, a nickel aluminide coating on the surface.

[0012] Further areas of applicability will become apparent from the description provided herein. It should be understood that the description and specific examples are intended for purposes of illustration only and are not intended to limit the scope of the present disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The drawings described herein are for illustration purposes only and are not intended to limit the scope of the present disclosure in any way. In the drawings:

[0014] FIG. 1 is a flowchart illustrating operations that may be performed to apply an amorphous metal coating on a surface of a structure using a high velocity oxy fuel (HVOF) process;

[0015] FIG. 2 is a flowchart illustrating operations that may be performed to form a nickel aluminide coating on a surface using a spray process followed by a heating operation;

[0016] FIG. 3 is a flowchart illustrating operations that may be performed to form a nickel aluminide coating on a surface using a high velocity laser accelerated (HVLAD) deposition process; and

[0017] FIG. 4 is a flowchart illustrating operations that may be performed using a high velocity laser accelerated deposition process to apply a nickel aluminide coating to a substrate.

DETAILED DESCRIPTION

[0018] The following description is merely exemplary in nature and is not intended to limit the present disclosure, application, or uses. It should be understood that throughout the drawings, corresponding reference numerals indicate like or corresponding parts and features.

[0019] The present disclosure is directed to a plurality of coatings and methods for coating and/or treating components to significantly improve resistance to damage caused by cavitation and liquid impingement. An additional important consideration when coating components such as propellers used in military marine vessels, or in any other application where minimizing noise of the component is imperative, is that the coating has an acoustic impedance that exceeds the acoustic impedance of the substrate material. Thus, highly dense coatings with excellent interfacial bonds are required to maximize the coating acoustic impedance to increase the erosion resistance.

[0020] Ultra Hard Amorphous Metal Coatings

[0021] In one aspect, the present disclosure provides a coating process 10, shown in FIG. 1, that produces ultra-hard, corrosion-resistant, iron-based amorphous-metal coatings with the known high-velocity oxy-fuel (HVOF) spray process for the protection of underlying substrates. The HVOF process involves using fuel and oxygen to produce a high pressure flame to which a powdered metal is added. The result is a supersonic spray velocity which is instrumental in producing an extremely strong bond of the powdered coating material on the component.

[0022] Structural amorphous metal formulations, known as SAM2X5 and SAM1651, have been developed and used on an industrial scale. These materials have undergone extensive testing over several years, and have been shown to be more corrosion resistant in near-boiling geothermal brines than nickel-based Alloy C-22. More important for this application, these amorphous metals are much harder. For example, Type 316 stainless steel has a hardness of 150 HVN, Alloy C-22 has a hardness of 250 HVN, whereas the amorphous metals that will be investigated for resistance to cavitation and droplet impingement have Vickers hardness numbers ranging from 1100 to 1300 HVN.

[0023] In FIG. 1, the process 10 may involve selecting a specific structural amorphous metal coating, for example, but not limited to, SAM2X5 or SAM1651, as indicated at operation 12. The HVOF process may then be used to apply the selected material in amorphous metal powder form to the surface of a component or structure, as indicated at operation 14. At operation 16 an optional post processing operation may be performed on the just-coated component or structure. For

example, laser peening or subsequent heating, for example high power laser diode heating, may be performed on the just-coated component or structure to even further enhance its densification and/or hardness. Preliminary heating of the substrate may also be performed using any suitable heating means, for example diode heating. The preliminary heating may serve to soften the substrate. In this manner particulates deposited using the HVOF process may be expected to have even better penetration into the substrate resulting in a coating which has even better adhesion to the substrate.

[0024] Coatings applied using the above described operations of process 10 are able to be applied in a wide range of thicknesses, and more specifically in thicknesses ranging at least between about 15 mils to about 12 millimeters. Furthermore, structural amorphous metals coated on a component using the HVOF process, as described in FIG. 1, provide the added advantage of being thermally stable at temperatures between the glass transition temperature and the crystallization temperature, which is typically between about 600° C. and 700° C., making them suitable for some steam turbine applications.

[0025] In Situ Formation of Nickel Aluminide Coatings

[0026] In another aspect the present disclosure may involve the application of conformal pre-cursor coatings consisting of nickel and aluminum with a cold spray process, with subsequent conversion of this composite coating to nickel aluminide through the use of high-power diode arrays for localized heating. As will be appreciated by those skilled in the art, the cold spray process is a material deposition process by which particles of diameters typically between about 1 and 40 microns are impacted at high velocity onto a substrate. The particles are placed in a gas stream of nitrogen, helium or air. The stream is then heated and accelerated through a supersonic nozzle at speeds ranging from typically about 1000 meters per second to about 2500 meters per second. The particle stream is directed towards a substrate, where the particles are consolidated in the solid state. Preliminary heating of the substrate may also be done as an optional operation. The preliminary heating may be accomplished with any suitable means or devices, such as with diodes, to soften the substrate. The particulates deposited by the cold spray process are expected to have even better penetration in the substrate, and resulting coating is expected to have even better adhesion to the substrate.

[0027] Nickel aluminide is already used for the coating of blades in gas turbines and jet engines. Nickel aluminide includes three intermetallic compounds (NiAl, NiAl₃ and Ni₃Al), or ordered alloy phases formed between nickel and aluminum, with an unusually high strength-to-weight ratios and thermal conductivity at extreme temperature (typically about five times that of stainless steel at 800° C.). It has a density of about 7.26 g/cm³ and a hardness of about 12 HRC. An alloy is referred to as "ordered" if two or more sub-lattices are required to describe its atomic structure. The ordered structure exhibits superior elevated-temperature properties because of the long-range ordered superlattice, which reduces dislocation mobility and diffusion processes at elevated temperatures. One of the most common practical engineering materials based upon nickel aluminide is IC-221M, which consists not only of nickel and aluminum, but also chromium, molybdenum, zirconium and boron, with the boron addition enhancing both ductility and hardness. At a temperature of 800° C. the yield strength of this material is

in excess of about 700 MPa, compared to a yield strength of about 250 MPa for nickel-based Alloy 625.

[0028] Referring to FIG. 2, a process 100 for forming a nickel aluminide coating on a substrate via a cold spray process and subsequent diode heating is shown. At operation 102 a nickel conformal pre-cursor coating is applied to the substrate via a well known cold spray process. At operation 104 a conformal aluminum coating is then applied to the substrate via the cold spray process. It will be appreciated that operations 102 and 104 could be reversed in order. At operation 106 supplemental heating, such as by a laser, by high power laser diode heating, by induction heating or even by an electron beam, may be performed on the nickel and aluminum coatings to produce, in situ, the nickel aluminide coating. High power laser diode heating is described in the co-pending in co-pending patent publication no. WO/2013/081731, published Jun. 6, 2013, assigned to the assignee of the present application and incorporated by reference herein. At operation 108 an optional post processing operation, for example laser peening, may be performed on the nickel aluminide coating to further introduce compressive stress and reduce the risk of stress cracks.

[0029] It will be appreciated that other materials may be combined with the nickel and aluminum forming the nickel aluminide coating to provide even further enhanced characteristics for the coating. For example, one extremely abrasion-resistant material was made in 2005 by Dale E. Wittmer and Peter Filip at Southern Illinois University Carbondale by embedding diamonds in a nickel aluminide matrix. More specifically, this composite consisted of a mixture of nickel, aluminum, metal carbide and industrial diamond, and required processing at 1400 C. During subsequent testing it was found that this composite was at least 800 times more wear resistant than the carbide now used commercially in making mining tools, drill bits, ceramic tile routers and other such tools. Those skilled in the art will appreciate that still further materials such as carbides, borides, and various ultra-hard intermetallic compounds could potentially be used to create a nickel aluminide matrix in connection with the various processes described herein.

[0030] Friction Stir Processing with High Power Laser Diode Heating

[0031] In another aspect the present disclosure relates to the use of friction stir processing (FSP) on large castings of nickel-aluminum-bronze for the purpose of eliminating defects on propellers that can give rise to cavitation and noise generation on naval ships and submarines. It has been found that in addition to eliminating voids in the surface of these large castings, which may cause promote cavitation and noise generation, FSP also enhances passive film stability and corrosion resistance. The rate at which FSP can be performed is significantly enhanced through diode pre-heating of the area on which the FSP operation is to be performed. This methodology is described in detail in co-pending patent publication no. WO/2013/081731, referenced herein.

[0032] Referring to FIG. 3, a method 200 is set forth describing operations pertaining to using a friction stir processing operation to form an in situ nickel aluminide coating on a substrate. At operation 202 nickel and aluminum are provided on a surface of a structure to be acted on. At operation 204 pre-heating is performed on an area to be acted on by a friction stir operation. The pre-heating may be performed by a high power laser diode, or by a laser, or by electron beam heating, or by induction heating, or by any other suitable

heating means. At operation 206 a friction stir processing operation is performed on the surface to form, in situ, a nickel aluminide coating on the surface. At optional operation 208 a post processing operation such as laser peening may be performed to even further introduce compressive stress into the structure to further reduce the risk of stress cracks and improve surface homogenization, as well as to eliminate surface defects in the substrate. It will be appreciated that the operation of laser peening could instead be performed before the friction stir processing operation.

[0033] Refractory Coatings with Extreme Interfacial Bond Strength

[0034] The present disclosure also contemplates the application of ordinary and dispersion-strengthened refractory-metal coatings with extreme interfacial bond strength onto steel substrates with a High Velocity Laser Accelerated Deposition (HVLAD) process. The HVLAD process is described in co-pending U.S. patent application Ser. No. 13/229,840, filed Sep. 12, 2011, assigned to the assignee of the present application and hereby incorporated by reference into the present application. In general, the HVLAD process may use high power and high repetition rate production lasers for localized explosive bonding, thus producing a very broad range of advanced high-temperature and corrosion-resistant coatings with extreme interfacial bond strength. These interfacial bonds may approach the ultimate tensile strength of the substrate. The HVLAD process, as set forth in greater detail in the above referenced co-pending Ser. No. 13/229/840 can be summarized in terms of several discrete operations. During a first operation a high-performance corrosion resistant film material is advanced with a spool assembly, and bathed with water that serves as a tamper during laser pulse. At operation two a special laser pulse with a rectangular beam cross-section is imaged onto the advancing high-performance film material bathed with a thin layer of a tamping fluid, for example water. At operation three, the laser pulse generates a high temperature plasma and very large pressure, which acts to shear out a section of the film which it impinges. This accelerates the sheared out section of film to hypersonic velocities. At operation four, patches of ultra-hard and corrosion-resistant film are accelerated toward the substrate in a controlled, step-by-step process, as the film is advanced. At operation five, the film patches each hit the substrate at an oblique angle, where the high impact velocity induces plastic shear flow at the interface creating a coating having an extremely high-strength, explosive bond.

[0035] FIG. 4 sets forth a process 300 for providing a nickel aluminide coating on a substrate that makes use of the above described HVLAD process. At operation 302 a film is constructed to carry a nickel aluminide composition. The film is positioned closely adjacent a surface of the substrate. At operation 304 an extremely high power, high repetition rate laser is directed at the film while a tamping fluid, for example water, is also being directed at the film surface. At operation 306 the laser beam is used to shear off sections of the film carrying the nickel aluminide composition and accelerate the sheared off sections toward a surface of a substrate, at an oblique angle, to produce an explosively bonded nickel aluminide on the surface. The nickel aluminide coating will be bonded to the substrate with a strength that approaches the tensile strength of the substrate itself.

[0036] The present disclosure further may involve high acoustic impedance coatings of materials as described above deposited with physical and chemical vapor deposition meth-

ods. The coatings described herein may also be deposited from a liquid phase through the application of electroplating, electrolytic reduction, electrolytic oxidation, or electrophoretic deposition. The coatings described herein may also be deposited using powder coating processes. Still further, the coatings described herein may potentially be applied using any other form of additive manufacturing involving a powder or powder bed, with or without the assistance of laser, laser diode, induction or electron beam heating.

[0037] While various embodiments have been described, those skilled in the art will recognize modifications or variations which might be made without departing from the present disclosure. The examples illustrate the various embodiments and are not intended to limit the present disclosure. Therefore, the description and claims should be interpreted liberally with only such limitation as is necessary in view of the pertinent prior art.

What is claimed is:

1. A method of coating a substrate to enhance resistance of the substrate to at least one of cavitation and liquid impingement, the method comprising:

providing an amorphous metal composition able to be atomized;

applying the amorphous metal composition as an atomized spray to a surface of the substrate via a high velocity spray operation to coat the surface;

and wherein the coated surface has at least one of:

- a Vickers hardness number of at least about 1100 HVN;
- a yield strength of at least about 700 MPa; or
- a thermal stability between about 600° C. and about 700° C.

2. The method of the claim 1, further including a preliminary operation of pre-heating the substrate using a heat source to achieve substrate softening, to thus further enhance bonding with the substrate.

3. The method of claim 2, wherein the preliminary operation of pre-heating the substrate using a heat source comprises using light from diodes to pre-heat the substrate.

4. The method of claim 1, wherein the operation of applying the amorphous metal composition as an atomized spray comprises using a cold spray process.

5. The method of claim 1, wherein the operation of applying the amorphous metal composition comprises using a high velocity oxy fuel (HVOF) process.

6. The method of claim 5, wherein the amorphous metal composition comprises one of:

- structural amorphous metal 2x5 (SAM2x5); or
- structural amorphous metal 1651 (SAM1651).

7. The method of claim 4, further comprising using localized heating of the surface of the substrate subsequent to applying the amorphous metal composition, and wherein the amorphous metal composition is formed in situ into a nickel aluminide coating in response to the localized heating.

8. The method of claim 7, wherein the localized heating comprises using at least one of:

- a laser;
- a laser diode;
- induction heating; and
- an electron beam.

9. The method of claim 1, wherein the amorphous metal composition comprises nickel aluminide.

10. The method of claim 1, wherein the nickel aluminide comprises IC-221M.

11. The method of claim 1, further comprising using a laser peening operation to introduce compressive stresses into the substrate.

12. A method of coating a substrate to enhance resistance of the substrate to at least one of cavitation and liquid impingement, the method comprising:

providing an amorphous metal composition;

applying the amorphous metal composition onto a surface of the substrate via at least one of a cold spray process or a high velocity oxy fuel (HVOF) process to coat the surface;

using a post coating operation to further heat the coated surface; and

wherein the coated surface has a yield strength of at least about 700 MPa.

13. The method of claim 12, wherein the post coating operation comprises heating with a high power diode array.

14. The method of claim 12, wherein the amorphous metal composition comprises nickel aluminide.

15. The method of claim 12, wherein the coated surface has a Vickers hardness number of at least about 1100 HVN.

16. The method of claim 12, wherein the coated surface has a thermal stability between about 600° C. and about 700° C.

17. The method of claim 12, further comprising using a laser peening operation at least one of before the amorphous metal composition is applied to the substrate or after the amorphous metal composition is applied to the substrate.

18. The method of claim 12, wherein the localized heating comprises using at least one of:

- a laser;
- a laser diode;
- induction heating; and
- an electron beam.

19. A method for coating a substrate to enhance resistance of the substrate to at least one of cavitation and liquid impingement, the method comprising:

providing an amorphous metal composition on a portion of a film, the film being positioned over, and in proximity to, the substrate;

applying a tamping fluid to a surface portion of the film which is not facing the substrate;

applying a laser pulse to the surface portion of the film which is not facing the substrate, the laser pulse being of sufficient energy to shear off and accelerate a portion of the film carrying the amorphous metal composition onto the substrate to bond the amorphous metal composition to the substrate.

20. The method of claim 19, wherein the amorphous metal composition comprises nickel aluminide.

21. The method of claim 19, further comprising performing a laser peening operation on a surface of the structure at least one of before or after the amorphous metal composition is deposited on the surface.

22. A method of coating a substrate to enhance resistance of the substrate to at least one of cavitation and liquid impingement, the method comprising:

providing an amorphous metal composition including nickel and aluminum on a surface of a substrate;

preheating a portion of the surface to be acted on by a friction stir processing tool;

using the friction stir processing tool to perform a friction stir operation on the nickel and aluminum to form, in situ, a nickel aluminide coating on the surface.

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