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(54) SYSTEM AND METHOD FOR PRODUCING SUPERALLOYS UTILIZING ELECTROMETALLURGY

(57) A system and method for producing a rigid, heat-resistant part, such as a superalloy, via electrodeposition. The method can include the steps of coating a secondary alloy particulate with a superior alloy, forming a pre-coated particulate, dispensing a quantity of the pre-coated particulate into a container of an electrolytic solution, and applying a charge to the electrolytic solution such that the pre-coated particulate is electrodeposited onto a cathode or an external casing of the cathode. The pre-coated particulate can include particulate of non-uniform size and/or shape. The secondary alloy particulate is protected in the catalytic solution by the superior alloy coated thereon, such as nickel, iron, cobalt, and/or copper. The method also includes a step of vibrating or agitating the electrolytic solution before and/or during applying the charge to the electrolytic solution for even distribution of the pre-coated particulate onto the cathode or an external casing thereof.

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Description

BACKGROUND

[0001] Hypersonic flight and other applications require materials that can survive extreme conditions, especially high heat. Historically, aircraft materials suitable for such requirements have been made from nickel-based alloys where nickel is the primary alloy constituent and other elements such as cobalt, chrome, iron, titanium, and/or aluminum are provided for strengthening and resistance to elevated temperatures. However, even with these alloys, high temperatures can be problematic in some situations. For example, nickel alloy 718 significantly degrades beginning around 1250° F; and at 1,400° F, the materials strength and stiffness are no longer acceptable for the service conditions encountered by an aircraft. Furthermore, these alloys are traditionally difficult and expensive to cast, hot-work, roll, forge, extrude, and wrought-process. In addition, traditional methods to manufacture parts made from nickel-, iron-, or cobalt-based superalloys require numerous steps which result in low rolled throughput yield, high manufacturing cost, complex supply chain, and long lead times. Thus, in order to address the issues faced with global supply chain challenges and to keep up with the demand for such alloys in legacy applications as well as emerging ones, a more efficient and streamlined manufacturing approach is needed.

SUMMARY

[0002] The present invention solves the above-described problems and provides a distinct advance in the art of producing nickel-, iron-, or cobalt-based superalloys. Co-deposition of superior alloys and strengthening elements that are typically not electrodepositable (e.g., secondary alloys) via electrodeposition is possible by dispensing pre-coated particulate into electrolytic solution for electrodeposition, where secondary alloy particulate is pre-coated with the superior alloys. In one embodiment, a method for producing a rigid, heat-resistant part includes the steps of coating a secondary alloy particulate with an electroplating compatible alloy (e.g., a superior alloy), forming a pre-coated particulate, and dispensing a quantity of the pre-coated particulate into a container of an electrolytic solution. The superior alloy can be at least one of nickel, iron, cobalt, and copper and the electrolytic solution can comprise one or more alloying elements (e.g., nickel, cobalt, iron, tungsten, chromium, manganese, or molybdenum). The method can also include a step of applying a charge to the electrolytic solution such that the pre-coated particulate is electrodeposited onto a cathode or an external casing of the cathode. Furthermore, in some embodiments, the method can include a step of agitating the electrolytic solution at least one of before and during applying the charge. Thus, when such electrodeposition is performed in accordance with methods herein, upon subsequent heat treatment, the result is a strong, lightweight, oxidation-resistant part consisting of multiple alloy constituents, with useful applications at very high temperatures (e.g., triple or quadruple the strength of traditionally-used solid solution strengthened alloys at 1,500° F to 2,000° F).

[0003] Other embodiments provide a system for producing a rigid, heat-resistant, complex-contoured part. The system includes a container with electrolytic solution sealed therein, an anode, a cathode, an electrical source, a source of pre-coated particulate, and a vibrating device. The electrical source is electrically coupled to the anode and the cathode for selectively applying a charge to the electrolytic solution via the anode and the cathode. The source of pre-coated particulate is selectively dispensable into the container. The pre-coated particulate includes the secondary alloy particulate coated with an electroplating-compatible coating such as a superior alloy (e.g., nickel, iron, cobalt, and/or copper). When the charge is applied to the electrolytic solution, the pre-coated particulate is electrodeposited onto a surface of the cathode. The vibrating device applies a low frequency, high displacement resonance frequency to at least one of the container and the electrolytic solution sealed therein. Application of resonance or sub-resonance vibration allows more homogeneous dispersion/distribution of pre-coated powders in the plating solution and helps reduce residual stresses that result from electrodeposition; thereby allowing deposition of thicker parts within a given plating campaign, as well as producing components with higher degree of dimensional stability.

[0004] The invention is also described as following numbered clauses that illustrate various aspects and embodiments of the invention:

> Clause 1. A method for producing a rigid, heat-resistant part, the method comprising:
>
> > dispensing a quantity of a pre-coated particulate into a container of an electrolytic solution, wherein the pre-coated particulate is a secondary alloy particulate coated with a superior alloy; and
> > applying a charge to the electrolytic solution such that the pre-coated particulate is electrodeposited onto a cathode or an external casing of the cathode.
>
> Clause 2. The method of Clause 1, wherein the superior alloy is at least one of nickel, iron, cobalt, and copper.
>
> Clause 3. The method of Clause 1 or 2, wherein the secondary alloy particulate comprises particles of at least one of chromium (Cr), manganese (Mn), tungsten (W), molybdenum (Mo), rhenium (Re), ruthenium (Ru), titanium (Ti), aluminum (Al), niobium (Nb), tantalum (Ta), zirconium (Zr), vanadium (V), yttrium

(Y), cerium (Ce), lanthanum (La), boron (B), phosphorus (P) and carbon (C) with at least one of grain growth inhibitors and recrystallization inhibitors.

Clause 4. The method of any of Clauses 1 to 3, wherein the pre-coated particulate comprises particles of at least one of varying shapes and varying dimensions.

Clause 5. The method of any of Clauses 1 to 4, wherein the cathode or the external casing of the cathode has a complex, non-planar surface.

Clause 6. The method of any of Clauses 1 to 5, further comprising vibrating the container during the steps of dispensing the quantity of the pre-coated particulate and applying the charge to the electrolytic solution.

Clause 7. The method of any of Clause 6, wherein vibrating the container comprises applying a high amplitude, low frequency vibration to at least one of the container and the electrolytic solution.

Clause 8. The method of any one of Clauses 1 to 7, further comprising drawing partial vacuum from within the container during the step of applying the charge, such that hydrogen is removed from the container.

Clause 9. A method for producing a rigid, heat-resistant part, the method comprising:

- coating a secondary alloy particulate with a superior alloy, forming a pre-coated particulate, wherein the superior alloy is at least one of nickel, iron, cobalt, and copper;
- dispensing a quantity of the pre-coated particulate into a container of an electrolytic solution, wherein the electrolytic solution comprises one or more alloying elements;
- applying a charge to the electrolytic solution such that the pre-coated particulate is electrodeposited onto a cathode or an external casing of the cathode; and
- agitating the electrolytic solution at least one of before and during applying the charge.

Clause 10. The method of Clause 9, wherein the secondary alloy particulate comprises particles of at least one of chromium (Cr), manganese (Mn), tungsten (W), molybdenum (Mo), rhenium (Re), ruthenium (Ru), titanium (Ti), aluminum (Al), niobium (Nb), tantalum (Ta), zirconium (Zr), vanadium (V), yttrium (Y), cerium (Ce), lanthanum (La), boron (B), phosphorus (P) and carbon (C) with at least one of grain growth inhibitors and recrystallization inhibitors.

Clause 11. The method of Clause 9 or 10, wherein the pre-coated particulate comprises a plurality of particles of varying shapes and varying dimensions from each other.

Clause 12. The method of any one of Clauses 9 to 11, wherein the cathode or the external casing of the cathode has a non-planar surface having one or more complex contours.

Clause 13. The method of any one of Clauses 9 to 12, wherein agitating the electrolytic solution comprises vibrating the container during the steps of dispensing the quantity of the pre-coated particulate and applying the charge to the electrolytic solution, wherein vibrating the container comprises applying a high amplitude, low frequency vibration to at least one of the container and the electrolytic solution.

Clause 14. The method of any one of Clauses 9 to 13, further comprising heat-treating a resulting part formed on the cathode following the electrodeposition of the pre-coated particulate onto the cathode.

Clause 15. The method of any one of Clauses 9 to 14, further comprising drawing partial vacuum from within the container during the step of applying the charge, such that hydrogen between the electrolytic solution and the container is removed from the container.

Clause 16. A system for producing a rigid, heat-resistant, complex-contoured part, the system comprising:

- a container with electrolytic solution sealed therein;
- an anode;
- a cathode;
- an electrical source electrically coupled to the anode and the cathode and configured for selectively applying a charge to the electrolytic solution via the anode and the cathode;
- a source of pre-coated particulate selectively dispensable into the container, wherein the pre-coated particulate includes a secondary alloy particulate coated with a superior alloy, wherein the superior alloy is at least one of nickel, iron, cobalt, and copper, wherein when the charge is applied to the electrolytic solution the pre-coated particulate is electrodeposited onto a surface of the cathode; and
- a vibrating device configured for applying a low frequency, high displacement resonance frequency to at least one of the container and the electrolytic solution sealed therein.

Clause 17. The system of Clause 16, further comprising a temperature control tank for controlling a temperature of the electrolytic solution.

Clause 18. The system of Clause 16 or 17, wherein the pre-coated particulate comprises a plurality of particles of varying shapes and varying dimensions from each other.

Clause 19. The system of any one of Clauses 16 to 18, wherein the cathode comprises a shield and a mandrel, wherein the pre-coated particulate coats the mandrel, wherein the mandrel has a non-planar surface having one or more complex contours.

Clause 20. The system of any one of Clauses 16 to 19, wherein the secondary alloy particulate comprises particles of at least one of chromium (Cr), manganese (Mn), tungsten (W), molybdenum (Mo), rhenium (Re), ruthenium (Ru), titanium (Ti), aluminum (Al), niobium (Nb), tantalum (Ta), zirconium (Zr), vanadium (V), yttrium (Y), cerium (Ce), lanthanum (La), boron (B), phosphorus (P) and carbon (C) with at least one of grain growth inhibitors and recrystallization inhibitors.

Clause 21. A method for producing a part, the method comprising:

applying a charge to an electrolytic solution via an anode and a cathode within the electrolytic solution, such that one or more alloys are electrodeposited onto the cathode or an external casing of the cathode; and
vibrating the electrolytic solution before or during applying the charge to the electrolytic solution.

Clause 22. The method of Clause 21, wherein the alloy is a superior alloy, wherein the superior alloy is at least one of nickel, iron, cobalt, and copper.

Clause 23. The method of Clause 21 or 22, further comprising dispensing a quantity of a particulate into the electrolytic solution, wherein the particulate includes a material electrodepositable onto the cathode within the electrolytic solution, wherein the particulate comprises particles of at least one of varying shapes and varying dimensions.

Clause 24. The method of any one of Clauses 21 to 23, wherein the particulate is a secondary alloy particulate coated by a superior alloy, wherein the secondary alloy particulate comprises particles of at least one of chromium (Cr), manganese (Mn), tungsten (W), molybdenum (Mo), rhenium (Re), ruthenium (Ru), titanium (Ti), aluminum (Al), niobium (Nb), tantalum (Ta), zirconium (Zr), vanadium (V), yttrium (Y), cerium (Ce), lanthanum (La), boron (B), phosphorus (P) and carbon (C) with at least one of grain growth inhibitors and recrystallization inhibitors.

Clause 25. The method of any one of Clauses 21 to 24, wherein the cathode or the external casing of the cathode has a complex, non-planar surface.

Clause 26. The method of any one of Clauses 21 to 25, wherein the vibration is performed at a sub-resonant or resonant frequency of the part, providing in-situ stress relief to each layer of the part during electrodeposition.

Clause 27. The method of any one of Clauses 21 to 26, further comprising selectively pausing the vibrating between electrodeposition of different layers of the rigid, heat-resistant part and circulating the electrolytic solution while the vibrating is paused, thereby removing smut and other undesirable compounds from a last-deposited one of the different layers.

Clause 28. The method of any one of Clauses 21 to 27, wherein vibrating the electrolytic solution comprises applying a high amplitude, low frequency vibration to the electrolytic solution or a container holding the electrolytic solution.

Clause 29. The method of Clause 28, further comprising drawing partial vacuum from within the container from a space above the electrolytic solution during the step of applying the charge, such that hydrogen is removed from the container.

Clause 30. The method of any one of Clauses 21 to 29, wherein vibration performed prior to electrodeposition is a high aptitude, low frequency vibration, and vibration performed during electrodeposition is a high frequency, low aptitude ultrasonic vibration.

Clause 31. A method for producing a rigid, heat-resistant part, the method comprising:

dispensing a quantity of a particulate into a container of an electrolytic solution, wherein the particulate comprises a superior alloy electrodepositable onto a cathode within the electrolytic solution, wherein the particulate comprises particles of at least one of varying shapes and varying dimensions;
applying a charge to the electrolytic solution such that the particulate is electrodeposited onto the cathode or an external casing of the cathode; and
vibrating the container during at least one of: dispensing the quantity of the particulate, and applying the charge to the electrolytic solution.

Clause 32. The method of Clause 31, wherein the vibrating is performed prior to electrodeposition and during electrodeposition, wherein vibrating performed prior to electrodeposition is a high aptitude, low frequency vibration, and vibrating performed during electrodeposition is a high frequency, low aptitude ultrasonic vibration.

Clause 33. The method of Clause 31 or 32, wherein the particulate comprises a secondary alloy particulate coated by the superior alloy, wherein the secondary alloy particulate comprises particles of at least one of chromium (Cr), manganese (Mn), tungsten (W), molybdenum (Mo), rhenium (Re), ruthenium (Ru), titanium (Ti), aluminum (Al), niobium (Nb), tantalum (Ta), zirconium (Zr), vanadium (V), yttrium (Y), cerium (Ce), lanthanum (La), boron (B), phosphorus (P) and carbon (C) with at least one of grain growth inhibitors and recrystallization inhibitors.

Clause 34. The method of any one of Clauses 31 to 33, wherein the cathode or the external casing of the cathode has a complex, non-planar surface.

Clause 35. The method of any one of Clauses 31 to 34, wherein the vibration is performed at a sub-resonant or resonant frequency of the part, providing in-situ stress relief to each layer of the part during electrodeposition.

Clause 36. The method of any one of Clauses 31 to 35, further comprising selectively pausing the vibrating between electrodeposition of different layers of the rigid, heat-resistant part and circulating the electrolytic solution while the vibrating is paused, thereby removing smut and other undesirable compounds from a last-deposited one of the different layers.

Clause 37. The method of any one of Clauses 31 to 36, wherein vibrating the container comprises applying a high amplitude, low frequency vibration to at least one of the container and the electrolytic solution.

Clause 38. The method of any one of Clauses 31 to 37, further comprising drawing partial vacuum from within the container during the step of applying the charge, such that hydrogen is removed from the container.

Clause 39. A system for producing a rigid, heat-resistant, complex-contoured part, the system comprising:

> a container with electrolytic solution sealed therein;
> an anode;
> a cathode;
> an electrical source electrically coupled to the anode and the cathode and configured for selectively applying a charge to the electrolytic solution via the anode and the cathode; and
> a vibrating device configured for applying a low frequency, high displacement resonance frequency to at least one of the container and the electrolytic solution sealed therein.

Clause 40. The system of Clause 39, further comprising a source of particulate selectively dispensable into the container, wherein the particulate comprises a plurality of particles of varying shapes and varying dimensions from each other.

Clause 41. A method for producing a part, the method comprising:

> positioning an anode and a cathode in spaced apart relation to each other in an electrolytic solution, wherein the cathode has a complex, non-planar surface; and
> applying a charge to the electrolytic solution via the anode and the cathode, such that layers of one or more alloys are electrodeposited onto the cathode to form the part.

Clause 42. The method of Clause 41, wherein the anode has at least one of a shape and a position relative to the cathode or an external casing of the cathode such that there is a uniform distance between a majority of the anode and the cathode or the external casing of the cathode.

Clause 43. The method of Clause 41 or 42, wherein the alloy is a superior alloy, wherein the superior alloy is at least one of nickel, iron, cobalt, and copper.

Clause 44. The method of any one of Clauses 41 to 43, further comprising masking or electrically isolating one or more areas on a surface of one of the layers electrodeposited onto the cathode after a predetermined number of the layers are electrodeposited onto the cathode.

Clause 45. The method of Clause 44, wherein the one or more areas masked or electrically isolated create preferential deposition, hollow regions, or pockets once all of the layers are electrodeposited onto the cathode to form the part.

Clause 46. The method of Clause 44 or 45, wherein temporary materials are used for masking or electrically isolating the one or more areas, wherein the temporary materials are dissolvable or meltable.

Clause 47. The method of Clause 46, further comprising electrodepositing additional ones of the layers of the one or more alloys over the temporary materials, and then melting or dissolving the temporary materials, forming a hollow space where the temporary materials were melted or dissolved.

Clause 48. The method of any one of Clauses 41 to 47, further comprising a step of positioning permanent inserts at one or more areas on a surface of one of the layers electrodeposited onto the cathode after a predetermined number of the layers are electrodeposited onto the cathode such that electrodeposition bonds and incorporates or envelops the permanent inserts directly into the part.

Clause 49. The method of Clause 48, wherein the permanent inserts are support structures integrally stiffening the part between inner ones of the layers and outer ones of the layers.

Clause 50. The method of any one of Clauses 41 to 49, wherein the part electrodeposited onto the cathode is functionally graded, has variable thickness, or has variable properties.

Clause 51. A method for producing a part, the method comprising:

positioning an anode and a cathode in spaced apart relation to each other in an electrolytic solution, wherein the cathode has a complex, non-planar surface;
electrodepositing layers of one or more alloys onto the cathode to form the part via application of a charge to the electrolytic solution between the anode and the cathode; and
masking or electrically isolating one or more areas on a surface of one of the layers electrodeposited onto the cathode after a predetermined number of the layers are electrodeposited onto the cathode.

Clause 52. The method of Clause 51, wherein the anode has at least one of a shape and a position relative to the cathode or an external casing of the cathode such that there is a uniform distance between a majority of the anode and the cathode or the external casing of the cathode.

Clause 53. The method of Clause 51 or 52, further comprising electrodepositing additional ones of the layers of the one or more alloys over the one or more areas masked or electrically isolated, wherein the one or more areas masked or electrically isolated create preferential deposition, hollow regions, or pockets once all of the layers are electrodeposited onto the cathode to form the part.

Clause 54. The method of Clause 53, wherein temporary materials are used for masking or electrically isolating the one or more areas, wherein the temporary materials are dissolvable or meltable, the method further comprising melting or dissolving the temporary materials, forming a hollow space where the temporary materials were melted or dissolved.

Clause 55. The method of any one of Clauses 51 to 54, further comprising a step of positioning permanent inserts between electrodeposition of at least two of the layers onto the cathode such that electrodeposition bonds and incorporates or envelops the permanent inserts directly into the part, wherein the permanent inserts are support structures integrally stiffening the part between inner ones of the layers and outer ones of the layers.

Clause 56. The method of any one of Clauses 51 to 55, wherein the part electrodeposited onto the cathode is functionally graded, has variable thickness, or has variable properties.

Clause 57. The method of any one of Clauses 51 to 56, further comprising applying a high amplitude, low frequency vibration to the electrolytic solution during or between electrodeposition of the layers of the one or more alloys.

Clause 58. A system for producing a rigid, heat-resistant, complex-contoured part via electrodeposition of layers of one or more alloys, the system comprising:

a container with electrolytic solution sealed therein;
an anode within the electrolytic solution;
a cathode within the electrolytic solution in spaced relationship with the anode, wherein the cathode has a complex, non-planar surface, wherein the anode has at least one of a shape and a position relative to the cathode or an external casing of the cathode such that there is a uniform distance between a majority of the anode and the cathode or the external casing of the cathode;
an electrical source electrically coupled to the anode and the cathode and configured for selectively applying a charge to the electrolytic solution via the anode and the cathode; and
a vibrating device configured for applying a low frequency, high displacement resonance frequency to at least one of the container and the electrolytic solution sealed therein.

Clause 59. The system of Clause 58, further comprising temporary materials placed between the layers of the one or more alloys during electrodeposition, wherein the temporary materials are dissolvable or meltable such that melting or dissolving the temporary materials forms a hollow space in that rigid, heat-resistant, complex-contoured part where the temporary materials were melted or dissolved.

Clause 60. The system of Clause 58 or 59, further comprising permanent inserts positioned between at least two of the layers of the one or more alloys during electrodeposition, such that electrodeposition bonds and incorporates or envelops the permanent inserts directly into the rigid, heat-resistant, complex-contoured part.

[0005] This summary is intended to introduce a selection of concepts in a simplified form that are further described in the detailed description below. This summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter. Other aspects and advantages of the present invention will be apparent from the following detailed description of the embodiments and the accompanying drawing figures.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

[0006] Embodiments of the present invention are described in more detail below with reference to the attached drawing figures, wherein:

FIG. 1 is a schematic cross-sectional elevation view of a system for electrodeposition to form a rigid, heat-resistant part, in accordance with embodiments of the present invention;
FIG. 2 is a schematic cross-sectional elevation view of an alternative system for electrodeposition to form a rigid, heat-resistant part, in accordance with embodiments of the present invention;
FIG. 3a is a schematic cross-sectional elevation view of another alternative system for electrodeposition to form a rigid, heat-resistant part, in accordance with embodiments of the present invention;
FIG. 3b is an exploded cross-sectional elevation view of a cathode of the system of FIG. 3a, in accordance with embodiments of the present invention;
FIG. 4 is a schematic cross-sectional elevation view of yet another alternative system for electrodeposition to form a rigid, heat-resistant part, in accordance with embodiments of the present invention; and
FIG. 5 is a flow chart of a method for manufacturing a superalloy in accordance with embodiments of the present invention.

[0007] The drawing figures do not limit the present invention to the specific embodiments disclosed and described herein. The drawings are not necessarily to scale, emphasis instead being placed upon clearly illustrating the principles of the invention.

DETAILED DESCRIPTION

[0008] The following detailed description of embodiments of the invention references the accompanying drawings. The embodiments are intended to describe aspects of the invention in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments can be utilized and changes can be made without departing from the scope of the claims. The following detailed description is, therefore, not to be taken in a limiting sense. The scope of the present invention is defined only by the appended claims, along with the full scope of equivalents to which such claims are entitled.

[0009] In this description, references to "one embodiment", "an embodiment", or "embodiments" mean that the feature or features being referred to are included in at least one embodiment of the technology. Separate references to "one embodiment", "an embodiment", or "embodiments" in this description do not necessarily refer to the same embodiment and are also not mutually exclusive unless so stated and/or except as will be readily apparent to those skilled in the art from the description. For example, a feature, structure, act, etc. described in one embodiment may also be included in other embodiments but is not necessarily included. Thus, the present technology can include a variety of combinations and/or integrations of the embodiments described herein.

[0010] Systems and methods herein are suitable for electrodeposition to create existing complex nickel-, iron-, or cobalt-based precipitation hardened, super alloys (e.g., Nickel 718, Nickel, 718 Plus, Nickel 263, or off-stoichiometric alloys), or other alloy formulations that are difficult to produce with ingot metallurgy due to solid solubility limits and alloy segregation (micro and macro) directly from chemical solution. The systems and methods herein eliminate the need for conventional pyro-metallurgy, melting, casting, forging, rolling, drawing, sintering, and even metal forming operations.

[0011] Electrodeposition and Electroless deposition of nickel and cobalt alloys is an alternative being considered for such applications, and nickel and iron or nickel and cobalt can even be co-deposited for such a component, however only materials that are within the same element classification can be directly co-deposited from an electrolytic solution using prior art methods. So while co-deposition of simple alloys such as brass (copper and zinc), iron-nickel or nickel-cobalt, and deposition of simple solid solution strengthened alloys can be performed using such prior art methods when the electrode potentials of the constituent metallic elements are not very different from one another, such co-deposition is not suitable for other dissimilar elements. In traditional use cases where similar elements are co-deposited, the anode can be made from the simple alloy to be deposited, and the plating bath contains a mixture of electrolytes that otherwise would have been employed separately for each of the metallic elements individually. So, while this solution may be suitable for relatively simple solid solution-strengthened superalloys containing a certain group of transitional metal elements, such solution is limited in what combination of alloy constituents can be combined into complex superalloys which rely on multiple strengthening mechanisms to achieve superior room temperature and elevated temperature mechanical properties.

[0012] To address these and other such disadvantages in regard to heat resistance, strength, and oxidization of traditional materials used in manufacturing structural parts for aircraft, the present invention provides an improved method for producing a rigid, heat-resistant part using electroplating, also referred to herein as electrodeposition. Specifically, applicant has discovered that adding a pre-coated particulate as described herein to the electrolytic solution can form complex alloys containing secondary elements that are traditionally difficult or expensive to directly electrodeposit.

[0013] Electroplating and electrodeposition refer to a process of coating a superior alloy over a base material (e.g., an inferior alloy or inferior metal) by passing direct current through an electrolytic solution containing soluble salt of the coating metal. In an electroplating process, positively charged ions of the plated metal (e.g., can consist of one or more compatible alloying elements) from the electrolytic solution combine with the electrons flowing through the negatively charged cathode and as a result deposit a layer of the plated metal onto the cathode. Factors affecting electroplating may include temperature, concentration, and distance between electrodes. Note that in all embodiments of this invention, factors such as current density, temperature, electrolyte conductivity, current polarization, selection of continuous or pulsed current, control use of reverse current electroplating, and use of additional agent(s) are all important considerations for plating, and therefore, must be effectively controlled just as they are for conventional plating or electroforming applications.

[0014] Such electroplating or electrodeposition methods are commonly used to plate a single element such as nickel, chromium, copper, zinc, cadmium, gold, silver, cobalt, for example. These methods have also been used to plate alloys made from compatible elements such as brass (a copper-zinc alloy), nickel-cobalt alloy, and even nickel-tungsten alloy. However, in order to produce complex alloys containing secondary elements that are difficult or expensive to electrodeposit directly onto a cathode, the system and methods described herein add such secondary elements to the electrolytic solution after first coating those secondary elements with a primary alloy constituent or electroplating-compatible coating.

[0015] Specifically, the system and methods herein allow co-deposition of major alloying constituents or primary alloying constituents (e.g., nickel, cobalt, iron, or copper) that can be co-electrodeposited into an electrolytic solution with those that traditionally cannot. That is, particulate or powder of secondary elements that cannot be deposited directly (or would be difficult / expensive to be deposited directly) from the electrolytic solution onto the cathode or mandrel can be pre-coated with at least one of the primary alloying constituents and carried along with the primary alloying constituent to the cathode during electrodeposition. For example, Electroless nickel-coated powders, chemical vapor deposition (CVD) nickel-coated powders, or physical vapor deposition (PVD) nickel-coated powders of secondary elements such as titanium, aluminum, carbon, chromium, niobium, tantalum, metalloids, and/or rare earth elements can be incorporated into the deposited layer due to the techniques described herein. The resultant nickel-, iron-, or cobalt-based alloy may contain many (or if desired all) of the following elements below: manganese (Mn), tungsten (W), molybdenum (Mo), rhenium (Re), ruthenium (Ru), titanium (Ti), aluminum (Al), niobium (Nb), tantalum (Ta), zirconium (Zr), vanadium (V), yttrium (Y), cerium (Ce), lanthanum (La), boron (B), phosphorus (P) and carbon (C), with special grain growth inhibitors and recrystallization inhibitors (e.g., finely dispersed oxides, carbides, or borides can act as grain growth/recrystallization inhibitors). For example, nickel, iron, cobalt, copper, nickel-tungsten, nickel-cobalt, or the like can be co-deposited onto the cathode from the electrolytic solution, and other elements can be incorporated by addition of nickel-coated or cobalt-coated secondary elements or powders. The above list of alloying elements is not meant to be exclusive of other elements which can be incorporated.

[0016] In one embodiment disclosed herein, as depicted in FIG. 1, a system 10 for producing a rigid, heat-resistant, complex-contoured part comprises a container 12 with electrolytic solution 14 contained and/or sealed therein, an anode 16, a cathode 18, an electrical source 20, a source (e.g., a hopper 22) of a pre-coated particulate 24, and a heat source 26. Furthermore, an agitation device 28 or a vibrating device configured for applying a low frequency, high-displacement resonance frequency to at least one of the container 12 and the electrolytic solution 14 sealed therein can optionally be included in this embodiment, as depicted in FIG. 1.

[0017] The container 12 is any liquid-holding container made of materials that do not react with the electrolytic solution 14. In some embodiments, the container 12 can contain a thermal jacket 30 having two spaced apart walls, with space therebetween fluidly coupled with the heat source 26 (e.g., a temperature control tank), as later descried herein. The container 12 can include a solution-holding basin 32 and/or a lid 34 sealable onto the solution-holding basin 32. One or more ports 36 may extend through the solution-holding basin 32, the lid 34, and/or the thermal jacket 30, with said ports 36 being selectively openable and closable via a valve 38 or other device for selectively sealing off an opening within a port or passageway leading to the container 12.

[0018] In some embodiments, the ports 36 of the container 12 may include a vacuum port (not shown). Specifically, in some embodiments the system 10 can further include a vacuum source (not shown) connected to the vacuum port in the container 12. For example, the container 12 can be sealed - thereby allowing application of partial vacuum to assist in removal of evolved gases such as hydrogen, as well as also allowing the increase of the kinetics of electrodeposition. Some embodiments of the container 12 can also include the port 36 fluidly coupling a solution chemical control tank 40 with the electrolytic solution 14 in the container 12, as depicted in FIG. 1. The solution chemical control tank 40 may be configured for filtering and/or otherwise controlling the electrolytic solution 14 per predetermined parameters. In some embodiments, between the solution chemical control tank 40 and the sealed container 12, there may also be at least one pump (not shown) for delivering the electrolytic solution 14 thereto.

[0019] In this embodiment, the electrolytic solution 14 held in and/or sealed in the container 12 is a chemical solution and may include one or more alloying elements such as nickel, cobalt, iron, tungsten, chromium, manganese, or molybdenum. For example, the electrolytic solution 14 can be formulated to allow deposition of nickel or co-deposition of Ni, W, Co, Fe onto the cathode. The electrolyte or electrolytic solution for co-deposition of nickel and cobalt may contain $NiSO_4$ (nickel sulfate), $CoSO_4$ (cobalt sulfate), boric acid, saccharin, and water, whereas the electrolytic solution for co-deposition of nickel and tungsten may contain nickel sulfate, Na_2WO_4 (sodium tungstate), $Na_3C_6H_5O_7$ (trisodium citrate), ammonium chloride, and sodium bromide. However, other electrolytic solutions can be used without departing from the scope of the technology described herein.

[0020] The anode 16 is located in the container 12 and at least partially covered by the electrolytic solution 14. The anode 16 is made of superior alloy or a primary alloy constituent, such as various coating metals or inert metals. For example, the anode 16 can be made of nickel, iron, cobalt, copper, or tungsten. In some embodiments, the anodes 16 may be conformal anodes made via 3D printing or other forming methods. The conformal anodes can, in some embodiments, help achieve more uniform thickness during electrodeposition. For making complex shapes, since the distance between various locations within the cathode and anode will be different as the result of the irregular shape of the desired object, throwing power (i.e., the ability of the electrolytic solution to produce uniform thickness) can become an issue that can be greatly mitigated by application of conforming anodes that allow more uniform distance between various areas of the anode and the cathode.

[0021] The cathode 18, on the other hand, is spaced apart from the anode 16 in the container 12, at least partially covered by the electrolytic solution 14, and comprises a base metal, such as stainless steel or nickel alloys to be used as permanent mandrels, or made from expendable (e.g., removable/recyclable) low melting alloys such as tin-zinc alloys, aluminum, or certain waxes. The expendable mandrels can be melted (zinc-tin or wax) or dissolved (aluminum) after the completion of the deposition. This feature allows deposition of complex alloys onto complex geometries including configurations that contain internal cavities.

[0022] In some embodiments, the cathode 18 may include or have placed thereon a composite material (e.g., a carbon composite-fiber composite material) and/or another external casing, mandrel, or mold. The cathode 18, the composite material, and/or the external casing or mold can have any shape or configuration (e.g., see embodiments depicted in FIGS. 3a, 3b, and 4 and described below). For example, the methods described herein can produce metallic alloys, as well as the matrix metal for metal matrix composites, by directly depositing on reinforcement fibers and consolidating into metal matrix parts, particularly when combined with techniques such as those described in U.S. Application Number 17/559,773, entitled "METHOD FOR MANUFACTURING METAL MATRIX COMPOSITE." In some embodiments, the composite material, and/or the external casing, mandrel, or mold has a non-planar surface having one or more complex contours. The electrodeposition may result in electroplating of the non-planar surface.

[0023] The electrical source 20 is electrically coupled to the anode 16 and the cathode 18 and configured for selectively applying a charge to the electrolytic solution 14 via the anode 16 and the cathode 18. Specifically, electrodeposition may be accomplished via direct or pulsed current or pulse reversal current. For example, the electrical source 20 can be a battery or another direct current source suitable for electroplating. Alternatively, as later described herein, an electrical source 20 can be incorporated into a control system or other electrical control devices. The voltage, pH, bath temperature, chemical concentration, and chemical ingredients can all vary based on material and solution selection. For example, Ni-Co can be co-deposited in a bath consisting of nickel and cobalt sulfate solution with boric acid with an electrolyte pH of 2 and temperature of 75 degrees F; whereas Ni-W deposit may use a different solution run at approximately 165 degrees F at a pH of 8.9.

[0024] Electrodeposition may be accomplished conventionally or via sediment deposition techniques, with the system 10 having different configurations for these two options. In conventional electrodeposition, the anode 16 and cathode 18 are placed substantially vertical, parallel to each other, and spaced apart from each other within the electrolytic solution 14, such that electrophoresis may force electrodeposition onto the cathode or a surface thereof, as depicted in FIGS. 1-3. Alternatively, using a sediment deposition technique ("SCD") includes the electrodes (i.e., the anode 16 and the cathode 18) immersed in the electrolytic solution 14, placed horizontally and parallel to each other, thereby taking advantage of gravitational force as part of the electrodeposition process, as opposed to the electrophoresis force alone.

[0025] The source of pre-coated particulate may include the hopper 22 or the like with a hopper valve 38, door, or the like configured for selectively dispensing the pre-coated particulate 24 into the container 12. Additionally or alternatively, the source of pre-coated particulate may include a plurality of individual hoppers (not shown) which can be used in order to independently control the addition of levels of the pre-coated particulate 24 into the electrolytic solution 14 in a more precise fashion. The pre-coated particulate 24 can be dispensed as dry pre-coated particulate and/or can be pre-wetted (e.g., in the form of a slurry) in any of the embodiments described herein.

[0026] The pre-coated particulate 24 includes a secondary alloy particulate (or particulate materials that are traditionally not electrodepositable on their own) coated with electroplating-compatible coating such as the superior alloy or the primary alloy constituent. The pre-coated particulate 24 can include particulate (e.g., a fine powder or nano powder) that is non-uniform in size and/or shape. For example, the pre-coated particulate my include particulates of different sizes and/or different shapes relative to each other. The electroplating-compatible coating can be the superior alloy or primary alloy constituent such as, for example, one or more of nickel, iron, cobalt, and/or copper. The secondary alloy particulate can be, in some embodiments, a non-electrodepositable particulate that would generally dissolve in the electrolytic solution. Furthermore, the secondary alloy particulate can be non-metals, alkaline-earth metals, rare earths, actinides and metalloids, even certain basic metals such as aluminum, or transitional elements such as titanium that are not known to be readily electrodeposited onto a cathode from an aqueous plating solution. Specifically, in some embodiments, the secondary alloy particulate can comprise particles of at least one of manganese (Mn), tungsten (W), molybdenum (Mo), rhenium (Re), ruthenium (Ru), titanium (Ti), aluminum (Al), niobium (Nb), tantalum (Ta), zirconium (Zr), vanadium (V), yttrium (Y), cerium (Ce), lanthanum (La), boron (B), phosphorus (P) and carbon (C). In one or more embodiments, the secondary alloy particulate can also include at least one of grain growth inhibitors and recrystallization inhibitors (e.g., finely dispersed oxides, carbides, or borides can act as grain growth/recrystallization inhibitors). Advantageously, because some secondary alloy particulates can dissolve in the electrolytic solution 14, the electroplating-compatible coating thereon allows co-depositing without such dissolving of these elements. Even for secondary elements that do not dissolve in the electrolytic solution, being coated as described herein can simplify the plating solution, reduce having extra chromium plating solutions, reduce environmental impact of hexavalent chrome, and/or increase deposition rates (e.g., the secondary element chromium is typically much slower to deposit). When charge is applied to the electrolytic solution 14, the pre-coated particulate 24 is electrodeposited onto a surface of the cathode 18, such as the non-planar surface described above. These secondary alloy particulates can be added for precipitation hardening, for example. In some example embodiments, nickel, iron, cobalt, copper, nickel-tungsten, nickel-cobalt, or the like can be co-deposited onto the cathode from the electrolytic solution and other elements can be incorporated by addition of the pre-coated particulate 24.

[0027] The heat source 26 can be, for example, a temperature control tank for controlling a temperature of the electrolytic solution 14. As the temperature increases, ions diffuse faster, and the amount of deposition increases. Thus, the temperature control tank can be set to any appropriate temperature for the materials being deposited, the electrolytic solution being used, and various desired qualities of the resulting part. In some embodiments, the temperature control tank is fluidly coupled to the thermal jacket 30 and provides heated fluid thereto in order to control a temperature of the electrolytic solution 14 contained in the container 12. Furthermore, a heat exchanger may be located around the temperature control tank or between the temperature control tank and the container 12. Examples of appropriate temperatures depending on the materials being deposited may include nickel being plated from a Watt's solution at 0.5 to 3 volts at 112° F to 150° F, 3 to 11 A/dm2, with 3 to 4.2 pH, or alternatively made from Sulfamate solution at 90° F to 140° F and pH of 3.5 to 4.5 at .5 to 32 A/dm2. In another example, Ni-Co can be co-deposited in a bath consisting of nickel and cobalt sulfate solution with boric acid with a electrolyte pH of 2 and temperature of 75° F; whereas Ni-W deposit may use a different solution run at approximately 165° F at a pH of 8.9. However, other such formulations and temperatures may be used without departing from the scope of the technology described herein.

[0028] The agitating device 28 or vibrating device may be configured for applying a low frequency, high displacement resonance frequency to at least one of the container 12 and the electrolytic solution 14 contained and/or sealed therein. Various solution agitation methods such as magnetic stirring, ultrasonic vibration, use of non-reactive or coated propellers, or pump agitation may be used to aid homogeneity and uniformity of distribution of the elements electrodeposited onto the cathode 18. In some embodiments, the agitating device 28 may be a vibration table, a shaker table, or a shaker platform configured to provide a low frequency, high displacement (e.g., high magnitude or amplitude), and/or resonance frequency vibration to the container 12 and thus to the electrolytic solution 14 therein. This agitating device 28 can move the container 12 in a back and forth or up and down reciprocal motion. However, any direction of movement may be used without departing from the scope of the technology described herein. In some embodiments, the resulting mechanical agitation can be performed prior to electrodeposition (e.g., high aptitude, low frequency), and/or during deposition if needed (e.g., high frequency, low aptitude ultrasonic vibration).

[0029] The agitating device 28 is thus configured to uniformly disperse alloying elements for precipitation hardening, dispersion hardening, and the like. This may be particularly useful where the pre-coated particulate 24 is of varying dimensions, sizes, and/or shapes, so that there is a substantially uniform distribution of larger versus smaller particles being electrodeposited onto the cathode 18 or the non-planar surface thereon or associated therewith. Thus, the vibration of the agitation device 28 enables proper (uniform) distribution of the pre-coated particulate 24, irrespective of particle size, density, and/or percentage. Advantageously, the ability to effectively mix particles of varying dimensions, sizes, and/or shapes allows use of cheaper powder or particulate that cannot generally be used for additive manufacturing or metal injection molding (which conversely use particulate of uniform size and shape). In some embodiments, mechanical agitation involving low frequency high amplitude vibration via acoustic resonant mixing, resonance or sub-resonance frequency vibration can be employed by the agitating device 28 not only to help disperse the coated powders, but also as means to perform in-situ stress relief of the electrodeposited layers onto the cathode or mandrel, thereby allowing the ability to rapidly form thicker sections.

[0030] Other example embodiments of the system 10 are depicted in FIGS. 2-4, providing additional system elements and/or alternative configurations. For example, FIG. 2 depicts a system 210 that is similar to the system 10 described above, including a container 212 with electrolytic solution 214 contained and/or sealed therein, an anode 216, a cathode 218, an electrical source 220, a source (e.g., a hopper 222) of pre-coated particulate 224, and a heat source 226. These elements can be similar or identical to each of the following, respectively: the container 12 with the electrolytic solution 14 contained and/or sealed therein, the anode 16, the cathode 18, the electrical source 20, the source (e.g., the hopper 22) of the pre-coated particulate 24, and the heat source 26. Furthermore, the system 210 in FIG. 2 includes an agitation device 228 or a vibrating device configured for applying a low frequency, high displacement resonance frequency to at least one of the container 212 and the electrolytic solution 214 sealed therein, similar to or identical to the agitation device 28 described above.

[0031] In FIG. 2, a system 210 is depicted with a container 212, an electrolytic solution 214, an electrical source 220, a hopper 222 with pre-coated particulate 224 dispensable into the container 212, an anode 216, a cathode 218, and a heat source 226, each the same or substantially similar to the system 10, the container 12, the electrolytic solution 14, the electrical source 20, the hopper 22, the pre-coated particulate 24, the anode 16, the cathode 18, and the heat source 226 respectively, as described above. Furthermore, the system 210 may likewise include an agitating device 228 and a solution chemical control tank 240 that is the same or substantially similar to the agitating device 28 and the solution chemical control tank 40 described above.

[0032] However, in addition to these similar or identical components, this alternative embodiment of the system 210 further includes a control system 270 having a processor, memory, communication components, user input components, one or more displays, sensors, and/or a power supply. The user input components may comprise, for example, a keyboard, a touchpad, a mouse, a mousepad, and/or a communications port for receiving user input from a wired or wireless remote user device. The one or more displays can include, for example, an electronic screen or a physical dial associated with one or more readings/measurements. However, other user input components and displays can be used as part of the control system 270 without departing from the scope of the technology described herein.

[0033] The sensors can include, for example, a sensor 272 extending into the electrolytic solution and configured for controlling the electrolytic solution by providing signals to the processor which, based on those signals, controls or instructs the chemical control tank 240, actuates pumps associated therewith, or otherwise actuates or adjusts other variables associated therewith. Furthermore, the power supply of the control system 270 can power the control system and/or provide charge to the anode 216 and the cathode 218. That is, the power supply of the control system 270 may be the electrical source 220. In some embodiments, the control system 270 can further be electrically and/or communicably coupled to the hopper 222 and/or a valve or door associated therewith for dispensing the pre-coated particulate 224. Furthermore, in some embodiments, the control system 270 can power and/or provide instructions to the agitating device 228, based on preset or preprogrammed information (such as the desired frequency and amplitude). Likewise, the control system 270 can be programmed to control an amount of heat to be applied to the electrolytic solution 214, how much pre-coated particulate 224 to add thereto, what charge to apply and for how long, and/or what electrolytic solution 214 to add to the container 212. The control system 279 may be implemented in hardware, software, firmware, or any combination thereof.

[0034] The control system 270 may include any number of processors, controllers, integrated circuits, programmable logic devices, or other computing devices and resident or external memory for storing data and other information accessed and/or generated by various components of the system 210. The control system 270 is preferably coupled with the other components of the system 210 through wired or wireless connections to enable information to be exchanged between the various components. In some embodiments the control system 270 can be programmed with the sequence, duration, and/or other parameters for mixing the pre-coated particulate. Such parameters to be programmed, controlled, and/or adjusted may include an amount of particulate to dispense from the hopper, timing of pre-coated particulate addition, whether to continue or stop vibration of the agitating device when electric current is applied to the electrolytic solution, parameters for application of pulsed or direct current for electrodeposition of primary elements, and/or programming of when to stop plating a layer. However, other parameters can be programmed into the control system 270 without departing from the scope of the technology described herein.

[0035] The control system 270 may implement a computer program and/or code segments to perform the functions described herein. The computer program may comprise an ordered listing of executable instructions for implementing logical functions in the control system 270 such as some of the steps illustrated in FIG. 5 and described below. For example, the computer program may be a software program configured to run on a computer, such as a personal computer, laptop, tablet, or the like. The computer program can be embodied in any computer-readable medium for use by or in connection with an instruction execution system, apparatus, or device, and execute the instructions. In the context of this application, a "computer-readable medium" can be any physical means that can contain, store, communicate, propagate, or transport the program for use by or in connection with the instruction execution system, apparatus, or device. The computer-readable medium can be, for example, but not limited to, an electronic, magnetic, optical, electromagnetic, infrared, or semi-conductor system, apparatus, or device. More specific, although not inclusive, examples of the computer-readable medium would include the following: an electrical connection having one or more wires, a portable computer diskette, a random access memory (RAM), a read-only memory (ROM), an erasable, programmable, read-only memory (EPROM or Flash memory), a portable compact disk read-only memory (CDROM), an optical fiber, multi-media card (MMC), reduced-size multi-media card (RS MMC), secure digital (SD) cards such as microSD or miniSD, and a subscriber identity module (SIM) card.

[0036] In FIGS. 3a and 3b, a system 310 is depicted with a container 312, an electrolytic solution 314, a hopper 322 with pre-coated particulate 324 dispensable into the container 312, an anode 316, a cathode 318, and an agitation device 328, each the same or substantially similar to the system 10, the container 12, the electrolytic solution 14, the hopper 22, the pre-coated particulate 24, the anode 16, the cathode 18, and the agitation device 28 respectively, as described above.

[0037] However, the embodiments in FIGS. 3a and 3b depict the cathode 318 comprising a shield 380 and a mandrel 382 onto which the pre-coated particulate is electrodeposited into an electrodeposited part 384. That is, the pre-coated particulate 324 can coat the mandrel 382, such as a non-planar surface of the mandrel 382 having one or more complex contours. The shield 380 can be made of stainless steel, or nickel alloys, while the mandrel 382 can be made of electrically conductive or non-conductive material. Examples of conductive material are stainless steel or nickel alloys for configurations in which the electrodeposited part can be removed from the mandrel (for example parts with no re-entrant shapes), or alternatively from expendable mandrel material made from zinc-tin alloys. Examples of non-conductive mandrels are plastics or wood that needs to be rendered conductive by application of a thin metallic film, for example silver or nickel. Nickel can be applied in the form of Electroless nickel, while silver can be, for example, sprayed on the plastic surface with solution from a dual nozzle spray gun that reacts together to form a silver film on the plastic surface.

[0038] In FIG. 4, a system 410 is depicted with a container 412, an electrolytic solution 414, anodes 416, and a cathode 418, each the same or substantially similar to the system 10, the container 12, the electrolytic solution 14, the anode 16, and the cathode 18 respectively, as described above. However, unlike other embodiments described above, system 410 includes at least two anodes 416 spaced apart from each other, and the cathode 418 is posited between the at least two anodes 416. Similar to the embodiments of FIGS. 3a and 3b, the cathode 418 can include a shield 480 and a mandrel 482 onto which the pre-coated particulate is electrodeposited into an electrodeposited part 484. Note that any number of anodes and cathodes can be used in the systems described herein and for the methods described herein.

[0039] In use, the system 10 (and/or any of systems 210, 310, and/or 410) can perform a process to make simple flat or complex shapes directly from electrolytic solution by employing conforming cathodes and anodes via electroforming. Homogenization and heat treatment processes such as solution treatment and aging allow inter-diffusion, mixing and homogenizing chemistry and integrating all alloy elements. As described above, the alloy elements may include the pre-coated particulate, such as elements deposited from powder into a homogenous alloy matrix that can form intermetallic dispersoids that are formed when atoms from the deposited pre-coated particulate combine with those from elements directly electrodeposited onto the cathode. The method steps described herein using the system 10 can further produce a superalloy that is precipitation hardened for optimum strength, creep, and fatigue resistance. Once the electrodeposition is complete, and the resulting electrodeposited part is heat treated, the form can be inspected, trimmed, and drilled as required for a given final part.

[0040] The flow chart of FIG. 5 depicts the steps of an exemplary method 500 for manufacturing a part via electrodeposition in more detail. In some embodiments of the invention, various steps may be omitted and/or steps may occur out of the order depicted in FIG. 5 without departing from the scope of the invention. For example, two blocks shown in succession in FIG. 5 may in fact be executed substantially concurrently, or blocks may sometimes be executed in the reverse order depending upon the functionality involved.

[0041] The exemplary method 500 includes the steps of selecting specific alloys and/or specific alloy formulations, as depicted in block 502, and formulating an electrolytic solution, as depicted in block 504, for co-deposited primary alloying elements that can be plated directly from that formulated electrolytic solution. For example, alloying elements can be selected that are capable of being directly co-deposited simultaneously from electrolytic solution (e.g., nickel, iron, cobalt, copper, nickel-tungsten, nickel-cobalt, or the like), and corresponding electrolytic solutions can be prepared (e.g., those containing Ni, Co, Fe, Cu, W, Cu, Ag, and the like). The method 500 may further include preparing chemical solutions containing elements that can be electrodeposited from the same formulated electrolytic solution, as depicted in block 506. Depending on complexity of the alloy, more than one bath / electrolytic solution can be used. In some embodiments, the preparing step 506 can further include positioning the anode and the cathode in spaced apart relation to each other in the prepared chemical solutions (i.e., the electrolytic solution), particularly in embodiments where the cathode has a complex, non-planar surface.

[0042] In some embodiments, the method 500 can also include a step of programming the control system with the sequence, duration, and/or other parameters, as depicted in block 508. Such parameters to be programmed, controlled, and/or adjusted may include parameters for mixing the pre-coated particulate, an amount of particulate to dispense from the hopper, timing of pre-coated particulate addition, whether to continue or stop vibration of the agitating device when electric current is applied to the electrolytic solution, other parameters or variables for operation of the agitating device, parameters for application of pulsed or direct current for electrodeposition of primary elements, and/or programming of when to stop plating a layer being electrodeposited. However, other parameters can be programmed into the control system without departing from the scope of the technology described herein.

[0043] Furthermore, the method 500 includes a step of coating the secondary alloy particulates with the electroplating-compatible coating or superior alloy (e.g., nickel, iron, cobalt, and/or copper), as depicted in block 510, and then dispensing a quantity of the resulting pre-coated particulate to the electrolytic solution(s), as depicted in block 512. For example, the particulate may be powder or particulate of varying dimensions and/or shapes and can be coated with nickel or other chemically compatible coatings to prevent dissolution, allow wetting and deposition onto the cathode via CVD, PVD, or chemical plating processes (for example Electroless nickel coating). Examples of such secondary alloy particulates can include chromium, aluminum, titanium, niobium, tantalum, carbon, or boron powder. Boron and phosphorous can also be provided by Electroless nickel plating. Various methods for coating the secondary alloy particulate can be used, such as Electroless nickel plating to pre-coat this powder or secondary alloy particulate. Alternatively, pre-coating both metallic and non-metallic powders may be performed via chemical or physical vapor deposition prior to suspending the pre-coated particulate in the electrolytic solution.

[0044] As depicted in FIG. 5, the method 500 also includes a step of electrodepositing using both the electrolytic solution and/or dispersion of the pre-coated particulate, as depicted in block 514. For example, this electrodeposition may be triggered by applying a charge to the electrolytic solution via the anode and cathode such that the pre-coated particulate is electrodeposited onto a cathode, an external casing or mandrel of the cathode, and/or a previously-electrodeposited layer. Via electrodeposition in this step, positively charged ions of the plated metal from the electrolytic solution combine with the electrons flowing through the negatively charged cathode and as a result deposit a layer of the plated metal onto the cathode. Simultaneously, the pre-coated particulate added to the electrolytic solution is carried along with the plated metal to be co-deposited onto the cathode or mandrel described herein. Any desired number of layers and/or any desired thickness of electroplating can be performed via electrodeposition as described herein. This electrodeposition allows deposition of alloys that can contain nickel, iron or cobalt alloys, for example, secondary alloy particulate such as Mn, W, Mo, Re, Ru, Ti, Al, Nb, Ta, Zr, V, Y, Ce, La, B, P, and C, with at least one of grain growth inhibitors and recrystallization inhibitors (e.g., finely dispersed oxides, carbides, or borides can act as grain growth/recrystallization inhibitors). In some example embodiments, easily dissolvable element powders (e.g., carbon) can be coated with an organic material or a metal (e.g., nickel or copper) via CVD, PVD, Electroless nickel (EN) coating, or by mechanical alloying prior to addition to the electrolytic solution to prevent premature dissolution and to help effective suspension/mixing of alloying elements. In addition, certain alloying elements such as yttrium or lanthanum can be added to improve oxidation and corrosion resistance or for grain refinement.

[0045] In addition to the metallic elements added in the form of the pre-coated particulate described herein, note that oxides or carbides can be added via one or more of these electrodeposition method steps to form oxide, carbon, or carbide dispersion hardened alloys. Additionally or alternatively, elements added as powders or particulates can combine to form reaction-induced coherent or semi-coherent intermetallic dispersoids by combining with each other or by combining with electrodeposited elements from the electrolytic solution to further enhance strength and creep resistance.

[0046] Method step 514 can include electrodepositing any number of layers required to form the desired electrodeposited part. In some embodiments, after a predetermined number of layers are electrodeposited via electrodeposition, one or more areas can be masked and/or electrically isolated to achieve area coverage, preferential deposition, and/or pockets in the resulting electrodeposited form (e.g., once all layers are electrodeposited onto the cathode to form the part). This can include, for example, fabricating complex shapes (both profile and depth) and/or hollow structure by use of temporary materials (e.g., dissolvable or meltable materials) in removable patterns that the desired part or at least some layers thereof can be electrodeposited on. Once the electrodeposited part has been produced, the temporary materials can be removed via melting or dissolution and a hollow structure can thus be made.

[0047] Additionally or alternatively, some embodiments of the method described herein may include positioning inserts (not shown) such that electrodeposition bonds and incorporates or envelops the insert directly into the electrodeposited part. This can allow for forming configurations with variable thickness or properties. Due to the layered deposition nature of the process, functionally graded structures can also be made using the electrodeposition techniques described herein. Support systems, reinforcement features, columns and other permanent inserts (e.g., support structures) can additionally or alternatively be incorporated to tie the outer and inner walls and make light weight integrally stiffened hollow structures consisting of inner walls, outer wall, and support structures. In accordance with these embodiments, any of the systems described herein can additionally include the temporary materials and/or the permanent inserts without departing from the scope of the technology described herein.

[0048] In some embodiments, the method 500 further comprises a step of vibrating the container and/or otherwise agitating the electrolytic solution, as depicted in block 516. This step may be performed in order to ensure effective dispersion of the pre-coated particulate. In some embodiments, the vibrating or agitating may be performed via the agitation device described above or any other device capable of such vibration or agitation of the electrolytic solution and may be performed during the steps of dispensing the quantity of the pre-coated particulate and applying the charge to the electrolytic solution for electrodeposition. In some embodiments, vibrating the container comprises applying a high amplitude, low frequency vibration to at least one of the container and the electrolytic solution. For example, low-frequency, high-energy (G-force) resonant or sub-resonant frequency vibration such as resonant acoustic mixing and pulsed current plating can assist in controlling resulting grain size during electrodeposition.

[0049] "Resonance acoustic mixing" (also known by the acronym RAM) as used herein refers to generating a high level of energy by seeking and operating, at all times, at a resonant condition of the mechanical system being used. As with all objects, a system using resonance acoustic mixing has a specific resonant frequency (e.g., between 58 Hz to 62 Hz) that is constant when at rest but is continually monitoring, adjusting, and changing when in operation. So, employing resonant acoustic mixing to the methods described herein can include monitoring mixing condition changes multiple times per second, for example, to balance kinetic energy or mixing forces and potential energy or stored forces. This balancing action allows a resonant acoustic mixer to apply all forcing energy (e.g., up to 100 g) directly to the ingredients being mixed. Thus, resonance acoustic mixing can be used to continually adjust to the changing damping characteristics in the container to stay at the resonant frequency of the entire system including the materials being mixed therein. Using resonance acoustic mixing can deliver the greatest amplitude or displacement using the least amount of power for maintaining the resonant condition.

[0050] Shaped cathodes, mandrels, and conforming containers as described herein can be used during electrodeposition to allow direct deposition of preforms into complex shape. In this way, electrodeposition can produce complex shapes directly with no need for further forming of forging operations. One disadvantage of prior art electroforming of complex shapes is that residual stresses can break away the deposit from the mandrel. However, using the methods described herein, resonant frequency mixing / vibrating can advantageously result in in-situ stress relief of the deposit, thereby allowing direct deposition of complex shapes. Thus, sub-resonant or resonant frequency vibration can be applied via the agitation device after deposition layer has ended to relieve plating stresses.

[0051] Application of resonant acoustic mixing during the vibrating or agitating step may in some embodiments require the container to be enclosed, which may enable vacuum assisted electrodeposition that can remove gasses such as hydrogen gas and accelerate deposition rates. Specifically, the method 500, in some embodiments, further includes a step of drawing at least partial vacuum from within the container during or after the step of applying the charge, as depicted in block 518, such that hydrogen is removed from the container. For example, soft vacuum or partial vacuum can be applied during electrodeposition and/or after electrodeposition.

[0052] The method 500 further includes post-deposition processing of the resulting electrodeposited layer, form, or part, as depicted in block 520. In some embodiments, such post-deposition processing can occur between layers of deposition. For example, in one embodiment, once a first layer is deposited, the electric current is stopped, the vibration is stopped, and the electrolytic solution is manually or automatically circulated in order to remove smut and undesirable compounds, thereby bringing electrolytic solution chemistry under control. Whether or not the electrolytic solution chemistry is under control may be determined, for example, by the solution sensor coupled with the control system, as in FIG. 2. With or without such processing between depositions of one or more of the layers, note that the steps 512 - 516 may be repeated as many times as needed to achieve a desired thickness of the resulting electrodeposited part.

[0053] The post-deposition processing additionally includes cleaning and drying the complete electrodeposited part, followed by homogenization and heat treating for a sufficient time at a temperature to sinter/metallurgically bond the electrodeposited layers in order to render the electrodeposited part into a true alloy encompassing all of the alloying elements. In some embodiments, the post-deposition processing can also include solution treating the part in order to create a solution-annealed alloy for solution hardening alloy formulations (with or without dispersoids) or to create supersaturated solid solution for precipitation hardening alloys. The post-deposition processing can also include precipitation hardening to achieve maximum strength and creep resistance.

[0054] The subsequent post-deposition processing, especially thermal processing (e.g., homogenization and solution treatment and precipitation hardening for certain alloys) are essential in some embodiments of the present invention. Specifically, homogenization and solution treatment remove inhomogeneity/chemical segregation within the electrodeposited part and allow the individual alloying elements to dissolve and mix into an alloy via diffusion, as the electrodeposited part is heated at a high temperatures (below the solidus temperature) of the alloy for a sufficient time. Solution heat treatment will cause the one or more of the constituents to enter into a solid solution followed by cooling at appropriate rates to keep these elements in solid solution as the part is cooled to room temperature. Many malleable solid solution strengthened alloys such as 300 series stainless steels, and Nickel 625 can be used in their solution treated or solution annealed conditions. However, complex alloys such as Nickel 718 achieve their desired mechanical properties through formation controlled nucleation and growth of precipitates that impede dislocation resulting in significant increase in strength, hardness and creep resistance of the alloy. Thus, in some embodiments herein, heat treatment (e.g., homogenization, solution treatment for solid solution strengthened alloys and homogenization, solution treatment for precipitation hardening alloys) is a key step in the methods described herein.

[0055] The heat treatment described above is different from degassing or baking treatments used for other prior art electrodeposited structures, as it includes solution / homogenization treatment to create true alloy mixtures and precipitation hardening to increase strength of the electrodeposited structures. In some embodiments, the homogenization and subsequent heat treatment is essential for homogenization of alloying constituents and converting them from incoherent particles in order to create true alloy mixtures via solid state diffusion, followed by the solution treatment and precipitation hardening or dispersion hardening to increase strength, creep resistance, and fatigue performance of the electrodeposited structures. Heat treatment in order to attain precipitation hardening or dispersion hardening of the alloy by solution treatment and controlled precipitation of such hardening agents via in-situ reaction among the alloying elements advantageously provides an added degree of freedom for formulating complex alloys beyond what is possible by mere electro co-deposition of colloidal dispersoids onto the cathode. Furthermore, heat treatment allows formation of indigenous precipitates. By providing the option for both creating indigenous and exogenous precipitates, dispersoids and hardening compounds, the system and methods herein allow alloy formulation and manufacture of complex alloys including nonstoichiometric compositions, and compositions that are not effectively achievable via ingot metallurgy due to macro or micro-segregation during solidification of large ingots. Specialized heat treatment solution treats and ages the part to achieve desired mechanical properties and desired corrosion resistance optimizing homogenization without undue grain growth or particle coarsening. Optionally, Hot Isostatic Pressing of the part can also be performed prior to solution treatment and aging.

[0056] Finally, the method 500 includes a step of drilling or trimming the resulting electrodeposited form, as depicted in block 522. For example, such drilling or trimming can be performed following heat treatment thereof for the purpose of fastening the part to another part and otherwise machining it to desired parameters. Using the method steps described herein, forming complex alloys can be made directly from electrolytic solution into near net shape or net shape components (with subsequent heat treatment, drilling, and/or trimming), eliminating any need for melt refinement, melting, casting, forging, and forming. In some embodiments, even machining of the form is not required, with the exception of trimming and drilling. In addition, processes such as electrodeposition with in-situ stress relief negates the need for using any leveler or additives that can adversely affect mechanical properties.

[0057] Using the systems and methods described herein, virtually any nickel, iron or cobalt base composition can be produced and electroformed into the final shape, thus producing simple highly formable solid solution or dispersion hardened alloys. The alloys produced thereby can be of any desired shape and thickness. In addition to these advantages, electrodeposition of the pre-coated particulate described herein allows formulation of any type of alloy including precipitation hardened alloys which can increase strength and creep resistance several fold once the preform deposit has been homogenized and heat treated. Conversely, prior art co-deposition methods using electrolytic solution were limited to only being able to co-deposit materials that are within the same element classification.

[0058] Using the system and methods described herein, all alloying constituents can be electrodeposited onto successive plated layers and virtually any alloy composition consisting of all classes of nickel, iron, or cobalt base alloys can be formed via electrodeposition. For example, this may include highly formable and oxidation solid solution strengthened, dispersion-hardened alloys, including both those containing coherent or semi-coherent dispersoids made by formation of intermetallic due to subsequent thermal processing or alternatively dispersion of non-metallic particles. Specifically, the system and methods described herein allow incorporation of coherent or semi-coherent intermetallic precipitates as well as any class of dispersoids, carbides or oxide particulates to help control microstructure, and to help improve mechanical properties of the alloy. Intermetallic compounds are composed of an ordered mixture of two or more elements in definite proportions and with distinctive crystalline structures. Controlled precipitation of intermetallic compounds as the result of elemental diffusion via subsequent heat treatment can allow significant increase in strength and elevated temperature mechanical properties such as elevated temperature strength, fatigue resistance, stress rupture and creep.

[0059] For example gamma prime strengthening of nickel base superalloys through formation of gamma prime (NI_3Al or Ni_3Ti), or through the formation of gamma double prime Ni_3Nb/Ni_3Ta phases are primarily responsible for the excellent elevated temperature resistance of precipitation hardened nickel-base super alloys. The systems and methods described herein allow additions to be made either: (1) in elemental form that, upon further heat treatment, will form intermetallic compound, carbide, or oxide dispersoids via reacting with other alloying elements, or (2) directly incorporated into the alloy in the final form by using coated pre-formed intermetallic, carbide, or oxide powders. In some examples, alloys formed by the methods herein may additionally or alternatively include oxide or carbides such as oxide dispersion-hardened nickel base superalloys or alloys that are conventionally made by mechanically alloying, precipitation hardening alloys, and even off-stoichiometric alloy compositions that cannot be effectively made by conventional ingot metallurgy. In addition, in cases where significant increases in oxidation resistance is required, silicide formation or formation of yttrium, lanthanum, or cerium oxides can be made by incorporation of nickel coated rare earth elements or silicon powder into the electrodeposited alloy. Oxides, carbides, or silicides can be either added in the form of pre-made powders or alternatively formed by reaction with other elements within the alloy following heat treatment, or even by reacting with the atmosphere (e.g., yttrium or lanthanum within the electrodeposited alloy) forming oxides upon use at elevated temperatures.

[0060] Part configuration incorporating all major and minor constituents for the specified alloy formulations can be electrodeposited through various embodiments of this invention. However, the deposited part may need to undergo subsequent thermal processing, including homogenization followed by solution heat treatment or annealing for solid solution strengthened alloy systems in order to develop optimum combination of properties. These operations typically dissolve and mix-in the various components into a true alloy form (solid solution) via diffusion of the elemental atoms. Alloy systems that are to be further strengthened by hardening and tempering require the deposited parts to be homogenized followed by hardening and tempering to achieve proper desired properties. Parts made from age hardenable alloy compositions typically include homogenization, solution treatment followed by precipitation hardening to achieve the desired heat treat condition.

[0061] In summary this invention allows application of electrodeposition process to create complex nickel, iron, or cobalt base precipitation hardening alloys such as Nickel 718, Nickel 263, even new off-stoichiometric alloys, or alloy formulations that are difficult to produce with traditional ingot metallurgy. By deposition directly from chemical solution(s), the process eliminates the need for existing pyro-metallurgy, melting, casting processes as well as also eliminating forging, rolling, drawing, and metal forming operations. This invention allows co-deposition of major alloying constituents in a single deposition operation from an electrolytic bath. As an example, nickel, cobalt, iron, and/or copper may be alloyed with a dispersed pre-coated powders of other alloying elements which cannot be electrodeposited directly from the electrolytic solution onto the cathode (mandrel). In this way using Electroless, CVD or PVD nickel coated powders elements such as such as titanium, aluminum, carbon, chromium, niobium, tantalum, metalloids, and or rare earth elements can be incorporated into the electrodeposited layer. The process can use direct or pulsed electric current for electrodeposition as well as using effective methods to uniformly distribute pre-coated powders before, and/or during electrodeposition.

[0062] With this invention all alloying constituents can be electrodeposited in successive plated layers and virtually any alloy composition consisting of all classes of nickel, iron, or cobalt base alloys can be manufactured. This invention not only allows production of simple solution hardened alloys with or without dispersion of exogenous dispersoids, but also allows formation of complex precipitates and dispersoids which are formed in-situ by reaction between indigenous atoms upon subsequent heat treatment. This feature allows production of precipitation hardened alloys with significant improvement in elevated temperature properties such as stress rupture or creep resistance by in-situ formation of copiously distributed and highly stable precipitates such as gamma prime precipitates for nickel base superalloys. Formation of precipitates through heat treatment allows control over size and distribution of hardening particles via judicious selection of solution treatment and aging parameter. In addition, exogenous and indigenous precipitates/dispersoids can be simultaneously incorporated to increase volume percent of hardening elements without undo depletion of base metal elements. As an example, most of carbides in form of highly stable VC, TaC or WC as well as chromium carbide(s) can be exogenously introduced in desired amount and sizes into the alloy, while low volume of carbon atoms can react with chromium in the matrix to form additional chromium carbide in a ferrous, cobalt or nickel base alloy via subsequent heat treatment. This way higher volume percent carbides can be incorporated into the alloy with very minimum risk of depletion of chromium; preserving the alloy's good corrosion and oxidation resistance without compromising hardness and wear resistance. In addition, the ability to judiciously engineer precipitate size and content by incorporating both exogenous and indigenous dispersoids provides an additional degree of freedom in formulating complex alloys. This added flexibility allows manufacture of alloys that are no longer bound by stoichiometry, nor by micro or macro segregation of solute elements during solidification as experienced with conventional ingot metallurgy. This opens up a whole new opportunity to formulate alloys that are not bound by stoichiometry, nor by solidification rate.

[0063] Although the invention has been described with reference to example embodiments illustrated in the attached drawing figures, it is noted that equivalents may be employed and substitutions made herein without departing from the scope of the invention as described and claimed herein.

Claims

1. A method for producing a rigid, heat-resistant part, the method comprising:

dispensing a quantity of a pre-coated particulate into a container of an electrolytic solution, wherein the pre-coated particulate is a secondary alloy particulate coated with a superior alloy; and
applying a charge to the electrolytic solution such that the pre-coated particulate is electrodeposited onto a cathode or an external casing of the cathode.

2. The method of claim 1, wherein the superior alloy is at least one of nickel, iron, cobalt, and copper.

3. The method of claim 1 or 2, further comprising vibrating the container during the steps of dispensing the quantity of the pre-coated particulate and applying the charge to the electrolytic solution.

4. The method of claim 3, wherein vibrating the container comprises applying a high amplitude, low frequency vibration to at least one of the container and the electrolytic solution.

5. The method of any preceding claim, further comprising drawing partial vacuum from within the container during the step of applying the charge, such that hydrogen is removed from the container.

6. A method for producing a rigid, heat-resistant part, the method comprising:

coating a secondary alloy particulate with a superior alloy, forming a pre-coated particulate, wherein the superior alloy is at least one of nickel, iron, cobalt, and copper;
dispensing a quantity of the pre-coated particulate into a container of an electrolytic solution, wherein the electrolytic solution comprises one or more alloying elements;
applying a charge to the electrolytic solution such that the pre-coated particulate is electrodeposited onto a cathode or an external casing of the cathode; and
agitating the electrolytic solution at least one of before and during applying the charge.

7. The method of any preceding claim, wherein the cathode or the external casing of the cathode has a non-planar surface, optionally having one or more complex contours.

8. The method of claim 6 or 7, wherein agitating the electrolytic solution comprises vibrating the container during the steps of dispensing the quantity of the pre-coated particulate and applying the charge to the electrolytic solution, wherein vibrating the container comprises applying a high amplitude, low frequency vibration to at least one of the container and the electrolytic solution.

9. The method of any one of claims 6 to 8, further comprising heat-treating a resulting part formed on the cathode following the electrodeposition of the pre-coated particulate onto the cathode.

10. The method of any one of claims 6 to 9, further comprising drawing partial vacuum from within the container during the step of applying the charge, such that hydrogen between the electrolytic solution and the container is removed from the container.

11. A system for producing a rigid, heat-resistant, complex-contoured part, the system comprising:

a container with electrolytic solution sealed therein;
an anode;
a cathode;
an electrical source electrically coupled to the anode and the cathode and configured for selectively applying a charge to the electrolytic solution via the anode and the cathode;
a source of pre-coated particulate selectively dispensable into the container, wherein the pre-coated particulate includes a secondary alloy particulate coated with a superior alloy, wherein the superior alloy is at least one of nickel, iron, cobalt, and copper, wherein when the charge is applied to the electrolytic solution the pre-coated particulate is electrodeposited onto a surface of the cathode; and
a vibrating device configured for applying a low frequency, high displacement resonance frequency to at least one of the container and the

electrolytic solution sealed therein.

12. The system of claim 11, further comprising a temperature control tank for controlling a temperature of the electrolytic solution.

13. The system of claim 11 or 12, wherein the cathode comprises a shield and a mandrel, wherein the precoated particulate coats the mandrel, wherein the mandrel has a non-planar surface having one or more complex contours.

14. The method of any one of claims 1 to 10, or the system of any one of claims 11 to 13, wherein the precoated particulate comprises a plurality of particles of varying shapes and varying dimensions from each other.

15. The method of any one of claims 1 to 10 or of claim 14, or the system of any one of claims 11 or 14, wherein the secondary alloy particulate comprises particles of at least one of chromium (Cr), manganese (Mn), tungsten (W), molybdenum (Mo), rhenium (Re), ruthenium (Ru), titanium (Ti), aluminum (Al), niobium (Nb), tantalum (Ta), zirconium (Zr), vanadium (V), yttrium (Y), cerium (Ce), lanthanum (La), boron (B), phosphorus (P) and carbon (C) with at least one of grain growth inhibitors and recrystallization inhibitors.

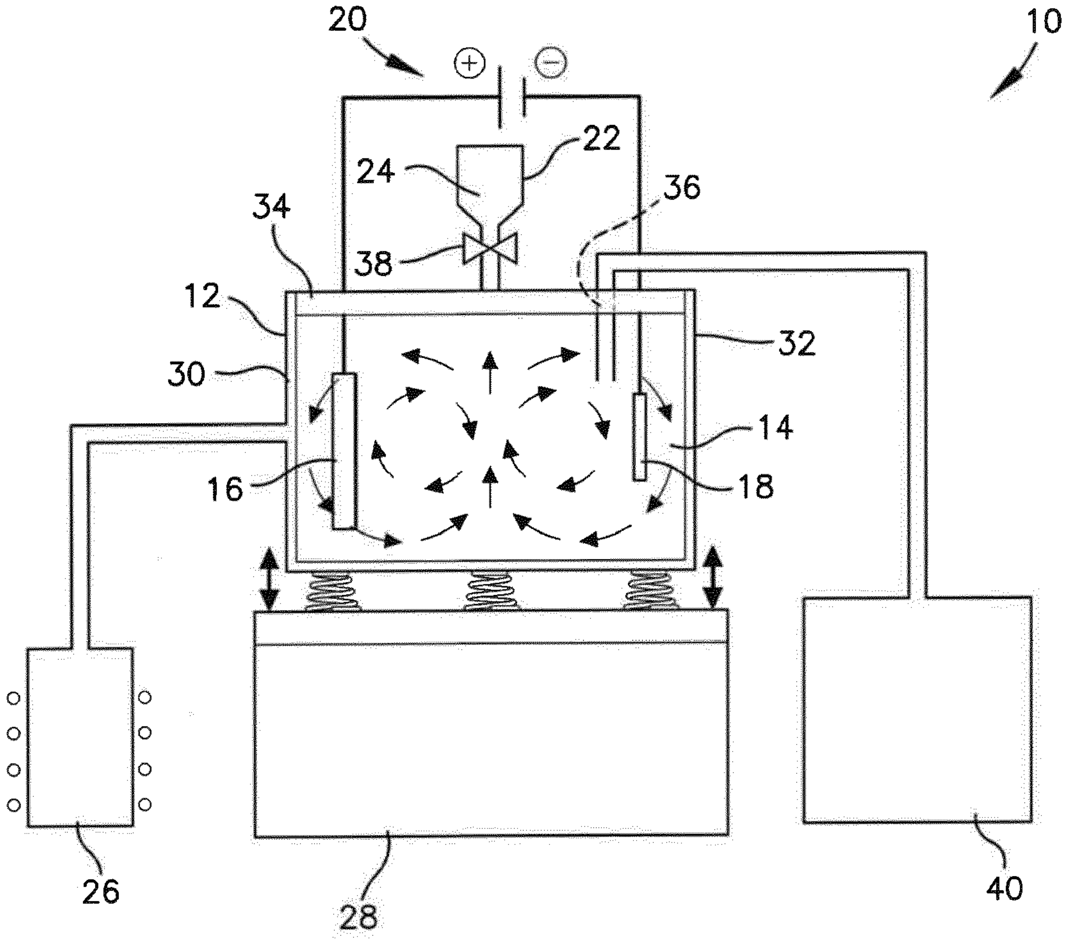

Fig. 1

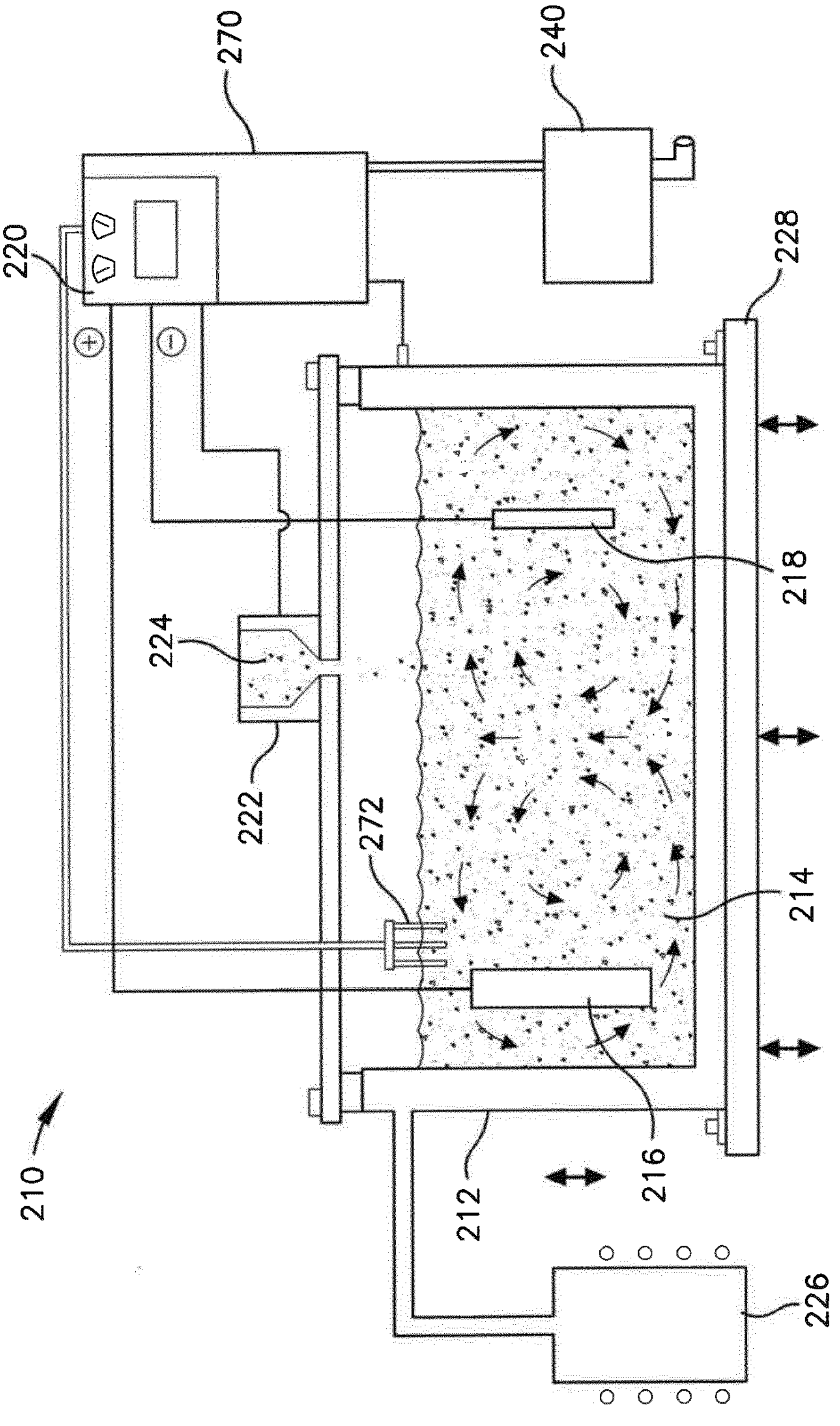

Fig. 2

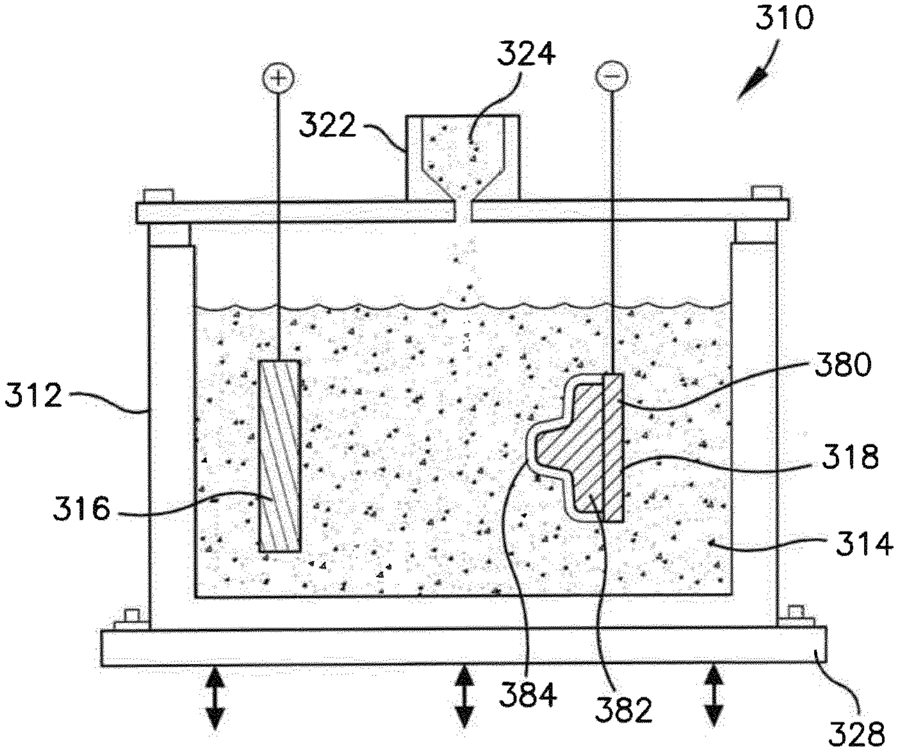

Fig. 3a

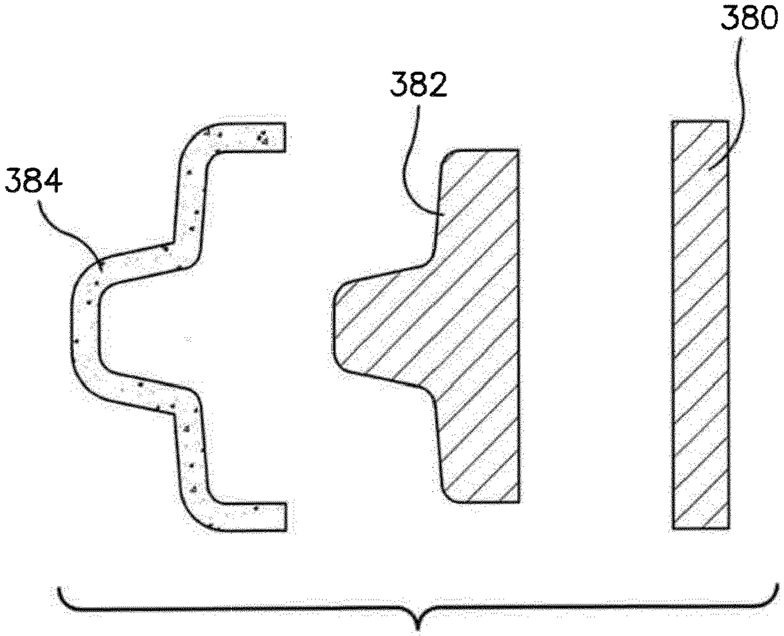

Fig. 3b

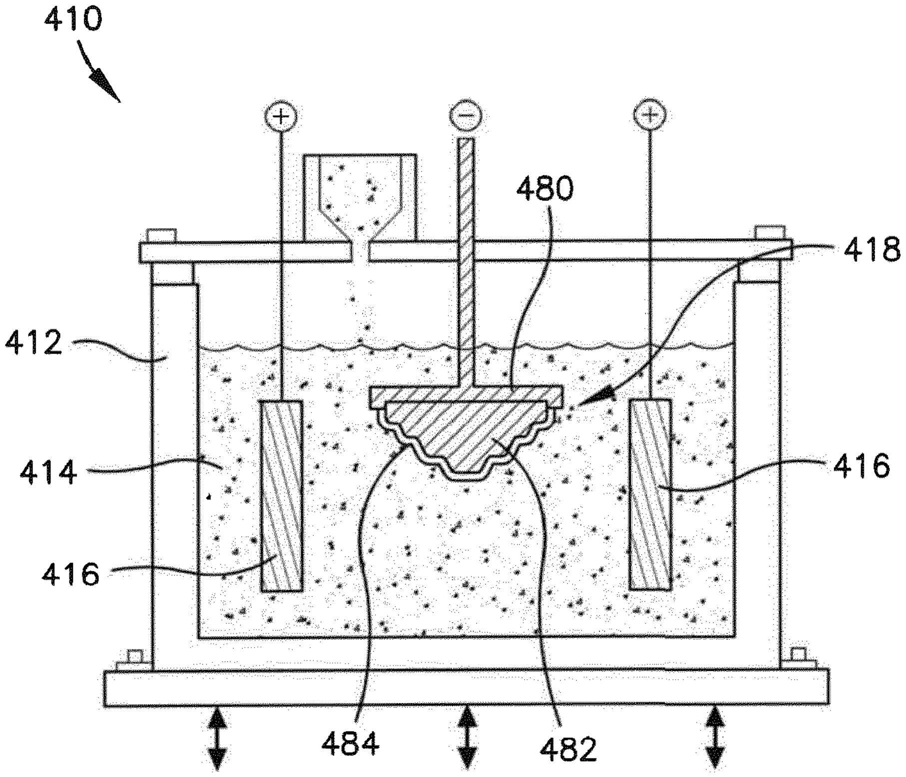

Fig. 4

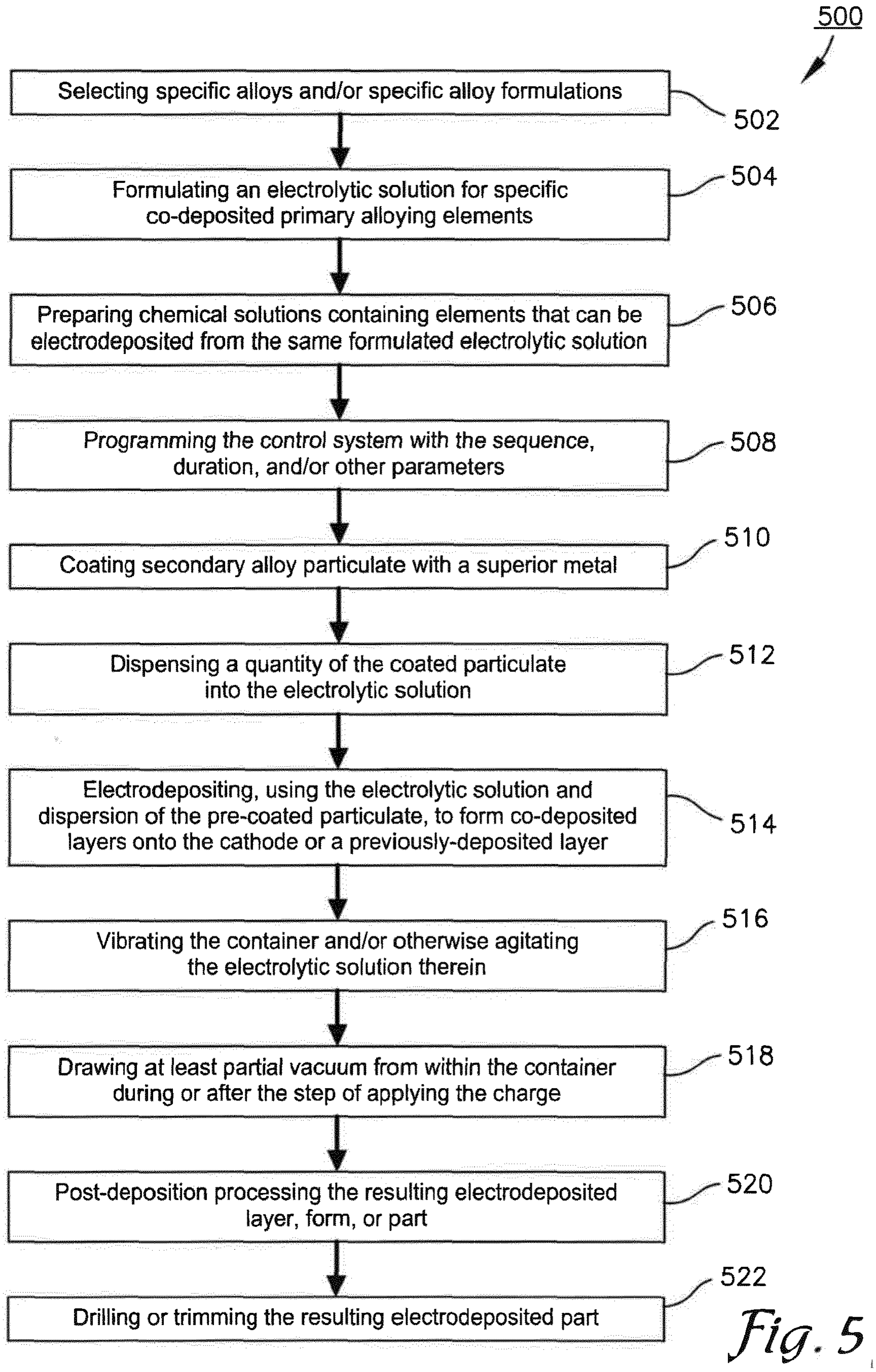
500
Selecting specific alloys and/or specific alloy formulations
502
Formulating an electrolytic solution for specific co-deposited primary alloying elements
504
Preparing chemical solutions containing elements that can be electrodeposited from the same formulated electrolytic solution
506
Programming the control system with the sequence, duration, and/or other parameters
508
Coating secondary alloy particulate with a superior metal
510
Dispensing a quantity of the coated particulate into the electrolytic solution
512
Electrodepositing, using the electrolytic solution and dispersion of the pre-coated particulate, to form co-deposited layers onto the cathode or a previously-deposited layer
514
Vibrating the container and/or otherwise agitating the electrolytic solution therein
516
Drawing at least partial vacuum from within the container during or after the step of applying the charge
518
Post-deposition processing the resulting electrodeposited layer, form, or part
520
Drilling or trimming the resulting electrodeposited part
522

Fig. 5

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

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