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Chen et al.

(54) ALLOY COMPOSITION, METHOD AND APPARATUS THEREFOR

- (71) Applicant: Wisconsin Alumni Research Foundation, Madison, WI (US)
- (72) Inventors: Lianyi Chen, Rolla, MO (US); Qilin Guo, Madison, WI (US)
- (73) Assignee: Wisconsin Alumni Research Foundation, Madison, WI (US)
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Primary Examiner — Dana Ross

Assistant Examiner — Adam M Eckardt

(74) Attorney, Agent, or Firm - Crawford Maunu PLLC

(57) ABSTRACT

Aspects of the disclosure are directed to forming a threedimensional (3D) structure by depositing an alloy composition on a target, and solidifying portions of the alloy composition to form the 3D structure. The solidifying includes producing a martensitic structure by destabilizing a ferrite phase of the alloy composition while solidifying the alloy composition.

21 Claims, 8 Drawing Sheets



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	Spec	3D-printed	Invention
C	15-17.5	16.7	14.5-16
Ņ	ŝ	4 Ú	4-5.5
3	ş	4	3-5.5
Nb+Ta	0.15-0.45	0.3	0.15-0.45
Mn		0.22	0
0	0-0'0	0.02	0
a	0-0.04	0.011	0
s	0-0.03	0.003	0
Si	6	0.34	0
Fe	Bai	Bal	Bai

FIG. 2



Intensity, a.u.





Time, s







ALLOY COMPOSITION, METHOD AND APPARATUS THEREFOR

This invention was made with government support under 2011354 awarded by the National Science Foundation. The ⁵ government has certain rights in the invention.

BACKGROUND

Alloys are used for a multitude of structures, and may be ¹⁰ formed in a variety of manners such as by casting, threedimensional (3D) printing, and other approaches. However, for some applications it can be challenging to produce a product having a desirable structure. For instance, when cooling metal alloys, various phases of material and corre-¹⁵ sponding crystalline structures may form based on a variety of factors.

Stainless steel is an alloy used in a variety of applications. For instance, precipitation-hardened (PH) stainless steel known as 17-4 PH (otherwise known as AISI 630 or SAE $\ ^{20}$ Type 630) has a chemical makeup of approximately 15-17.5% chromium and 3-5% nickel, as well as 3-5% copper. 17-4 PH stainless steel may be manufactured as a fully martensitic stainless steel via methods such as forging, casting or welding. However, additively manufactured 17-4 25 PH has a strong tendency of reserving residual ferrite and austenite phases at room temperature upon solidification, which may provide undesirable mechanical and corrosion performance. For instance, in manufacturing with low cooling rates, 17-4 PH undergoes phase transformations as: 30 liquid (L)— δ -ferrite (δ)—austenite (γ)—martensite (α '). However, with additive manufacturing, transformation to fully martensite (e.g., at least 90% or at least 95% martensite) can be challenging. As such, it can be challenging to obtain desired phases in materials built using additive manu- 35 facturing (AM) with multi-stage phase transformations, because such materials may be sensitive to complex AM processing conditions, such as rapid heating/cooling and chemical variation. For instance, 17-4 PH may undergo different solidification paths during solidification in AM 40 processes, which leads to the formation of different unwanted phases in the printed parts.

It may also be challenging to obtain equiaxed grains in additive manufacturing, especially in powder bed fusion. Due to the high temperature gradient, columnar grains ⁴⁵ epitaxially grow from a previously deposited layer, along the build direction, and may be observed in additive manufactured parts. The columnar grains are generally coarse and characterized by anisotropic mechanical properties, which may be detrimental for applications involving multi-direc- ⁵⁰ tional stresses.

These and other matters have presented challenges to the selection of materials and formation of structures, for a variety of applications.

SUMMARY

Various example embodiments are directed to a composition of matter, its implementation and resulting apparatuses thereof. Such embodiments may be useful for forming 60 3D structures, in a manner that addresses challenges including those noted above.

As may be implemented in accordance with one or more embodiments, a three-dimensional (3D) structure is formed by depositing an alloy composition on a target, and solidifying portions of the alloy composition to form the 3D structure. The solidification includes producing a martensitic

structure by destabilizing a ferrite phase of the alloy composition while solidifying the alloy composition.

Another embodiment is directed to a method for additively manufacturing a three-dimensional (3D) structure. A first layer of the 3D structure is formed by depositing alloy powder on a target, liquefying the alloy powder via application of laser energy, and solidifying the liquefied alloy powder to produce a martensitic structure by destabilizing a ferrite phase of the alloy powder. Subsequent layers of the 3D structure are formed over the first layer by, for each subsequent layer, depositing additional alloy powder of the same composition of the alloy powder used in forming the first layer, liquefying the additional alloy powder via application of laser energy, and also solidifying the liquefied additional alloy powder to produce a martensitic structure by destabilizing a ferrite phase of the additional alloy powder.

Another embodiment is directed to an alloy powder composition of matter for forming martensitic 17-4 stainless steel via laser powder bed fusion additive manufacturing. The alloy powder comprises iron, chromium, nickel, copper, niobium, and tantalum.

The above discussion/summary is not intended to describe each embodiment or every implementation of the present disclosure. The figures and detailed description that follow also exemplify various embodiments.

BRIEF DESCRIPTION OF FIGURES

Various example embodiments may be more completely understood in consideration of the following detailed description and in connection with the accompanying drawings, in which:

FIG. 1 shows a method for forming a structure, as may be implemented in accordance with one or more embodiments;

FIG. **2** shows components of an alloy composition, in accordance with various embodiments, and with reference to 17-4 specification values as well as 3D-printed values;

FIGS. 3A, 3B, 3C and 3D show phase transformation behavior of an alloy as may be implemented in accordance with one or more embodiments, in which:

FIG. **3**A shows a phase constitution after cooling to room temperature,

FIGS. **3**B and **3**C show X-ray diffraction results showing the phase transformation behavior, and

FIG. **3**D shows an enhanced view of a portion of FIG. **3**C; and

FIGS. **4A-4**B show a scan approach as may be implemented to achieve as built equiaxed fine grains utilizing an alloy composition as characterized herein, as may be implemented in accordance with one or more embodiments, in which:

FIG. 4A depicts scan patterns for four stacked layers, and FIG. 4B depicts an example scan pattern for one of the layers shown in FIG. 4A, with hatch spacing.

While various embodiments discussed herein are amenable to modifications and alternative forms, aspects thereof have been shown by way of example in the drawings and ⁵⁵ will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the scope of the disclosure including aspects defined ⁶⁰ in the claims. In addition, the term "example" as may be used throughout this application is by way of illustration, and not limitation.

DETAILED DESCRIPTION

Aspects of the present disclosure are believed to be applicable to a variety of different types of articles of manufacture, apparatuses, systems and methods involving the formation of 3D structures, as may include additive manufacturing, and which may involve what is often referred to as 3D printing and/or casting. In certain implementations, aspects of the present disclosure have been shown to be beneficial when used in the context of forming 3D metal structures using a composition of materials that facilitate a near fully or fully martensitic structure. While not necessarily so limited, various aspects may be appreciated through a discussion of examples using such exemplary contexts.

According to various example embodiments, a liquid alloy includes a composition of matter that operates to destabilize a ferrite phase of the alloy composition while it is solidified. This may involve, for instance, transforming δ -ferrite to austenite and otherwise mitigating the formation of δ -ferrite phase material in a solidified form of the alloy. Substantially all of the austenite may further be transformed to martensite, for instance such that the volume of the final 20 structure is 90-100% martensite.

The liquid alloy may be provided, for example, as part of a casting or 3D printing operation, and may be formed by liquefying a powder alloy composition. In this context, an alloy composition may be deposited/provided on a target, 25 and portions of the alloy composition may be solidified to form a 3D structure while destabilizing the ferrite phase to product a martensitic structure. In some instances, laser powder-bed fusion is utilized to effect laser melting successive layers of the alloy composition in powder form based on 30 a 3D computer aided design (CAD) model.

Destabilizing the ferrite phase as characterized herein may be carried out in a variety of manners. In some embodiments, the alloy includes a composition of materials that reduces a temperature at which δ -ferrite phase material 35 forms during cooling of the alloy, relative to a temperature at which δ -ferrite phase material forms during cooling of a 17-4 PH alloy composition. In other embodiments, the alloy includes a composition of materials that increases a temperature at which δ -ferrite phase material, which is formed 40 of a liquid phase provided at block 110 to δ -ferrite, transfrom the alloy, transitions to y-austenite phase material during cooling of the alloy, relative to a temperature at which δ -ferrite phase material transitions to γ -austenite during cooling of a 17-4 PH alloy composition. In certain embodiments, the composition of materials in the alloy are 45 selected to effect both of the aforementioned aspects relating to reducing the temperature at which δ -ferrite phase material forms and to increases the temperature at which the δ -ferrite material transitions to y-austenite. For each of these embodiments, the reference 17-4 PH alloy referred to as being 50 relative to the δ -ferrite transitions may refer to that formed from an Argon-atomized powder 17-4 PH composition, which is liquefied as it is deposited in an additive manufacturing procedure.

In connection with particular embodiments, it has been 55 recognized/discovered that an increase of Ni and Cu in a 17-4 PH composition can shorten the lifetime of δ -ferrite, promote the earlier formation of austenite, and reduce the δ-ferrite fraction during solidification. It has been further recognized that, compared with increasing Ni and Cu, 60 increasing Cr exhibits the opposite trend. Mn may be excluded from the composition to mitigate high temperature volatility, and C and Si may be excluded from the composition to mitigate a drop of Ms temperature (the temperature at which martensite begins to form). The presence of impu- 65 rity type elements such as O, N, P, and S may be maintained as low as possible.

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In certain embodiments, an alloy composition having materials consisting of iron, chromium, nickel, copper, niobium and tantalum is provided (e.g., deposited), and the composition of the respective materials is used to destabilize the ferrite phase of the alloy composition as it is solidified. For instance, a powder form of the alloy composition may be deposited, liquefied with a laser, and solidified to form a 3D martensitic structure as characterized herein.

In some implementations, the alloy composition is as 10 follows: Fe: 74.7%, Cr: 15.2%, Ni: 4.8%, Cu: 5.0% and Nb: 0.3%. This composition is utilized to achieve the δ -ferrite phase transition temperatures as noted above with an additive manufacturing process, with a lattice parameter of the δ phase being 0.29403 nm upon initial solidification, relative to a lattice parameter of 0.29437 nm 17-4 PH, using an atomized Argon powder deposition with laser heating. Accordingly, the δ phase forms at a lower temperature such that its formation is delayed via the alloy composition, relative to δ phase formation in the 17-4 PH composition. The γ phase lattice parameter in the alloy composition is 0.36873 nm, whereas the Argon-atomized 17-4 PH lattice parameter is 0.36748 nm. Accordingly, the δ - γ transfer temperature in the alloy composition is higher than that of the 17-4 PH composition, which permits more time for the δ - γ transformation process to complete.

Turning now to the figures, FIG. 1 shows a flow diagram, as may be implemented in accordance with one or more embodiments. At block 100, an alloy composition is provided, such as by depositing and melting an alloy composition powder. At block 110, the alloy composition is melted or otherwise liquefied, such as by applying a laser to deposited powder as noted above. Certain approaches involve casting the alloy, in which blocks 100 and 110 are utilized to provide a melted alloy into a cast. At block 120, the alloy composition melt is solidified while mitigating the formation of δ -ferrite as characterized herein. When utilized in an additive manufacturing procedure, operations at blocks 100, 110 and 120 are repeated, as represented at 130.

Block 120 may further include facilitating transformation formation of the δ -ferrite to γ -austenite, and transformation of the γ -austenite to α' martensite, utilizing the composition provided at block 100 to lower a temperature at which δ -ferrite forms, to increase a temperature at which δ -ferrite transitions to γ -austenite, and to increase a temperature at which y-austenite transforms to a' martensite. This is depicted at blocks 121, 122 and 123.

Various approaches may be implemented in connection with the method depicted in FIG. 1. In connection with a particular embodiment, in-situ laser-melting is performed with a composition of material of: Fe (74.7%), Cr (15.2%), Ni (4.8%), Cu (5.0%), and Nb (0.3%). Destabilization of δ -ferrite is achieved, as indicated by a short-lived δ -ferrite peak as well as complete δ (110)- γ (111) transformation. On the other hand, the γ - α ' (austenite-martensite) transformation is also completed, with a high Ms temperature of $\sim 170^{\circ}$ C. (characterized by a lattice parameter of 0.28800 nm), which may be achieved via the exclusion of certain minor elements sometimes included in 17-4 PH. In this manner, fully martensite may be achieved at room temperature. The cooling rate in the sample may be increased from 1.88×10^{4} C./s to $8.66 \times 10^{4\circ}$ C./s and achieve fully martensite, with nearly identical solidification behavior in which a primarysolidified short-lived &-ferrite transforming completely into austenite, and ending with a complete γ - α ' transformation with a high Ms temperature in the range of 150° C.-190° C. Such a complete γ - α ' transformation may also be achieved

when impurities are introduced (e.g., during a manufacturing process), such as may result in increased O and N concentration.

In accordance with a particular embodiment, it has been recognized/discovered that a composition of matter having 5 parameters in the ranges noted for the Alloy depicted in FIG. **2** can produce as-built fully martensitic structure through additive manufacturing, by mitigating formation of a stabilized δ -ferrite phase, and mitigating formation of a stabilized austenite phase. This recipe can be used for a wide range of 10 additive manufacturing conditions. FIG. **2** further depicts exemplary comparisons to specified and 3D-printed 17-4 PH compositions that may utilize an Argon-atomized powder that is melted via laser energy and subsequently solidified.

In connection with various embodiments utilizing com- 15 positions as characterized herein, it has been recognized/ discovered that fully martensitic 17-4 PH can be built via additive manufacturing, with an increase of martensite fraction along with decreased residual δ -ferrite fraction in a final structure under elevated cooling rates. Surprisingly, the 20 higher cooling rate leads to less residual δ -ferrite, with destabilized primary-solidified δ -ferrite such that a δ - γ transformation has a higher degree of completion. An increased austenite start temperature, denoted by a larger lattice parameter, has been recognized/discovered under elevated 25 cooling rates, via stimulation of increased cooling rate on an earlier δ - γ transformation. Also surprisingly, additional martensite was achieved under elevated cooling rates, which may be a consequence of reduced residual δ -ferrite. It has further been recognized/discovered that a lower concentra- 30 tion of Cr and a higher concentration of Ni and Cu in a 17-4 PH alloy promotes earlier formation of austenite while reducing the stability of δ -ferrite.

The alloy composition may be deposited in a variety of manners. For instance, a liquid form of the alloy may be 35 deposited and transformed to ferrite, the ferrite then being transformed to austenite, and the austenite then being transformed to a martensitic structure. The alloy composition may be deposited as a powder with a laser being used to form liquid from the powder, the liquid being solidified 40 thereafter while a ferrite phase of the liquid is destabilized. Furthermore, layers may be formed by depositing, melting and solidifying additional powder of the alloy composition over a solidified or partially-solidified portion of the alloy composition.

In some embodiments, an alloy composition consisting of iron, chromium, nickel, copper, niobium and tantalum is utilized. For instance, a powder consisting of this alloy composition may be deposited and melted via laser, then solidified while destabilizing a ferrite phase of the solidify- 50 ing melt. In particular embodiments, the alloy composition consists of: 74-76% iron, 15-15.5% chromium, 4.5-5% nickel, 4.5-5% copper, and 0.15-0.45% of a mixture of niobium and tantalum, by weight. In other embodiments, the alloy composition consists of: 72.5-78.5% iron, 14.5-16% 55 chromium, 4-5.5% nickel, 3-5.5% copper, and 0.15-0.45% of a mixture of niobium and tantalum, by weight. It has been recognized/discovered that each of these alloy compositions may facilitate formation of a structure (e.g., additively manufactured) exhibiting substantially all martensite as 60 noted herein. Certain further embodiments exhibit additional minor elements, such as one or more of the following: 0-1.5% manganese, 0-0.1% carbon, 0-1.5% silicon, 0-0.1% oxygen, 0-0.15% nitrogen, 0-0.04% phosphorous, and 0-0.03% sulfur, by weight.

A martensitic structure as characterized herein may be produced using various approaches. For instance, the martensitic structure may be produced via solidification while continuing to deposit more of the alloy composition thereon. The resulting structure may include a 3D structure having a volume of which at least 90% is martensite, or of which at least 95% is martensite. Certain embodiments are directed to solidifying portions of the alloy composition to form the 3D structure by forming precipitation hardening martensitic stainless steel having equiaxed grains of a grain size that is less than 10 μ m, and in certain embodiments less than 5 μ m. It has been recognized/discovered that such a grain size can be achieved, using the alloy compositions and approaches characterized herein.

Another embodiment is directed to a method for additively manufacturing a three-dimensional (3D) structure. A first layer of the 3D structure is formed by depositing alloy powder on a target, liquefying the alloy powder using a laser, and solidifying the liquefied alloy powder to produce a martensitic structure while destabilizing a ferrite phase of the alloy powder. Subsequent layers of the 3D structure may be similarly formed over the first layer. For each subsequent layer, additional alloy powder is liquefied using the laser, and the liquefied additional alloy powder is solidified to produce a martensitic structure while destabilizing a ferrite phase of the additional alloy powder.

Destabilizing the ferrite phase in this context may include using approaches as characterized above. For instance, a composition of the alloy powder can be set to reduce a temperature at which δ -ferrite phase material forms during cooling of the liquefied alloy powder, relative to a temperature at which δ -ferrite phase material forms during cooling of a liquefied 17-4 PH alloy. The composition of the alloy powder may be set to increase a temperature at which δ -ferrite phase material transitions to γ -austenite phase during cooling of the liquefied alloy powder, relative to a temperature at which δ -ferrite phase material transitions to y-austenite during cooling of a liquefied 17-4 PH alloy. Both of the aforementioned reduction and increase in temperature may be obtained with a particular alloy composition (e.g., a powder consisting of iron, chromium, nickel, copper, niobium and tantalum may be used).

FIGS. 3A, 3B, 3C and 3D show phase transformation behavior of an alloy, as may be implemented in accordance with one or more embodiments. Beginning with FIGS. 3B and 3C, X-ray diffraction results are depicted respectively for cooling times corresponding to 0-1 seconds in FIG. 3C, and 1-19 seconds in FIG. 3B. FIG. 3D shows an enhanced view of inset 301 of FIG. 3C. FIG. 3D shows that, when solidification begins, δ -ferrite 331 at 301 exists for a very short time, upon which the material becomes γ -austenite 321. This is also shown in FIG. 3C with δ -ferrite at 331, 332 and 333 transitioning to γ -austenite at 321, 322 and 323.

Referring to FIG. **3B**, the γ -austenite **321**, **322**, **323** lasts for nearly 3 seconds before transforming into α' martensite **310**, **311** and **312**. The final phase may be fully or nearly fully α' martensite. Referring back to FIG. **3A**, shows a phase constitution of α' martensite **310**, **311** and **312**, as may be present after cooling to room temperature. Accordingly, such a resulting structure can be realized using compositions and related approaches as recognized/discovered and noted herein.

FIGS. **4A-4**B show a scan pattern as may be implemented to achieve as-built equiaxed fine grains utilizing an alloy composition as characterized herein, as may be implemented in accordance with one or more embodiments. FIG. **4**A depicts respective scan patterns as may be utilized to form successive layers, with each successive layer utilizing a scan pattern that is orthogonal relative to another or other layers immediately above and/or below the layer. FIG. **4**B depicts one of the scan patterns of FIG. **4**B with hatch spacing **400** (e.g., 0.05-0.2 mm).

Various embodiments are directed to achieving equiaxed 5 fine grains in additive manufacturing of a designed alloy via in-process heat-treatment. A continuous-wave fiber laser with a wavelength of 1070±10 nm, with a spot size of 150~300 µm and 300~500 W power may be used with a scan speed of 0.05~0.35 m/s. Feedstock powder supplied for 10 forming an apparatus may be gas-atomized with argon or nitrogen, with a composition as characterized in one or more embodiments herein. Multiple layers may be formed (e.g., as shown in FIG. 4A), with a spreading thickness of each layer being 35~150 µm. In a more particular implementation, the 15 laser spot size is set 230 µm, the laser power is set to 500 W, and the laser scan speed is set to 0.11 m/s, with a scan pattern that alternates 90 degrees for each layer (e.g., as shown in FIG. 4A, and with hatch spacing as shown in FIG. 4B being 0.05-0.2 mm).

Using this approach, it has been recognized/discovered that an as-built part may be fully composed of equiaxed fine grains with an average grain size of $\sim 3 \mu m$. Columnar grains and epitaxial growth are mitigated or prevented in the as-built part. Accordingly, an alloy composition and AM 25 processing conditions as characterized herein can be utilized to achieve equiaxed fine grains in an as-built AM part by controlling phase-transformation dynamics via in-process heat-treatment. It has further been recognized/discovered that forming a 3D structure in accordance with these 30 approaches may be implemented by forming precipitation hardening martensitic stainless steel having equiaxed grains of a grain size that is less than 10 µm. Certain embodiments are directed to such an approach, and embodiments are directed to a structure having such equiaxed grains and 35 related grain size, which has been unexpectedly attained via use of alloy compositions and related approaches herein.

Based upon the above discussion and illustrations, those skilled in the art will readily recognize that various modifications and changes may be made to the various embodi- 40 ments without strictly following the exemplary embodiments and applications illustrated and described herein. For example, the percentages of respective components in the alloys characterized herein may be varied while maintaining the recognized/discovered improvements relative to forma- 45 tion of a fully martensitic structure, such as those increasing the transition temperature of δ -ferrite to γ -austenite, and of γ -austenite to α' martensite. Further, approaches herein may utilize the compositions characterized in a variety of manufacturing approaches, including additive manufacturing as 50 well as casting. Various additive manufacturing procedures may be utilized as well, including laser powder bed fusion as noted herein, as well as blown powder additive manufacturing, wire-feed additive manufacturing, and foil-feed additive manufacturing. Further, different forms of product 55 such as powder, wire, and foil may be provided in accordance with such applications. Such modifications do not depart from the true spirit and scope of various aspects of the invention, including aspects set forth in the claims.

What is claimed is:

1. A method for forming a three-dimensional (3D) structure, the method comprising: depositing an alloy composition on a target, including adding a destabilizing component to the alloy composition that destabilizes the formation of ferrite during cooling; and solidifying portions of the alloy 65 composition to form the 3D structure, including producing a martensitic structure having a volume that is 90-100%

martensite by using the destabilizing component to destabilize the formation of a ferrite phase of the alloy composition while solidifying the alloy composition.

2. The method of claim 1, wherein destabilizing the ferrite phase includes facilitating transformation of δ -ferrite in the alloy composition to austenite and mitigating the formation δ -ferrite phase material from the alloy composition, to produce the martensitic structure from the austenite.

3. The method of claim **2**, wherein depositing the alloy includes depositing alloy powder and heating the powder to form a liquid, and wherein solidifying the portions of the alloy composition includes transforming substantially all of the austenite to martensite while solidifying the liquid and prior to further heat treatment.

4. The method of claim 1, wherein destabilizing the ferrite phase includes depositing the alloy composition with materials that reduce a temperature at which δ-ferrite phase material forms from the alloy composition during cooling 20 thereof, relative to a temperature at which δ-ferrite phase material forms during cooling of a 17-4 PH alloy composition.

5. The method of claim **1**, wherein destabilizing the ferrite phase includes depositing the alloy composition with materials that increase a temperature at which δ -ferrite phase material formed from the alloy composition transitions to a γ -austenite phase material during cooling thereof, relative to a temperature at which δ -ferrite phase material transitions to γ -austenite during cooling of a 17-4 PH alloy composition.

6. The method of claim 1, wherein destabilizing the ferrite phase includes depositing the alloy composition with the destabilizing component including materials that:

- reduce a temperature at which δ -ferrite phase material forms from the alloy composition during cooling thereof, relative to a temperature at which δ -ferrite phase material forms during cooling of a 17-4 PH alloy composition; and
- increase a temperature at which δ -ferrite phase material formed from the alloy composition transitions to a γ -austenite phase material during cooling thereof, relative to a temperature at which δ -ferrite phase material transitions to γ -austenite during cooling of a 17-4 PH alloy composition.

7. The method of claim 6, wherein the 17-4 PH alloy composition includes Argon-atomized powder.

8. The method of claim **6**, wherein producing the martensitic structure by destabilizing a ferrite phase of the alloy composition while solidifying the alloy composition includes forming austenite and transforming substantially all of the austenite to martensite.

9. The method of claim **1**, wherein depositing the alloy composition includes depositing an alloy composition consisting of: iron, chromium, nickel, copper, niobium and tantalum.

10. The method of claim **1**, wherein destabilizing the ferrite phase of the alloy composition while solidifying the alloy composition includes depositing the alloy composition having materials consisting of iron, chromium, nickel, copper, niobium and tantalum, and using the composition of the respective materials to destabilize the ferrite phase thereof.

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11. The method of claim **1**, wherein depositing the alloy composition includes depositing an alloy composition consisting of: 72.5-78.5% iron, 14.5-16% chromium, 4-5.5% nickel, 3-5.5% copper, and 0.15-0.45% of a mixture of niobium and tantalum, by weight.

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12. The method of claim **1**, wherein producing the martensitic structure via the solidifying includes producing the martensitic structure while continuing to deposit more of the alloy composition thereon.

13. The method of claim **1**, wherein producing the martensitic structure via the solidifying includes solidifying all of the deposited alloy composition to form the 3D structure.

- 14. The method of claim 1, wherein:
- depositing the alloy composition on a target includes depositing a liquid form of the alloy; and
- producing the martensitic structure via the solidifying includes transforming the liquid alloy to ferrite, transforming the ferrite to austenite, and transforming the austenite to the martensitic structure.

15. The method of claim **1**, wherein producing the martensitic structure includes forming the 3D structure having a volume of which at least 95% is martensite.

16. The method of claim **1**, wherein:

- depositing the alloy composition includes depositing the alloy composition as a powder; and 20
- solidifying the portions of the alloy composition includes forming layers of the alloy composition by using a laser to form liquid from the powder and thereafter solidifying the liquid while destabilizing a ferrite phase of the liquid, including melting and solidifying powder of 25 the alloy composition that is deposited over a solidified portion of the alloy composition.

17. The method of claim 1, wherein solidifying the portions of the alloy composition to form the 3D structure includes forming martensitic stainless steel having equiaxed $_{30}$ grains of a grain size that is less than $10 \ \mu m$.

18. A method for additively manufacturing a three-dimensional (3D) structure, the method comprising: forming a first layer of the 3D structure by depositing alloy powder on a target, liquefying the alloy powder via application of laser

energy, and solidifying the liquefied alloy powder to produce a martensitic structure having a volume that is 90-100% martensite by destabilizing the formation of a ferrite phase of the alloy powder; forming subsequent layers of the 3D structure over the first layer by, for each subsequent layer, depositing additional alloy powder of the same composition of the alloy powder used in forming the first layer, liquefying the additional alloy powder via application of laser energy, and solidifying the liquefied additional alloy powder to produce a martensitic structure having a volume that is 90-100% martensite by destabilizing the formation of a ferrite phase of the additional alloy powder.

19. The method of claim 18, wherein forming the first layer and forming the subsequent layers include:

- destabilizing the ferrite phase using a composition of alloys in the alloy powder to reduce a temperature at which δ -ferrite phase material forms during cooling of the liquefied alloy powder, relative to a temperature at which δ -ferrite phase material forms during cooling of a liquefied 17-4 PH alloy; and
- increasing a temperature at which δ -ferrite phase material transitions to γ -austenite phase during cooling of the liquefied alloy powder, relative to a temperature at which δ -ferrite phase material transitions to γ -austenite during cooling of a liquefied 17-4 PH alloy.

20. The method of claim 18, wherein the alloy powder consists of: iron, chromium, nickel, copper, niobium and tantalum.

21. An alloy powder composition of matter for forming martensitic 17-4 stainless steel having a volume that is 90-100% martensite via laser powder bed fusion additive manufacturing, the alloy powder comprising: iron; chromium; nickel; copper; niobium; and tantalum.

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