



US 20240002986A1

(19) **United States**

(12) **Patent Application Publication**
Amram et al.

(10) **Pub. No.: US 2024/0002986 A1**

(43) **Pub. Date: Jan. 4, 2024**

(54) **IRON-CONTAINING ALLOYS AND
ASSOCIATED SYSTEMS AND METHODS**

C22C 38/06 (2006.01)

C22C 33/02 (2006.01)

C22C 38/12 (2006.01)

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C22C 38/10 (2006.01)

C22C 38/08 (2006.01)

C22C 38/16 (2006.01)

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(52) **U.S. Cl.**

CPC *C22C 38/002* (2013.01); *C22C 38/18*
(2013.01); *C22C 38/008* (2013.01); *C22C*

38/14 (2013.01); *C22C 38/06* (2013.01); *C22C*

33/0257 (2013.01); *C22C 38/12* (2013.01);

C22C 38/10 (2013.01); *C22C 38/08* (2013.01);

C22C 33/0278 (2013.01); *C22C 38/16*

(2013.01); *C22C 2200/04* (2013.01); *B22F*

2998/10 (2013.01); *B22F 2999/00* (2013.01);

B22F 1/054 (2022.01)

(21) Appl. No.: **18/316,792**

(22) Filed: **May 12, 2023**

Related U.S. Application Data

(63) Continuation of application No. 15/970,322, filed on
May 3, 2018, now abandoned.

(60) Provisional application No. 62/649,178, filed on Mar.
28, 2018, provisional application No. 62/646,282,
filed on Mar. 21, 2018, provisional application No.
62/501,240, filed on May 4, 2017.

Publication Classification

(51) **Int. Cl.**

C22C 38/00 (2006.01)

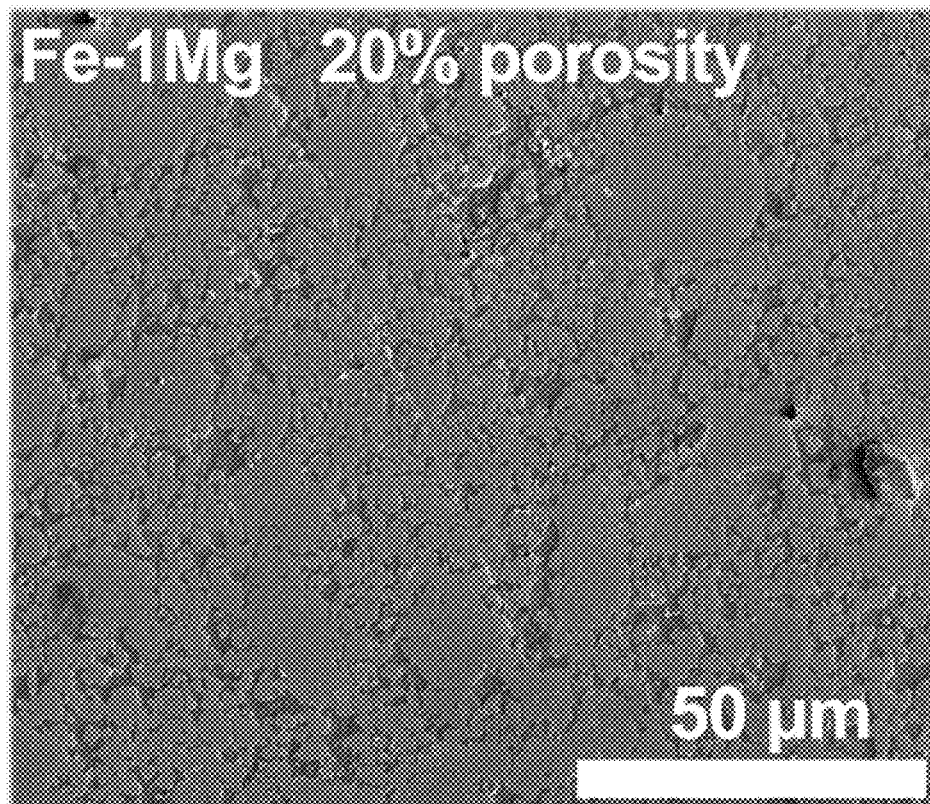
C22C 38/18 (2006.01)

C22C 38/14 (2006.01)

(57)

ABSTRACT

Iron-containing alloys, and associated systems and methods,
are generally described. The iron-containing alloys are,
according to certain embodiments, nanocrystalline. Accord-
ing to certain embodiments, the iron-containing alloys have
high relative densities. The iron-containing alloys can be
relatively stable, according to certain embodiments. Inven-
tive methods for making iron-containing alloys are also
described herein. The inventive methods for making iron-
containing alloys can involve, according to certain embodi-
ments, sintering nanocrystalline particulates comprising iron
and at least one other element (e.g., at least one other metal
or a metalloid) to form an iron-containing nanocrystalline
alloy.



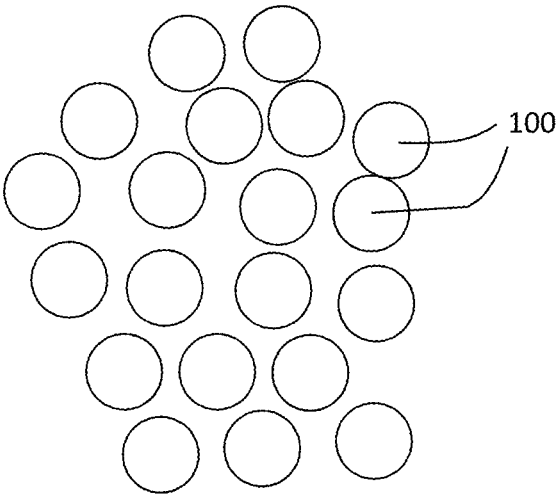


FIG. 1A

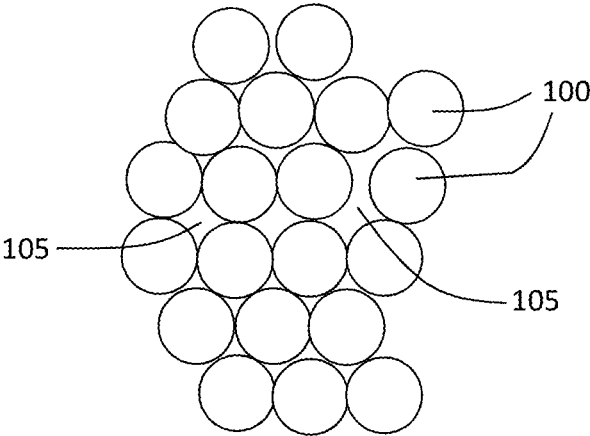


FIG. 1B

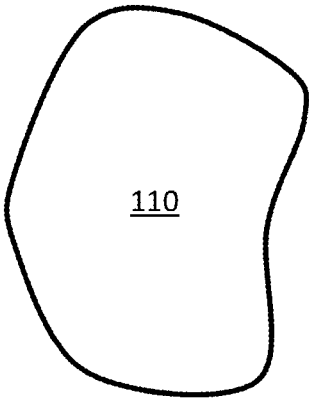
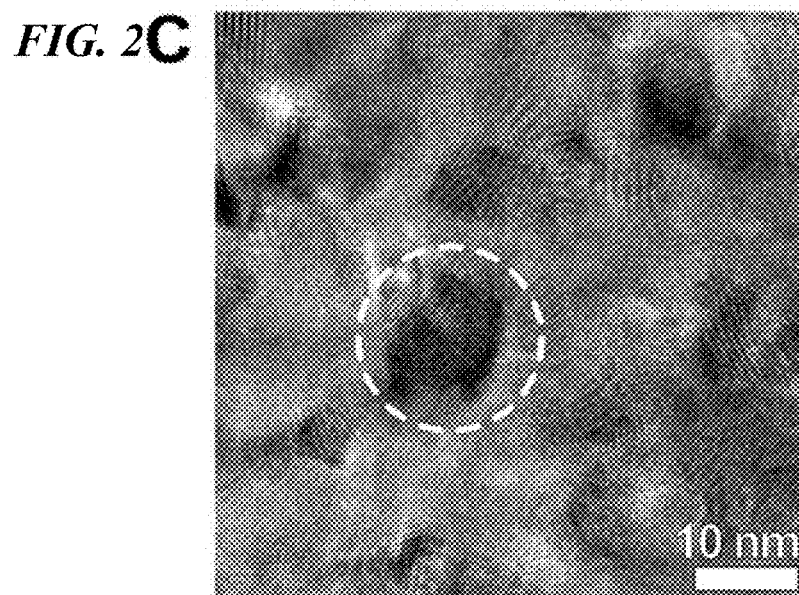
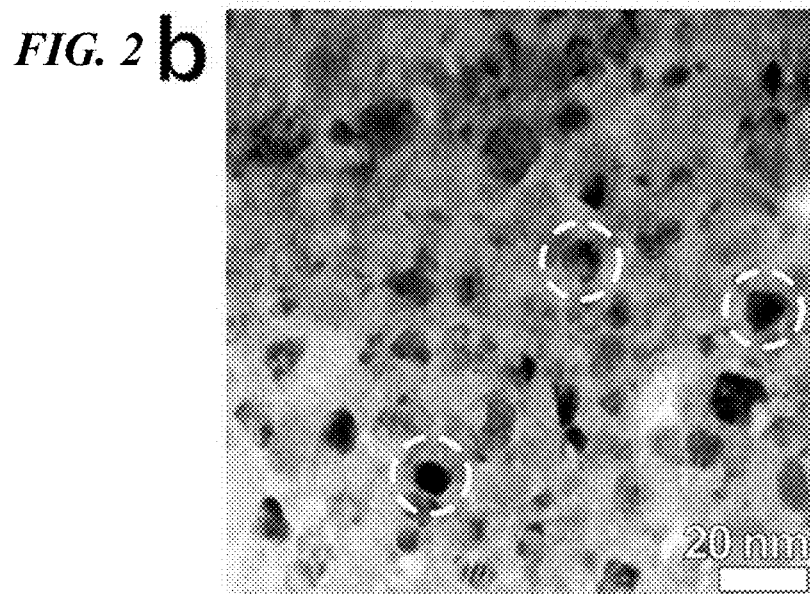
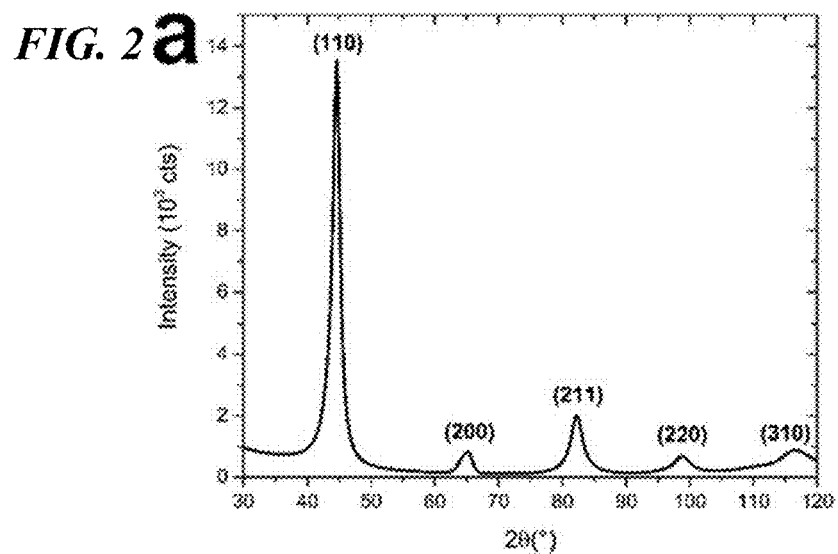


FIG. 1C



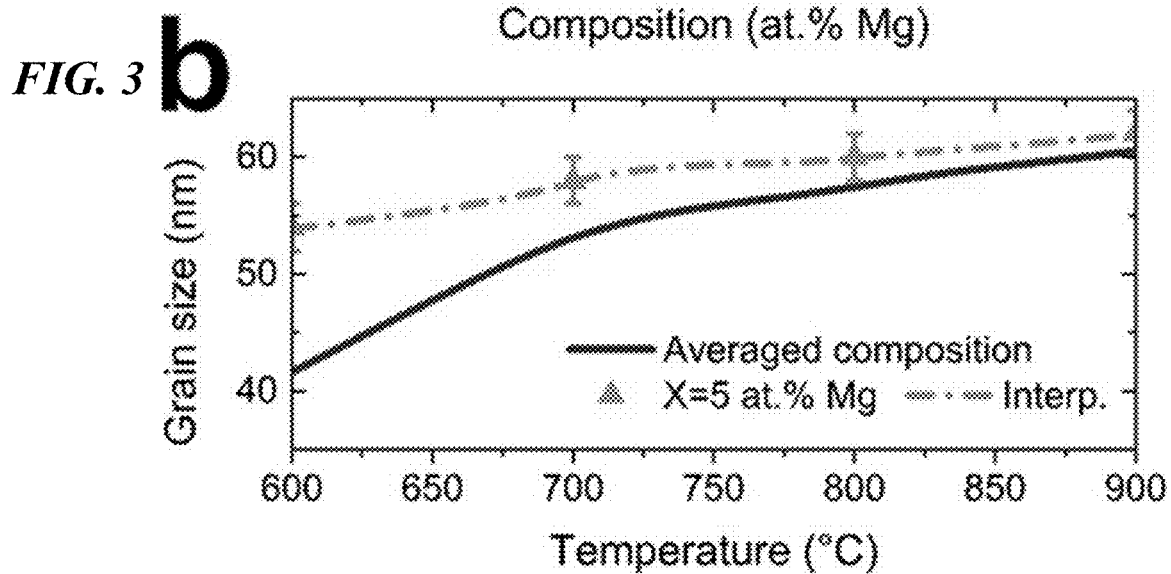
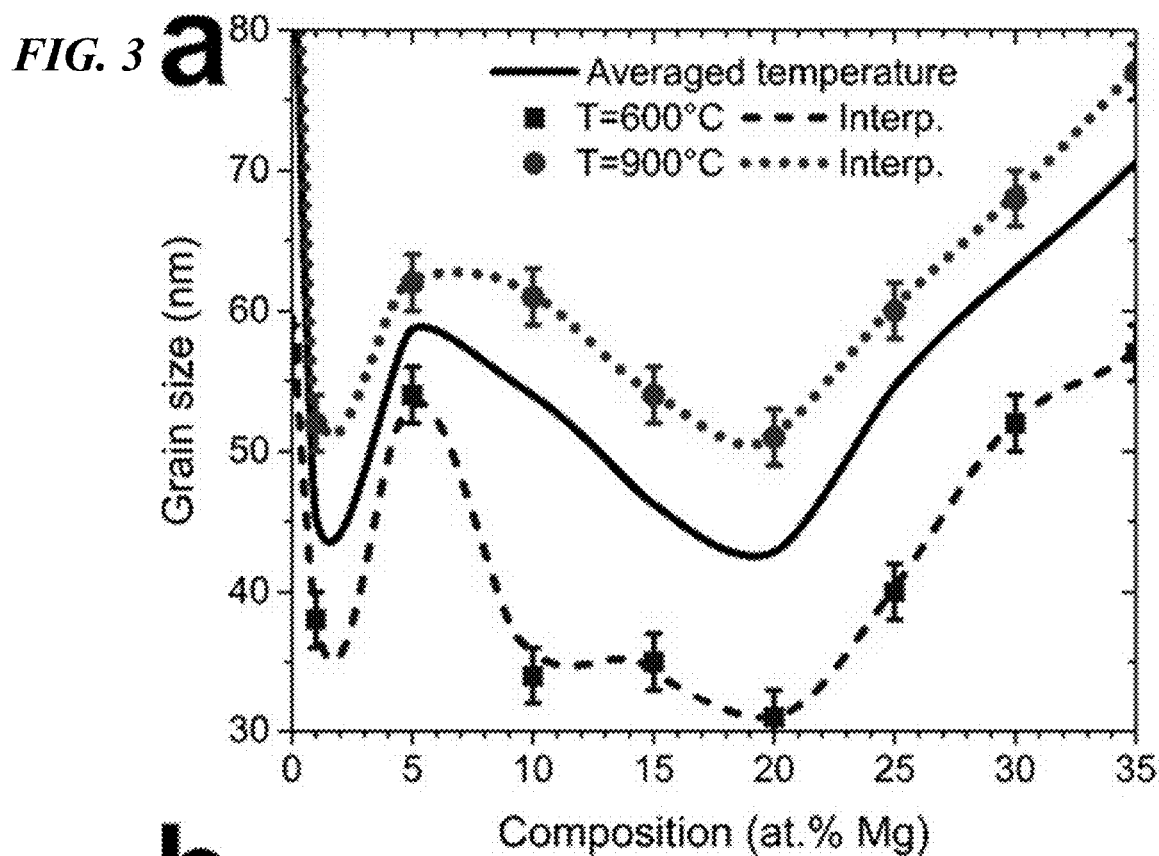


FIG. 4A

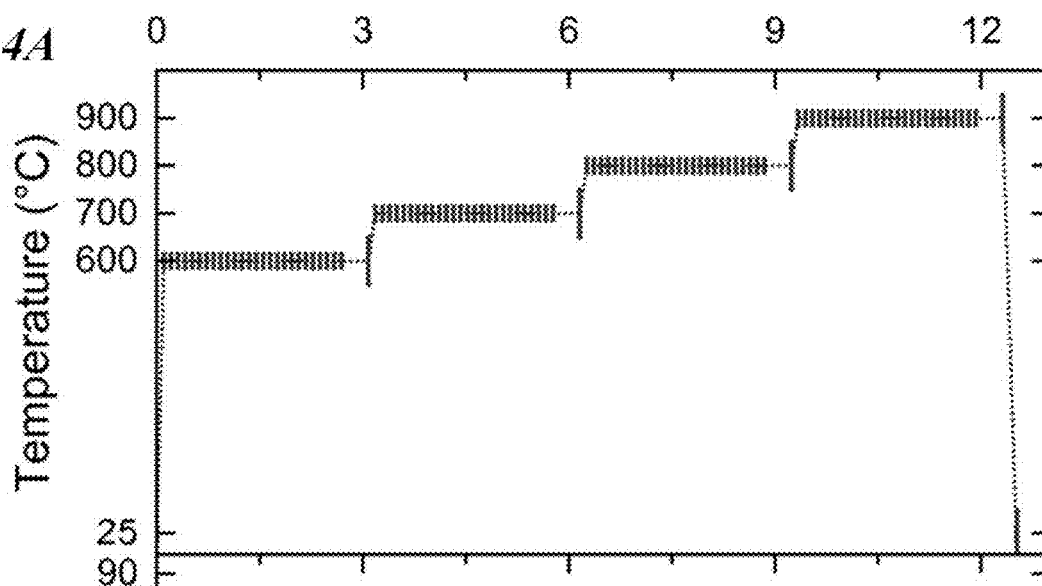


FIG. 4B

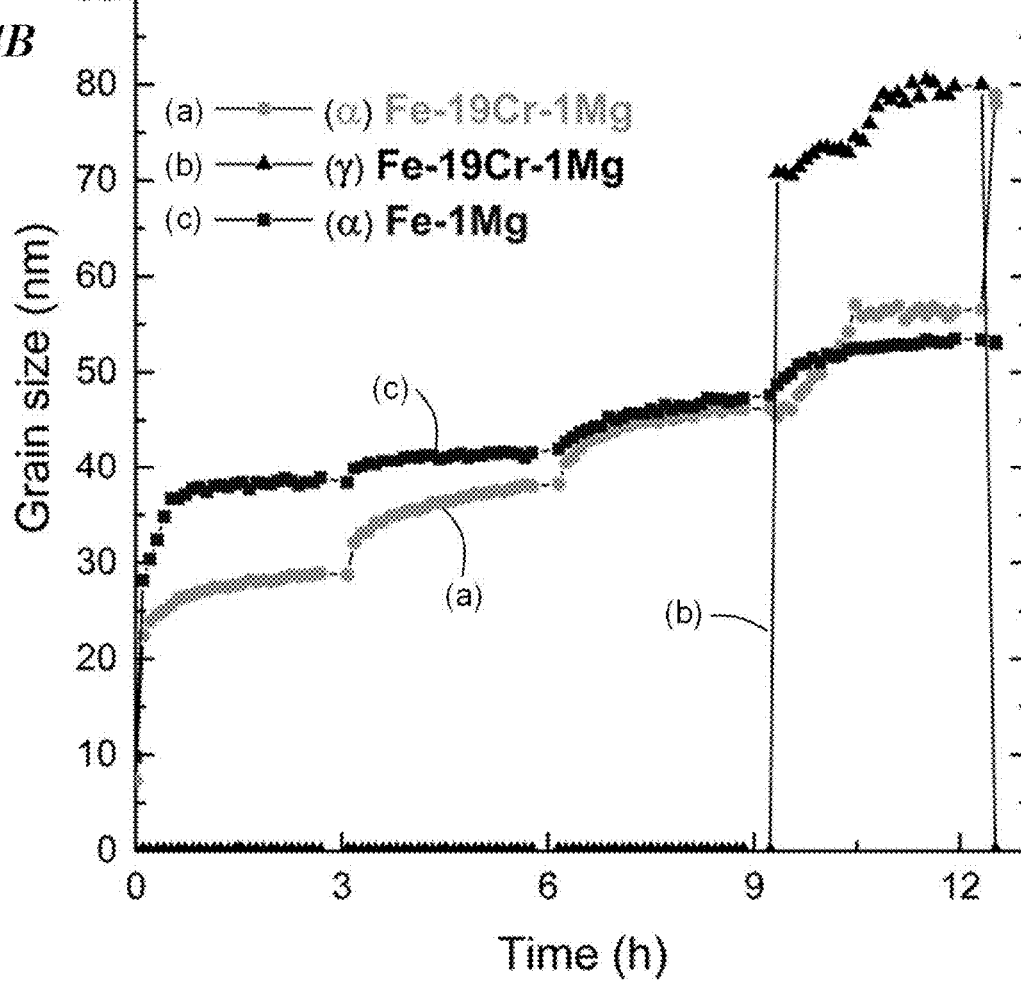


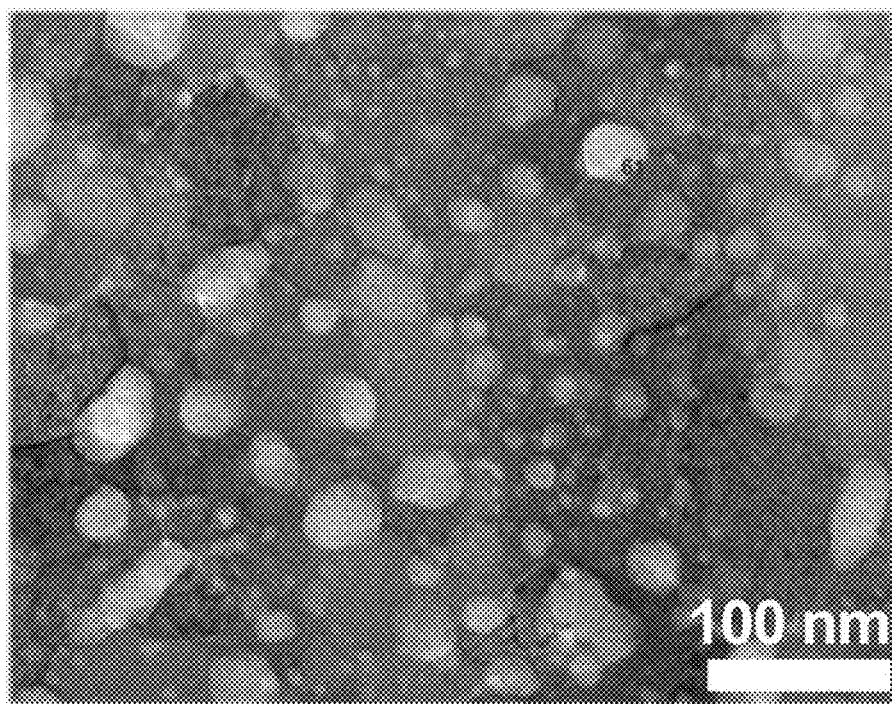
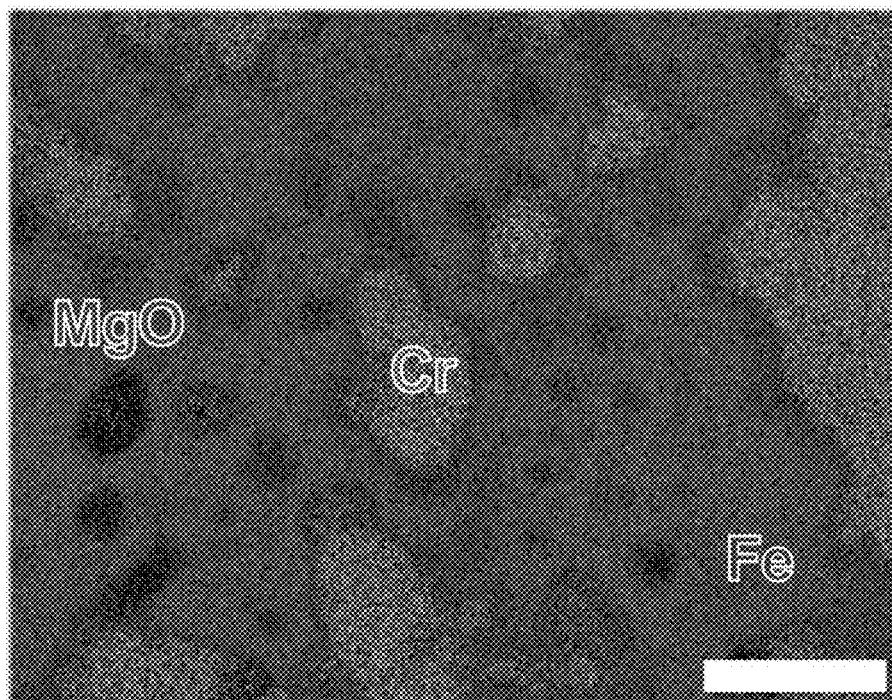
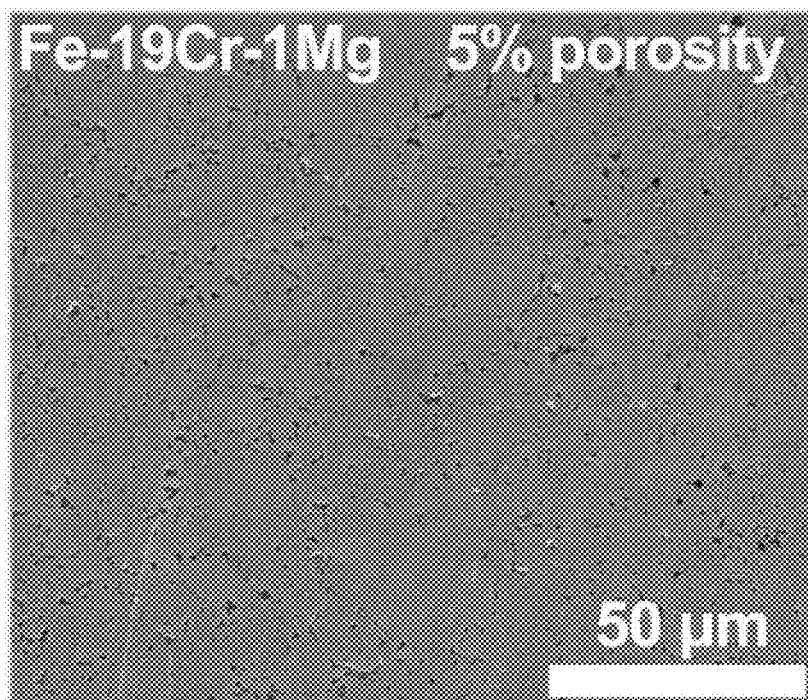
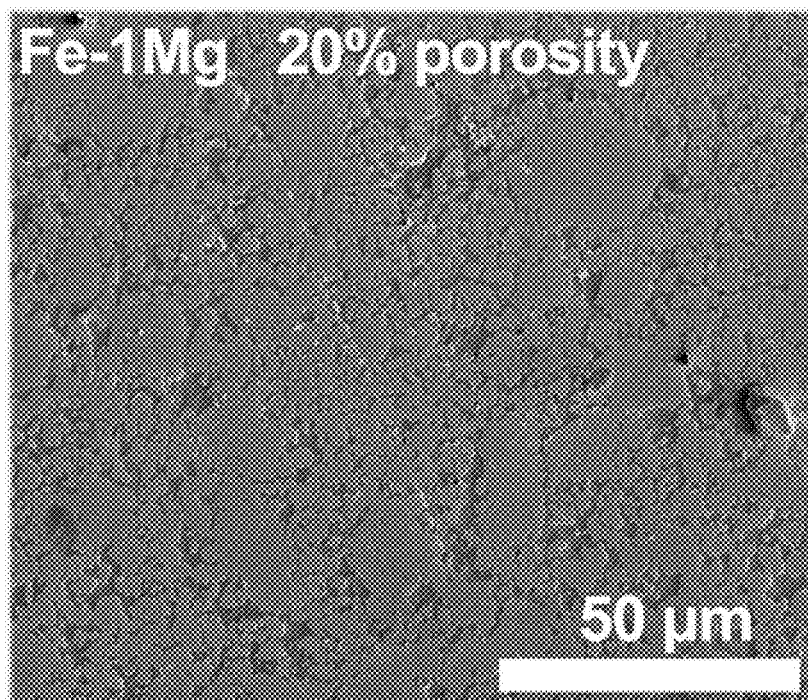
FIG. 5A*FIG. 5B*

FIG. 6A**FIG. 6B**

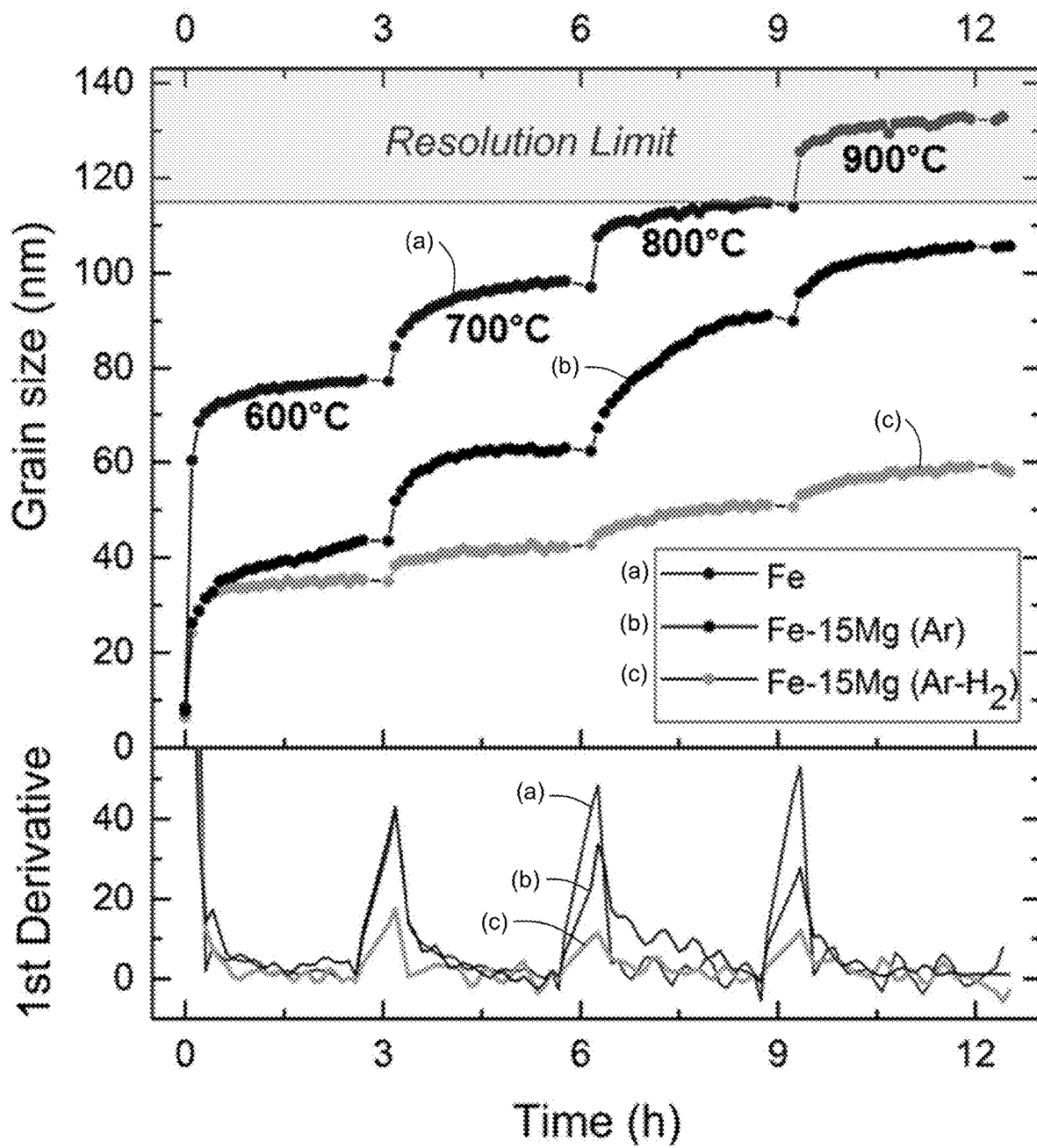


FIG. 7

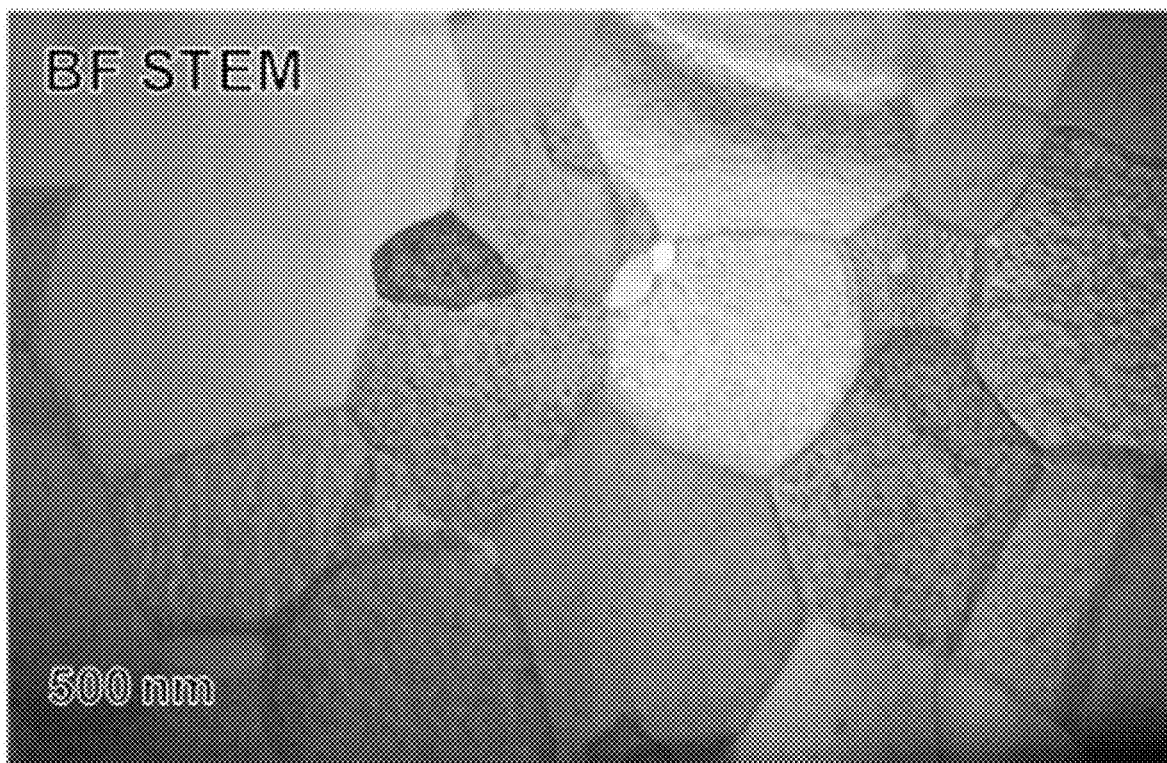


FIG. 8A

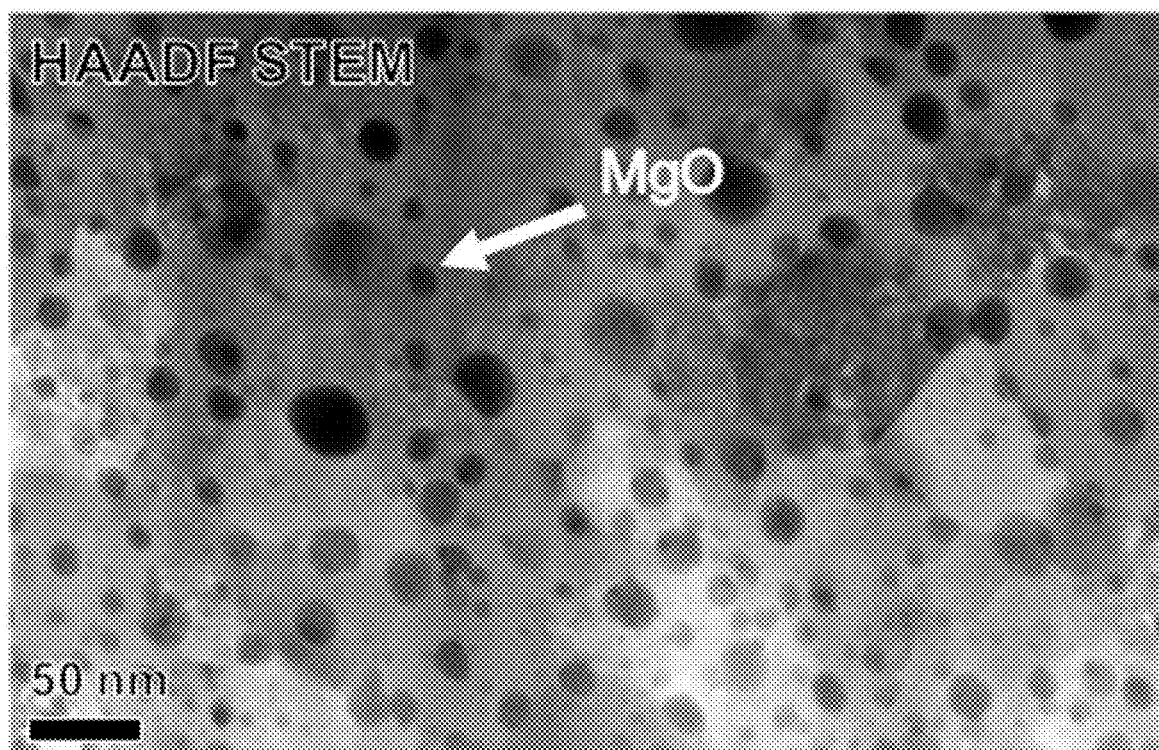


FIG. 8B

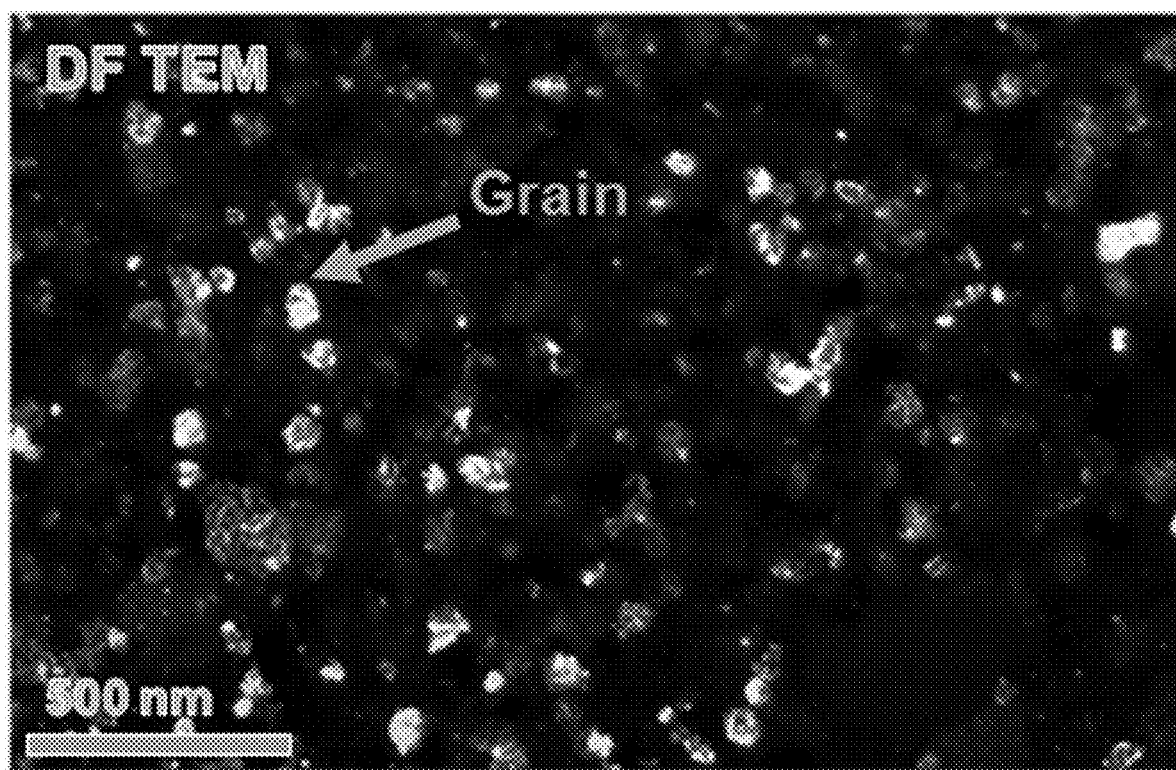


FIG. 8C

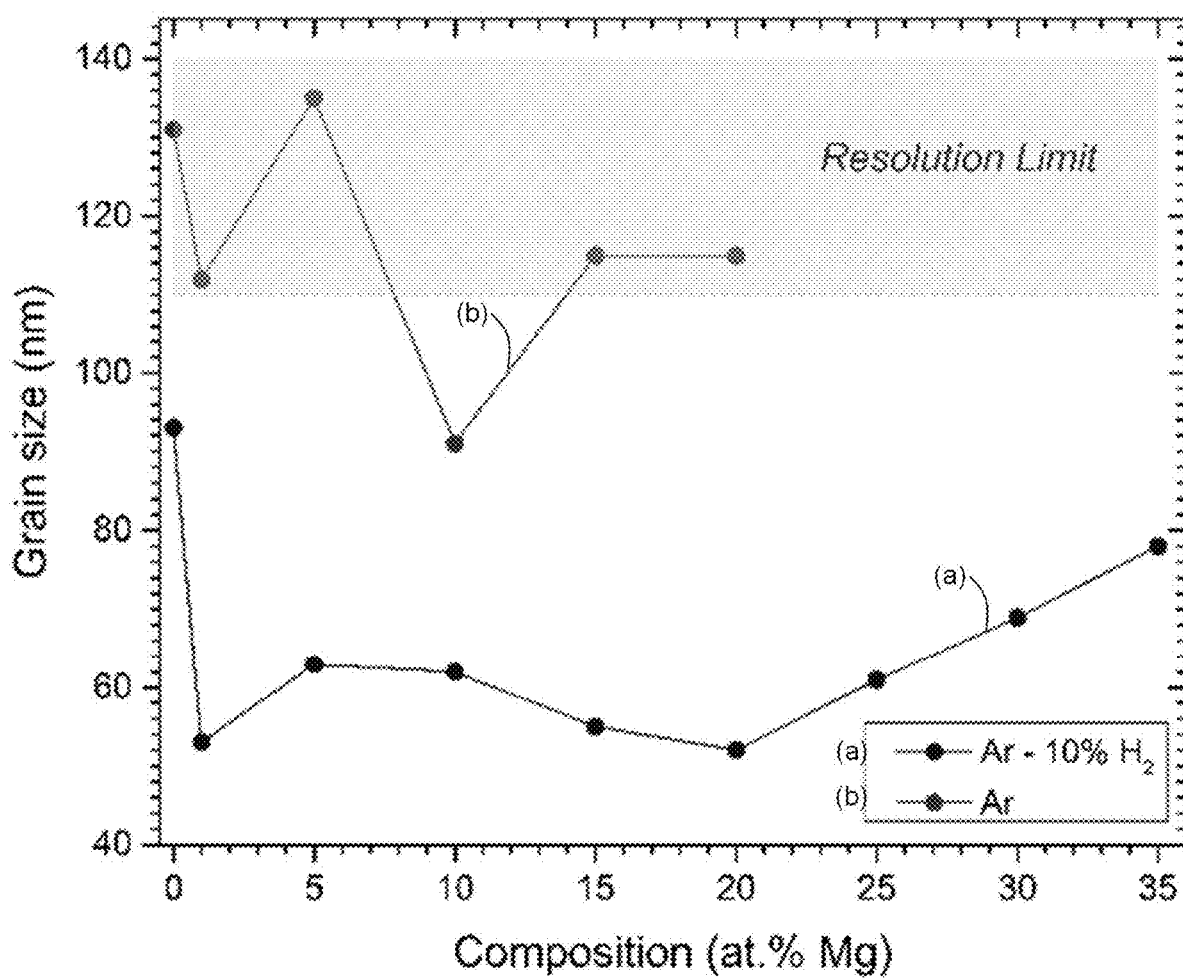
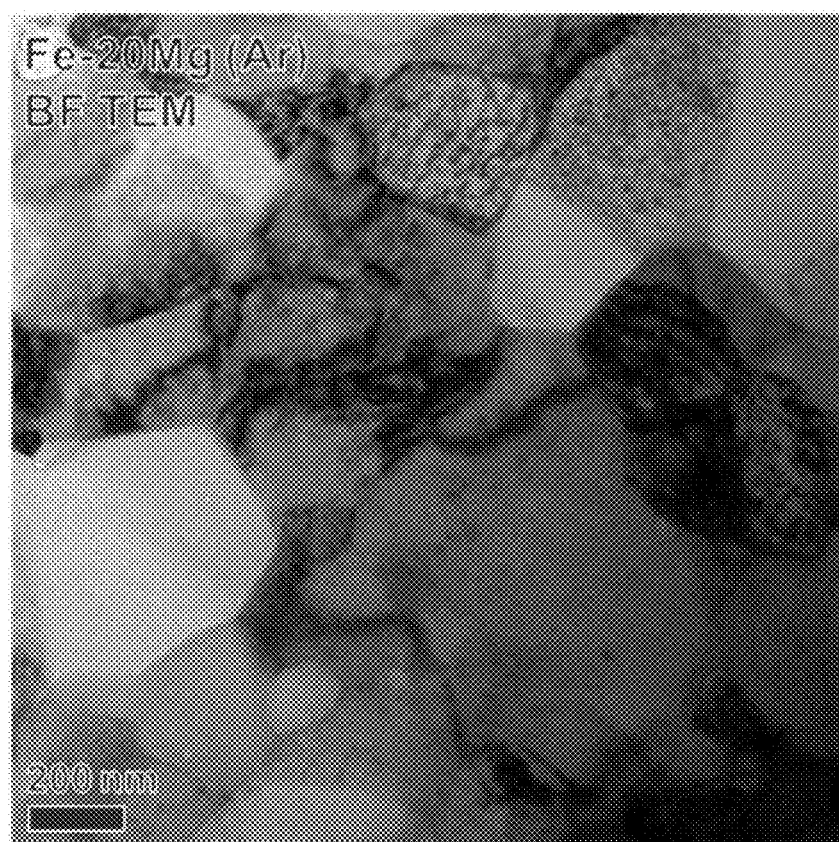
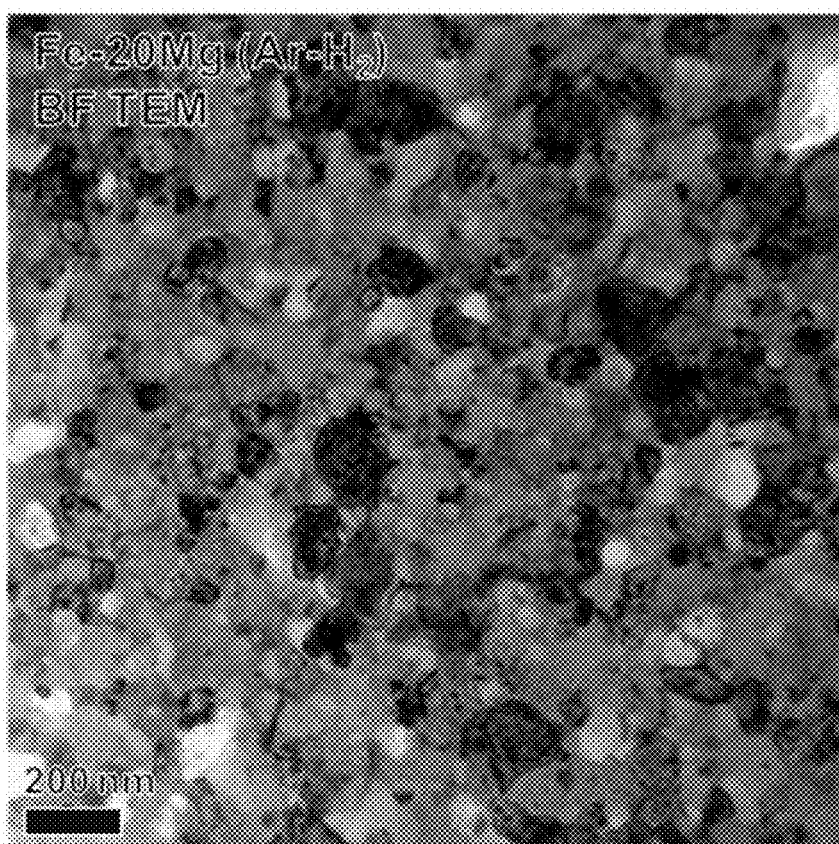
**FIG. 9**

FIG. 10A**FIG. 10B**

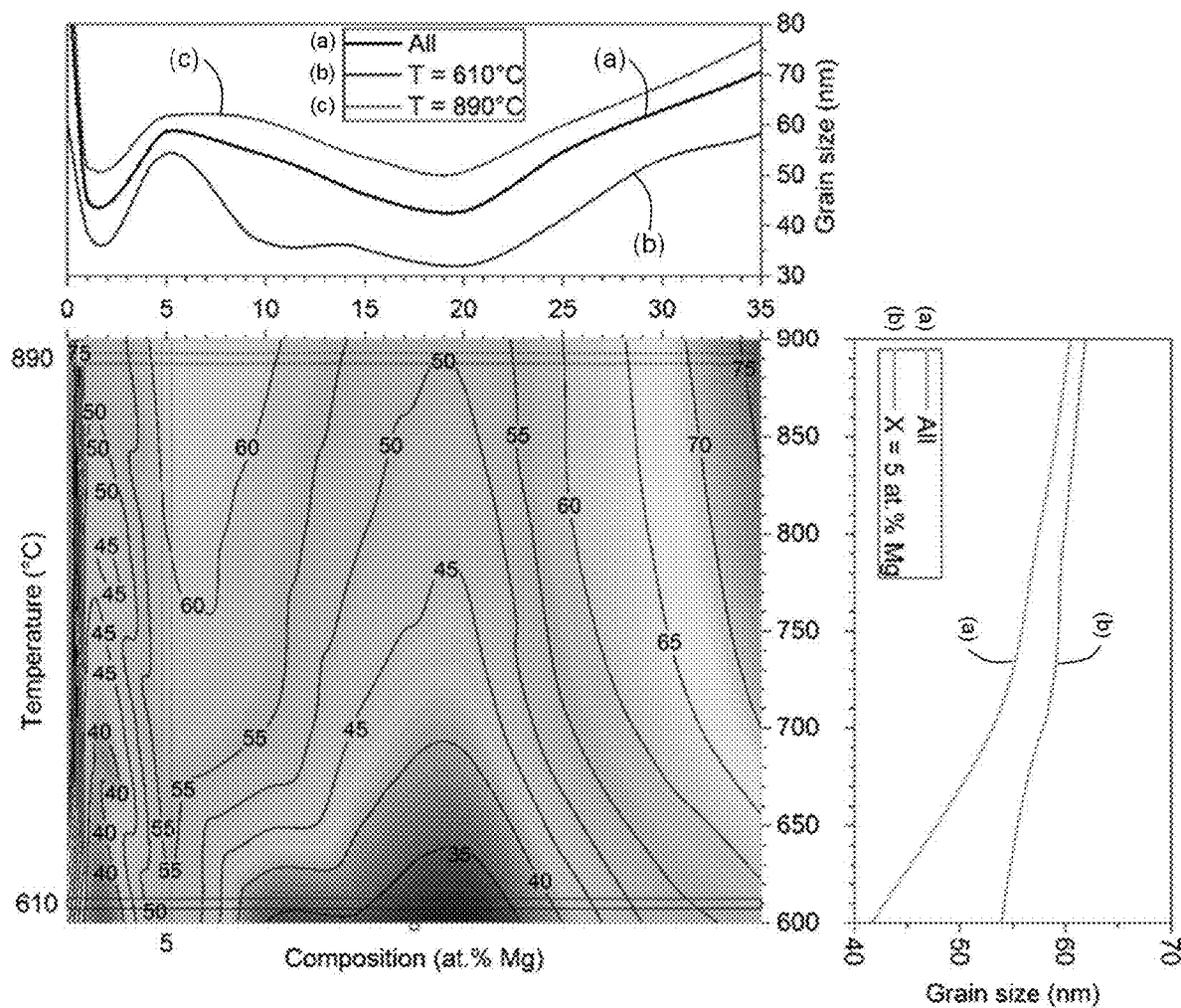


FIG. 11

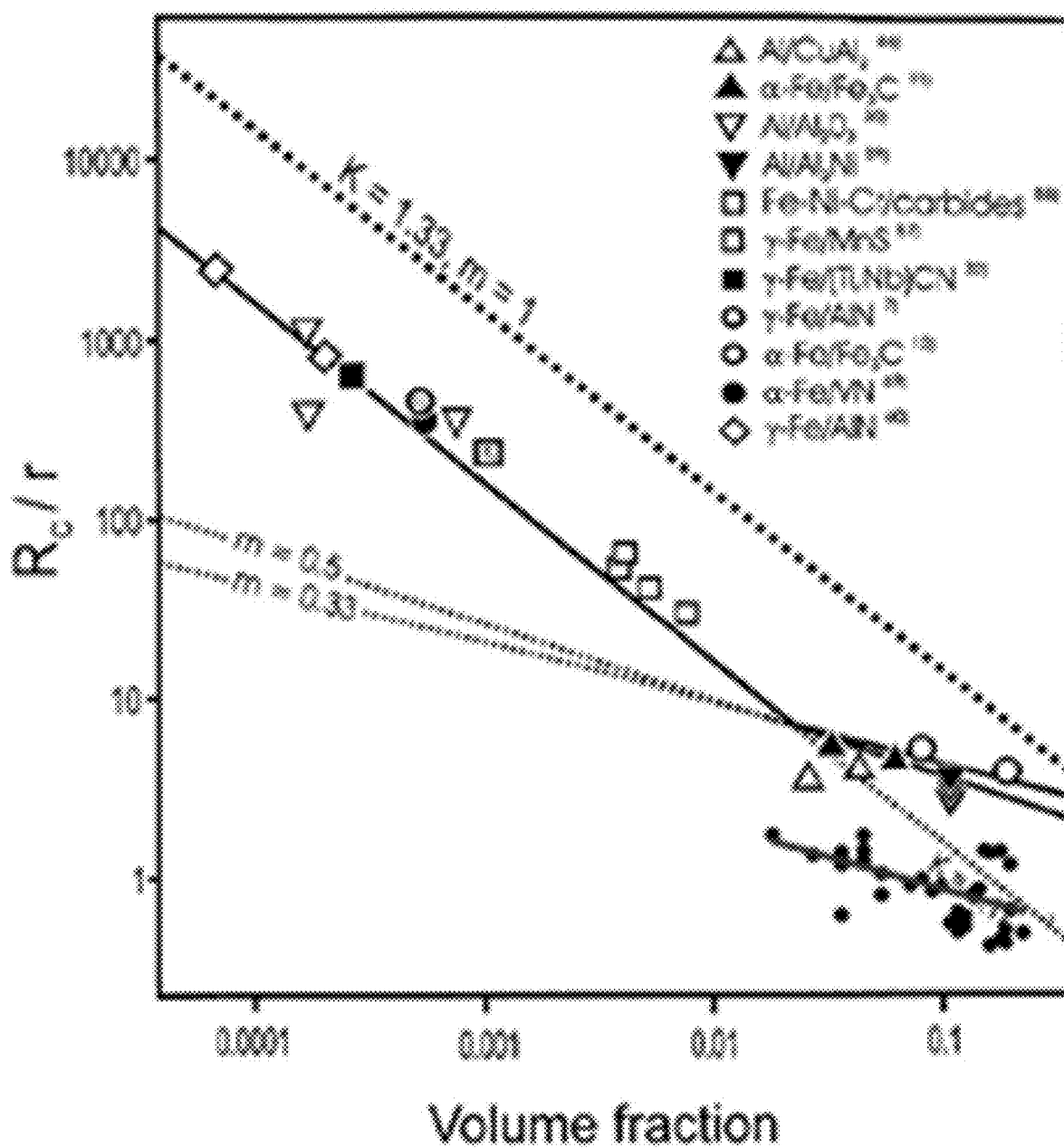


FIG. 12

IRON-CONTAINING ALLOYS AND ASSOCIATED SYSTEMS AND METHODS

RELATED APPLICATIONS

[0001] This application is a continuation of U.S. patent application Ser. No. 15/970,322, filed on May 3, 2018, and entitled “Iron-Containing Alloys and Associated Systems and Methods”; which claims priority under 35 U.S.C. § 119(e) to U.S. Provisional Application No. 62/501,240, filed May 4, 2017, and entitled “Thermally Stable Nanocrystalline Iron Alloys”; and to U.S. Provisional Application No. 62/646,282, filed Mar. 21, 2018, and entitled “Thermally Stable Nanocrystalline Iron Alloys and Associated Systems and Methods”; and to U.S. Provisional Application No. 62/649,178, filed Mar. 28, 2018, and entitled “Thermally Stable Nanocrystalline Iron Alloys and Associated Systems and Methods”; each of which is incorporated herein by reference in its entirety for all purposes.

GOVERNMENT SPONSORSHIP

[0002] This invention was made with Government support under Grant No. W911NF-14-1-0539 awarded by the Army Research Office. The Government has certain rights in the invention.

TECHNICAL FIELD

[0003] Iron-containing alloys and associated systems and methods are generally described.

BACKGROUND

[0004] Nanocrystalline materials can be susceptible to grain growth. In certain instances, prior sintering techniques for iron-based alloys have made it difficult to produce nanocrystalline materials, including bulk nanocrystalline materials, that have both small grain sizes and high relative densities. Improved systems and methods, and associated metal alloys, would be desirable.

SUMMARY

[0005] Iron-containing alloys, and associated systems and methods, are generally described. The iron-containing alloys are, according to certain embodiments, nanocrystalline. According to certain embodiments, the iron-containing alloys have high relative densities. The iron-containing alloys can be relatively stable, according to certain embodiments. Inventive methods for making iron-containing alloys are also described herein. The inventive methods for making iron-containing alloys can involve, according to certain embodiments, sintering nanocrystalline particulates comprising iron and at least one other element (e.g., at least one other metal or a metalloid) to form an iron-containing nanocrystalline alloy. The subject matter of the present invention involves, in some cases, interrelated products, alternative solutions to a particular problem, and/or a plurality of different uses of one or more systems and/or articles.

[0006] Certain embodiments are related to nanocrystalline metal alloys. In some embodiments, the nanocrystalline metal alloy comprises Fe; and a second element; wherein Fe is the most abundant element by atomic percentage in the nanocrystalline metal alloy, and the nanocrystalline metal alloy has a relative density of at least 80%.

[0007] In certain embodiments, the nanocrystalline metal alloy comprises Fe; and a second element; wherein the second element and Fe exhibit a miscibility gap, and the nanocrystalline metal alloy has a relative density of at least 80%.

[0008] In accordance with certain embodiments, the nanocrystalline metal alloy comprises Fe; and a second element; wherein the second element has a melting point that is lower than the melting point of Fe, and the nanocrystalline metal alloy has a relative density of at least 80%.

[0009] In certain embodiments, the nanocrystalline metal alloy comprises Fe; and a second element; wherein Fe is the most abundant element by atomic percentage in the nanocrystalline metal alloy, and the nanocrystalline metal alloy is substantially stable at a temperature that is greater than or equal to 100° C.

[0010] The nanocrystalline metal alloy comprises, in some embodiments, Fe; and a second element; wherein Fe is the most abundant element by atomic percentage in the bulk nanocrystalline metal alloy, and the nanocrystalline metal alloy has an average grain size of less than 300 nm.

[0011] Certain embodiments are related to a metal alloy comprising Fe; and Mg; wherein the metal alloy has a relative density of greater than or equal to 80%.

[0012] Some embodiments are related to methods of forming nanocrystalline metal alloys. In some embodiments, the method of forming a nanocrystalline metal alloy comprises sintering a plurality of nanocrystalline particulates to form the nanocrystalline metal alloy; wherein at least some of the nanocrystalline particulates comprise Fe and a second element, and Fe is the most abundant element by atomic percentage in at least some of the nanocrystalline particulates.

[0013] According to certain embodiments, the method of forming a nanocrystalline metal alloy comprises sintering a plurality of nanocrystalline particulates to form the nanocrystalline metal alloy; wherein at least some of the nanocrystalline particulates comprise Fe and a second element; and sintering the plurality of nanocrystalline particulates involves heating the nanocrystalline particulates to a first sintering temperature that is greater than or equal to 500° C. and less than or equal to 1100° C. for a sintering duration greater than or equal to 6 hours and less than or equal to 24 hours.

[0014] In some embodiments, the method of forming a nanocrystalline metal alloy comprises sintering a plurality of nanocrystalline particulates to form the nanocrystalline metal alloy; wherein at least some of the nanocrystalline particulates comprise Fe and a second element; and sintering the plurality of nanocrystalline particulates involves heating the nanocrystalline particulates such that the nanocrystalline particulates are not at a temperature of greater than or equal to 1100° C. for more than 24 hours.

[0015] In certain embodiments, the method of forming a nanocrystalline metal alloy comprises sintering a plurality of nanocrystalline particulates to form the nanocrystalline metal alloy; wherein at least some of the nanocrystalline particulates comprise Fe and a second element; Fe is the most abundant element by atomic percentage in at least some of the nanocrystalline particulates; and the sintering comprises heating the nanocrystalline particulates to a first sintering temperature lower than a second sintering temperature needed for sintering Fe in the absence of the second element.

[0016] In some embodiments, the method of forming a nanocrystalline metal alloy comprises sintering a plurality of nanocrystalline particulates to form the nanocrystalline metal alloy; wherein at least some of the nanocrystalline particulates comprise Fe and a second element; and the second element and Fe exhibit a miscibility gap.

[0017] In certain embodiments, the method of forming a nanocrystalline metal alloy comprises sintering a plurality of nanocrystalline particulates to form the nanocrystalline metal alloy; wherein at least some of the nanocrystalline particulates comprise Fe and a second element; Fe is the most abundant element by atomic percentage in at least some of the nanocrystalline particulates; and the nanocrystalline metal alloy has a relative density of at least 80%.

[0018] Certain embodiments are related to a method of forming a metal alloy comprising sintering powder comprising Fe and Mg to produce the metal alloy, wherein the metal alloy has a relative density of greater than or equal to 80%.

[0019] Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

[0021] FIGS. 1A-1C are exemplary schematic diagrams showing a sintering process, according to certain embodiments.

[0022] FIG. 2A shows an XRD pattern taken from an exemplary as-milled Fe-15Mg powder, with all reflections belonging to the α -Fe solid solution phase.

[0023] FIG. 2B and FIG. 2C show transmission electron microscopy (TEM) micrographs of the exemplary alloy of FIG. 2A.

[0024] FIG. 3A is a plot of grain size as a function of composition, in accordance with certain examples.

[0025] FIG. 3B is a plot of grain size as a function of temperature, in accordance with certain examples.

[0026] FIGS. 4A-4B show grain size obtained by XRD as a function of annealing temperature and time, in accordance with certain examples.

[0027] FIG. 5A shows a TEM micrograph of an exemplary sintered Fe-19Cr-1Mg alloy.

[0028] FIG. 5B is an elemental map showing the distribution of Fe, Cr and Mg (as MgO precipitates) in the same field of view as FIG. 5A.

[0029] FIG. 6A and FIG. 6B show scanning electron microscopy (SEM) micrographs of exemplary Fe-19Cr-1Mg and Fe-1Mg alloys, respectively, in accordance with certain examples.

[0030] FIG. 7 is a plot showing grain size and the first derivative of grain size as a function of heating time at different temperatures, in accordance with certain examples.

[0031] FIG. 8A shows a Bright Field (BF) Scanning TEM (STEM) micrograph of the Fe powder in FIG. 7A after annealing, in accordance with certain examples.

[0032] FIG. 8B shows a BF STEM micrograph of the Fe-15Mg powder in FIG. 7A after annealing in Ar, in accordance with certain examples.

[0033] FIG. 8C shows a Dark Field (DF) TEM micrograph of the Fe-15Mg powder in FIG. 7A after annealing in Ar with 10% H₂, in accordance with certain examples.

[0034] FIG. 9 is a plot of grain size as a function of composition (at % Mg) for two different annealing environments, in accordance with certain examples.

[0035] FIG. 10A shows a BF TEM micrograph of the Fe-20Mg powder after annealing in Ar, in accordance with certain examples.

[0036] FIG. 10B shows a DF TEM micrograph of the Fe-20Mg powder after annealing in Ar with 10% H₂, in accordance with certain examples.

[0037] FIG. 11 shows an exemplary contour plot of a surface of grain size over composition and temperature space, obtained from in-situ XRD data, and interpolated with composition and temperature steps of 0.1 at. % and 0.5° C., respectively.

[0038] FIG. 12 shows the ratio between limiting grain size and pinning particle size as a function of pinning particle volume fraction for different material systems ("Zener plot"), in accordance with certain examples. The full, small black circles at the bottom right are data for exemplary Fe—Mg alloys indicating improved stability relative to what is traditionally expected from Zener pinning alone.

DETAILED DESCRIPTION

[0039] Nanocrystalline metals have certain advantages over their microcrystalline counterparts due to the large volume fraction of grain boundaries. As one example, nanocrystalline alloys generally have remarkably higher tensile strength. However, nanocrystalline metals have primarily been processed as thin films, as retaining nanoscale grains in processing a bulk material is much more difficult.

[0040] This disclosure is generally directed to metal alloys comprising iron. The metal alloys comprising the iron are, according to certain embodiments, nanocrystalline metal alloys. Certain of the metal alloys described herein can have high relative densities while maintaining their nanocrystalline character. In addition, according to certain embodiments, the metal alloys can be bulk metal alloys. Certain of the metal alloys described herein are stable against grain growth.

[0041] In certain cases, the iron-containing alloys described herein comprise magnesium (Mg) and/or chromium (Cr), in addition to the iron (Fe).

[0042] In accordance with certain embodiments, the iron-containing alloy described herein can contain at least three elements (e.g., at least three metal elements). For example, in certain embodiments, the iron-containing alloys described herein comprise iron (Fe), a stabilizer element, and an activator element. In some embodiments, the iron-containing alloy comprises iron (Fe), magnesium (Mg), and chromium (Cr). The presence of three elements is not, however, strictly required, and in other embodiments, the iron-containing alloy may include only two elements.

[0043] Inventive methods for making iron-containing alloys are also described herein. For example, certain embodiments are directed to sintering methods in which the sintering is achieved at relatively low temperatures and/or over a relatively short period of time. In some embodiments, the sintering is performed with little or no applied pressure during the sintering process. According to some embodiments, and as described in more detail below, the sintering can be performed such that undesired grain growth is limited or eliminated (e.g., via the selection of materials and/or sintering conditions). Certain embodiments are directed to the recognition that one can sinter iron-containing materials over relatively short times, at relatively low temperatures, and/or with relatively low (or no) applied pressure while maintaining nanocrystallinity.

[0044] Certain of the embodiments described herein can provide advantages relative to prior articles, systems, and methods. For example, according to certain (although not necessarily all) embodiments, the iron-containing metal alloys can have high strength, high hardness, and/or high resistance to grain growth. According to some (although not necessarily all) embodiments, the methods for forming metal alloys described herein can make use of relatively small amounts of energy, for example, due to the relatively short sintering times, the relatively low sintering temperatures, and/or the relatively low applied pressures that are employed.

[0045] As noted above, certain embodiments are related to inventive metal alloys. The metal alloys comprise, according to certain embodiments, iron and at least one other metal.

[0046] According to certain embodiments, the metal alloy comprises iron (Fe). The metal alloy can contain, according to some embodiments, a relatively large amount of iron. For example, in some embodiments, Fe is the most abundant element (e.g., the most abundant metal) by atomic percentage in the metal alloy. (Atomic percentages are abbreviated herein as “at. %” or “at %”.) According to certain embodiments, Fe is present in the metal alloy in an amount of at least 50 at %, at least 55 at %, at least 60 at %, at least 65 at %, at least 70 at %, at least 80 at %, at least 90 at %, or at least 95 at %. In some embodiments, Fe is present in the metal alloy in an amount of up to 96 at %, up to 97 at %, up to 98 at %, up to 99 at %, up to 99.5 at %, or more. Combinations of these ranges are also possible. Other values are also possible.

[0047] The metal alloys described herein can comprise a second element. For example, the metal alloys described herein can comprise a second metal. The phrase “second element” is used herein to describe any element that is not Fe. The phrase “second metal” is used herein to describe any metal element that is not Fe. The term “element” is used herein to refer to an element as found on the Periodic Table. “Metal elements” are those found in Groups 1-12 of the Periodic Table except hydrogen (H); Al, Ga, In, Tl, and Nh in Group 13 of the Periodic Table; Sn, Pb, and Fl in Group 14 of the Periodic Table; Bi and Mc in Group 15 of the Periodic Table; Po and Lv in Group 16 of the Periodic Table; the lanthanides; and the actinides.

[0048] In some embodiments, the second element is a metalloid element. “Metalloid elements,” as the term is used herein, are boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te), and astatine (At).

[0049] According to certain embodiments, the second element is selected from the group consisting of magnesium

(Mg), boron (B), zirconium (Zr), gold (Au), chromium (Cr), nickel (Ni), vanadium (V), platinum (Pt), lead (Pb), copper (Cu), cobalt (Co), and tin (Sn). The metal alloy can comprise, in some embodiments, combinations of two or more of these. For example, as described elsewhere, the metal alloy can contain at least three elements (e.g., at least three metal elements), in some embodiments.

[0050] In some embodiments, the second element is Mg.

[0051] According to certain embodiments, the second element and Fe exhibit a miscibility gap. Two elements are said to exhibit a “miscibility gap” when the phase diagram of those two elements includes a region in which the mixture of the two elements exists as two or more phases. In some embodiments in which the second element and Fe exhibit a miscibility gap, the second element and Fe can be present in the metal alloy among at least two phases.

[0052] In some embodiments, the second element has a melting point that is lower than the melting point of iron (Fe). As would be understood by a person of ordinary skill in the art, the melting point of an element refers to the melting point of that element in its pure form. In the case of a metal, for example, the melting point of the metal refers to the melting point of that metal in its pure form. Similarly, in the case of a metalloid, the melting point of the metalloid refers to the melting point of that metalloid in its pure form.

[0053] According to some embodiments, the third element, when present, and Fe exhibit a miscibility gap. In some embodiments in which the third element and Fe exhibit a miscibility gap, the third element and Fe can be present in the metal alloy among at least two phases.

[0054] In some embodiments, Fe is at least partially soluble in the second element. For example, in some embodiments, Fe and the second element are in a solid solution.

[0055] The second element may be present in the metal alloy in a variety of suitable percentages. According to certain embodiments, the second element is present in the metal alloy in an amount of less than or equal to 40 at %, less than or equal to 35 at %, less than or equal to 32 at %, less than or equal to 30 at %, less than or equal to 25 at %, less than or equal to 22 at %, less than or equal to 20 at %, less than or equal to 15 at %, or less than or equal to 12 at %. In some embodiments, the second element is present in the metal alloy in an amount of at least 0.5 at %, at least 1 at %, at least 2 at %, at least 3 at %, at least 4 at %, at least 5 at %, at least 6 at %, at least 7 at %, at least 8 at %, at least 9 at %, at least 10 at %, or more. Combinations of these ranges are also possible. For example, in some embodiments, the second element is present in the metal alloy in an amount of from 0.5 at % to 40 at % of the metal alloy. In some embodiments, the second element is present in the metal alloy in an amount of from 1 at % to 40 at % of the metal alloy. In some embodiments, the second element is present in the metal alloy in an amount of from 8 at % to 32 at % of the metal alloy. Other values are also possible.

[0056] In some embodiments, the second element may be an activator element, relative to Fe. Activator elements are those elements that increase the rate of sintering of a material, relative to sintering rates that are observed in the absence of the activator element but under otherwise identical conditions. Activator elements are described in more detail below.

[0057] In certain embodiments, the second element may be a stabilizer element, relative to Fe. Stabilizer elements are

those elements that reduce the rate of grain growth of a material, relative to grain growth rates that are observed in the absence of the stabilizer element but under otherwise identical conditions. Stabilizer elements are described in more detail below. In some embodiments, the second element may be both a stabilizer element and an activator element. In some embodiments, the stabilizer element and the activator element are different elements.

[0058] According to certain embodiments, the second element (e.g., for forming an alloy with Fe) can be selected based on one or more of the following conditions:

- [0059] 1. thermodynamic stabilization of the nanocrystalline grain size;
- [0060] 2. phase separation region, which is extended above the sintering temperature;
- [0061] 3. second (e.g., solute) element with lower melting temperature; and/or
- [0062] 4. solubility of the Fe in the precipitated second phase.

[0063] According to some embodiments, the second element (e.g., Mg) forms precipitates within the Fe parent phase. For example, in some embodiments, the metal alloy comprises a structure consisting of Fe-rich grains and Mg-rich precipitates. In some embodiments, the precipitates of the second element (e.g., Mg) can populate the grain boundaries between Fe grains. In some embodiments, nanocrystalline structure with grain sizes of around 50 nm can be maintained even after 12 hours at 900° C. (which is above the melting temperature for Mg and 65% of the melting temperature for Fe). According to some embodiments, high relative densities can be achieved for Fe-1 at % Mg and Fe-20 at % Mg.

[0064] In some embodiments, the third element (e.g., Cr) forms a nano-duplex structure with the Fe. In some embodiments, the nano-duplex structure comprises Fe-rich grains and precipitates rich in the third element. The nano-duplex structure is, in some embodiments, substantially stable and/or nanocrystalline.

[0065] In some embodiments, the metal alloy comprises only Fe and the second element (i.e., Fe and the second element without additional metals or other elements). In other embodiments, the metal alloy comprises Fe, the second element, and a third element. For example, in some embodiments, the metal alloy comprises a third element (in addition to Fe and the second element). The third element can be, in some embodiments, a metal element. The phrase “third element” is used herein to describe an element that is not Fe and that is not the second element. That is to say, the third element, when present is different from Fe and the second element. In some embodiments, the metal alloy comprises a third metal, in which case the alloy comprises Fe, a second metal, and a third metal.

[0066] According to certain embodiments, the third element is selected from the group consisting of magnesium (Mg), boron (B), zirconium (Zr), gold (Au), chromium (Cr), nickel (Ni), vanadium (V), platinum (Pt), lead (Pb), copper (Cu), cobalt (Co), and tin (Sn).

[0067] In some embodiments, the third element is Cr or Au. In some embodiments, the third element is Cr.

[0068] In some embodiments, the third element has a melting point that is lower than the melting point of iron (Fe).

[0069] In some embodiments, the third element is a metalloid. For example, in some embodiments, the third element is boron (B).

[0070] The third element may be present in the metal alloy in a variety of suitable percentages. According to certain embodiments, the third element is present in the metal alloy in an amount of less than or equal to 40 at %, less than or equal to 35 at %, less than or equal to 30 at %, less than or equal to 25 at %, less than or equal to 22 at %, less than or equal to 20 at %, less than or equal to 15 at %, or less than or equal to 12 at %. In some embodiments, the third element is present in the metal alloy in an amount of at least 0.5 at %, at least 1 at %, at least 2 at %, at least 3 at %, at least 4 at %, at least 5 at %, at least 6 at %, at least 7 at %, at least 8 at %, at least 9 at %, at least 10 at %, or more. Combinations of these ranges are also possible. Other values are also possible.

[0071] According to certain embodiments, the third element may be a stabilizer element, an activator element, or both a stabilizer element and an activator element.

[0072] According to certain embodiments, the total amount of all metal and metalloid elements in the metal alloy that are not Fe (e.g., the second element (which may be a metal or metalloid), the optional third element (which may be a metal or a metalloid), and any additional optional elements (which may be metals or metalloids)) makes up less than 50 at %, less than or equal to 40 at %, less than or equal to 35 at %, less than or equal to 32 at %, less than or equal to 30 at %, less than or equal to 25 at %, less than or equal to 22 at %, less than or equal to 20 at %, less than or equal to 15 at %, or less than or equal to 12 at % of the metal alloy. In some embodiments, the total amount of all elements in the metal alloy that are not Fe (e.g., the second element (which may be a metal or metalloid), the optional third element (which may be a metal or a metalloid), and any additional optional elements (which may be metals or metalloids)) makes up at least 0.5 at %, at least 1 at %, at least 2 at %, at least 3 at %, at least 4 at %, at least 5 at %, at least 6 at %, at least 7 at %, at least 8 at %, at least 9 at %, at least 10 at %, or more. Combinations of these ranges are also possible. Other values are also possible.

[0073] In some embodiments, the total amount of magnesium (Mg), boron (B), zirconium (Zr), gold (Au), chromium (Cr), nickel (Ni), vanadium (V), platinum (Pt), lead (Pb), copper (Cu), cobalt (Co), and tin (Sn) present in the metal alloy is less than or equal to 40 at %, less than or equal to 35 at %, less than or equal to 30 at %, less than or equal to 25 at %, less than or equal to 22 at %, less than or equal to 20 at %, less than or equal to 15 at %, or less than or equal to 12 at % of the metal alloy. In some embodiments, the total amount of magnesium (Mg), boron (B), zirconium (Zr), gold (Au), chromium (Cr), nickel (Ni), vanadium (V), platinum (Pt), lead (Pb), copper (Cu), cobalt (Co), and tin (Sn) present in the metal alloy is at least 0.5 at %, at least 1 at %, at least 2 at %, at least 3 at %, at least 4 at %, at least 5 at %, at least 6 at %, at least 7 at %, at least 8 at %, at least 9 at %, at least 10 at %, or more. Combinations of these ranges are also possible. For example, in some embodiments, the total amount of magnesium (Mg), boron (B), zirconium (Zr), gold (Au), chromium (Cr), nickel (Ni), vanadium (V), platinum (Pt), lead (Pb), copper (Cu), cobalt (Co), and tin (Sn) present in the metal alloy is from 0.5 at % to 30 at % of the metal alloy. In some of these embodiments, at least 90 at % (or at

least 95 at %, at least 98 at %, at least 99 at %, or at least 99.9 at %) of the balance of the metal alloy is iron.

[0074] Those of ordinary skill in the art would understand that, to determine the total amount of magnesium (Mg), boron (B), zirconium (Zr), gold (Au), chromium (Cr), nickel (Ni), vanadium (V), platinum (Pt), lead (Pb), copper (Cu), cobalt (Co), and tin (Sn) present in a given metal alloy, one would simply sum the atomic percentages of each of these elements. For example, if the metal alloy contains 70 at % Fe, 29 at % Cr, and 1 at % Mg, then the total amount of magnesium (Mg), boron (B), zirconium (Zr), gold (Au), chromium (Cr), nickel (Ni), vanadium (V), platinum (Pt), lead (Pb), copper (Cu), cobalt (Co), and tin (Sn) present in that metal alloy would be 30 at % (i.e., 29 at % from Cr, 1 at % from Mg, and 0 at % for all other elements in the list). Those of ordinary skill in the art would also understand that, in making this calculation, not all of the elements in the list above would necessarily be present in the metal alloy. In the exemplary calculation described above, for example, boron (B), zirconium (Zr), gold (Au), nickel (Ni), vanadium (V), platinum (Pt), lead (Pb), copper (Cu), cobalt (Co), and tin (Sn) are not present in the Fe—Cr—Mg alloy.

[0075] In some embodiments, the total amount of magnesium (Mg), gold (Au), and chromium (Cr) present in the metal alloy is less than or equal to 40 at %, less than or equal to 35 at %, less than or equal to 30 at %, less than or equal to 25 at %, less than or equal to 22 at %, less than or equal to 20 at %, less than or equal to 15 at %, or less than or equal to 12 at % of the metal alloy. In some embodiments, the total amount of magnesium (Mg), gold (Au), and chromium (Cr) present in the metal alloy is at least 0.5 at %, at least 1 at %, at least 2 at %, at least 3 at %, at least 4 at %, at least 5 at %, at least 6 at %, at least 7 at %, at least 8 at %, at least 9 at %, at least 10 at %, or more. Combinations of these ranges are also possible. For example, in some embodiments, the total amount of magnesium (Mg), gold (Au), and chromium (Cr) present in the metal alloy is from 0.5 at % to 30 at % of the metal alloy. In some of these embodiments, at least 90 at % (or at least 95 at %, at least 98 at %, at least 99 at %, or at least 99.9 at %) of the balance of the metal alloy is iron.

[0076] In some embodiments, the metal alloy comprises Fe, Mg, and Cr. In some embodiments, the Fe is present in the metal alloy in an amount of at least 50 at % (e.g., from 50 at % to 99 at %), the Mg is present in the metal alloy in an amount of from 0.5 at % to 30 at %; and the Cr is present in the metal alloy in an amount of from 0.5 at % to 30 at %. In some embodiments, the Mg is present in the metal alloy in an amount of from 0.5 at % to 30 at %; the Cr is present in the metal alloy in an amount of from 0.5 at % to 30 at %; and at least 90 at % (or at least 95 at %, at least 98 at %, at least 99 at %, or at least 99.9 at %) of the balance of the metal alloy is the Fe. In some embodiments, the Mg is present in the metal alloy in an amount of from 0.5 at % to 1.5 at %; the Cr is present in the metal alloy in an amount of from 25 at % to 30 at %; and at least 90 at % (or at least 95 at %, at least 98 at %, at least 99 at %, or at least 99.9 at %) of the balance of the metal alloy is the Fe.

[0077] In certain embodiments, the metal alloy comprises the Fe, Mg, and Au. In some embodiments, the Fe is present in the metal alloy in an amount of at least 50 at % (e.g., from 50 at % to 99 at %); the Mg is present in the metal alloy in an amount of from 0.5 at % to 30 at % and the Au is present in the metal alloy in an amount of from 0.5 at % to 30 at %. In some embodiments, the Mg is present in the metal alloy

in an amount of from 0.5 at % to 30 at %; the Au is present in the metal alloy in an amount of from 0.5 at % to 30 at %; and at least 90 at % (or at least 95 at %, at least 98 at %, at least 99 at %, or at least 99.9 at %) of the balance of the metal alloy is the Fe. In some embodiments, the Mg is present in the metal alloy in an amount of from 0.5 at % to 1.5 at %; the Au is present in the metal alloy in an amount of from 25 at % to 30 at %; and at least 90 at % (or at least 95 at %, at least 98 at %, at least 99 at %, or at least 99.9 at %) of the balance of the metal alloy is the Fe.

[0078] According to certain embodiments, the metal alloys are nanocrystalline metal alloys. Nanocrystalline materials generally refer to materials that comprise at least some grains with a grain size smaller than or equal to 1000 nm. In some embodiments, the nanocrystalline material comprises grains with a grain size smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm. In some embodiments, the nanocrystalline materials comprise grains with a grain size of at least 1 nm or at least 5 nm. Accordingly, in the case of metal alloys, nanocrystalline metal alloys are metal alloys that comprise grains with a grain size smaller than or equal to 1000 nm. In some embodiments, the nanocrystalline metal alloy comprises grains with a grain size smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm. In some embodiments, the nanocrystalline metal alloy comprises grains with a grain size of at least 1 nm, at least 2 nm, or at least 5 nm. Other values are also possible.

[0079] The “grain size” of a grain generally refers to the largest dimension of the grain. The largest dimension may be a diameter, a length, a width, or a height of a grain, depending on the geometry thereof. According to certain embodiments, the grains may be spherical, cubic, conical, cylindrical, needle-like, or any other suitable geometry.

[0080] According to certain embodiments, a relatively large percentage of the volume of the metal alloy is made up of small grains. For example, in some embodiments, at least 50%, at least 75%, at least 90%, at least 95%, at least 99%, or substantially all of the volume of the metal alloy is made up of grains having grain sizes of smaller than or equal to 1000 nm, smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm (and/or, in some embodiments, as small as 5 nm, as small as 2 nm, or as small as 1 nm). Other values are also possible.

[0081] According to certain embodiments, the metal alloy may have a relatively small average grain size. The “average grain size” of a material (e.g., a metal alloy) refers to the

number average of the grain sizes of the grains in the material. According to certain embodiments, the metal alloy (e.g., a bulk and/or nanocrystalline metal alloy) has an average grain size of smaller than or equal to 1000 nm, smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm. In certain embodiments, the metal alloy has an average grain size of as little as 25 nm, as little as 10 nm, as little as 5 nm, as little as 2 nm, as little as 1 nm, or smaller. Combinations of these ranges are also possible. Other values are also possible.

[0082] According to certain embodiments, at least one cross-section of the metal alloy that intersects the geometric center of the metal alloy has a small volume-average cross-sectional grain size. The “volume-average cross-sectional grain size” of a given cross-section of a metal alloy is determined by obtaining the cross-section of the object, tracing the perimeter of each grain in an image of the cross-section of the object (which may be a magnified image, such as an image obtained from a transmission electron microscope), and calculating the circular-equivalent diameter, D_i , of each traced grain cross-section. The “circular-equivalent diameter” of a grain cross-section corresponds to the diameter of a circle having an area (A , as determined by $A=\pi r^2$) equal to the cross-sectional area of the grain in the cross-section of the object. The volume-average cross-sectional grain size ($G_{CS,avg}$) is calculated as:

$$G_{CS,avg} = \left(\frac{\sum_{i=1}^{i=n} D_i^3}{n} \right)^{1/3}$$

where n is the number of grains in the cross-section and D_i is the circular-equivalent diameter of grain i .

[0083] According to certain embodiments, at least one cross-section of the metal alloy that intersects the geometric center of the metal alloy has a volume-average cross-sectional grain size of smaller than or equal to 1000 nm, smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm. In certain embodiments, at least one cross-section of the metal alloy that intersects the geometric center of the metal alloy has a volume-average cross-sectional grain size of as small as 25 nm, as small as 10 nm, as small as 5 nm, as small as 2 nm, as small as 1 nm, or smaller. Combinations of these ranges are also possible. Other values are also possible.

[0084] According to certain embodiments, at least one cross-section of the metal alloy (that, optionally, intersects the geometric center of the metal alloy) has a volume-average cross-sectional grain size of smaller than or equal to 1000 nm, smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller

than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm (and/or as small as 25 nm, as small as 10 nm, as small as 5 nm, as small as 2 nm, as small as 1 nm, or smaller); and at least a second cross-section of the metal alloy that is orthogonal to the first cross section (that, optionally, intersects the geometric center of the metal alloy) has a volume-average cross-sectional grain size of smaller than or equal to 1000 nm, smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm (and/or as small as 25 nm, as small as 10 nm, as small as 5 nm, as small as 2 nm, as small as 1 nm, or smaller). Other values are also possible.

[0085] According to certain embodiments, at least one cross-section of the metal alloy (that, optionally, intersects the geometric center of the metal alloy) has a volume-average cross-sectional grain size of smaller than or equal to 1000 nm, smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm (and/or as small as 25 nm, as small as 10 nm, as small as 5 nm, as small as 2 nm, as small as 1 nm, or smaller); at least a second cross-section of the metal alloy that is orthogonal to the first cross section (that, optionally, also intersects the geometric center of the metal alloy, or otherwise) has a volume-average cross-sectional grain size of smaller than or equal to 1000 nm, smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm (and/or as small as 25 nm, as small as 10 nm, as small as 5 nm, as small as 2 nm, as small as 1 nm, or smaller); and at least a third cross-section of the metal alloy that is orthogonal to the first cross-section and that is orthogonal to the second cross-section (that, optionally, also intersects the geometric center of the metal alloy) has a volume-average cross-sectional grain size of smaller than or equal to 1000 nm, smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, or smaller than or equal to 20 nm (and/or as small as 25 nm, as small as 10 nm, as small as 5 nm, as small as 2 nm, as small as 1 nm, or smaller).

[0086] In some embodiments, the metal alloy comprises grains that are relatively equiaxed. In certain embodiments, at least a portion of the grains within the metal alloy have aspect ratios of less than or equal to 2, less than or equal to 1.8, less than or equal to 1.6, less than or equal to 1.4, less than or equal to 1.3, less than or equal to 1.2, or less than or equal to 1.1 (and, in some embodiments, down to 1). The aspect ratio of a grain is calculated as the maximum cross-sectional dimension of the grain which intersects the geometric center of the grain, divided by the largest dimension of the grain that is orthogonal to the maximum cross-sectional dimension of the grain. The aspect ratio of a grain is expressed as a single number, with 1 corresponding to an equiaxed grain. In some embodiments, the number average of the aspect ratios of the grains in the metal alloy is less than or equal to 2, less than or equal to 1.8, less than or equal to 1.6, less than or equal to 1.4, less than or equal to 1.3, less than or equal to 1.2, or less than or equal to 1.1 (and, in some embodiments, down to 1).

[0087] Without wishing to be bound by any particular theory, it is believed that relatively equiaxed grains may be present when the metal alloy is produced in the absence (or substantial absence) of applied pressure (e.g., via a pressureless or substantially pressureless sintering process).

[0088] In certain embodiments, the metal alloy comprises a relatively low cross-sectional average grain aspect ratio. In some embodiments, the cross-sectional average grain aspect ratio in the metal alloy is less than or equal to 2, less than or equal to 1.8, less than or equal to 1.6, less than or equal to 1.4, less than or equal to 1.3, less than or equal to 1.2, or less than or equal to 1.1 (and, in some embodiments, down to 1). The “cross-sectional average grain aspect ratio” of a metal alloy is said to fall within a particular range if at least one cross-section of the metal alloy that intersects the geometric center of the metal alloy is made up of grain cross-sections with an average aspect ratio falling within that range. For example, the cross-sectional average grain aspect ratio of a metal alloy would be less than 2 if the metal alloy includes at least one cross-section that intersects the geometric center of the metal alloy and in which the cross-section is made up of grain cross-sections with an average aspect ratio of less than 2. To determine the average aspect ratio of the grain cross-sections from which the cross-section of the metal alloy is made up (also referred to herein as the “average aspect ratio of grain cross-sections”), one obtains the cross-section of the metal alloy, traces the perimeter of each grain in an image of the cross-section of the metal alloy (which may be a magnified image, such as an image obtained from a transmission electron microscope), and calculates the aspect ratio of each traced grain cross-section. The aspect ratio of a grain cross-section is calculated as the maximum cross-sectional dimension of the grain cross-section (which intersects the geometric center of the grain cross-section), divided by the largest dimension of the grain cross-section that is orthogonal to the maximum cross-sectional dimension of the grain cross-section. The aspect ratio of a grain cross-section is expressed as a single number, with 1 corresponding to an equiaxed grain cross-section. The average aspect ratio of the grain cross-sections from which the cross-section of the metal alloy is made up (AR_{avg}) is calculated as a number average:

$$AR_{avg} = \frac{\sum_{i=1}^n AR_i}{n}$$

where n is the number of grains in the cross-section and AR_i is the aspect ratio of the cross-section of grain i.

[0089] According to certain embodiments, a metal alloy having a cross-sectional average grain aspect ratio falling within a particular range (e.g., any of the ranges described elsewhere herein) has a first cross-section intersecting the geometric center of the metal alloy and having an average aspect ratio of grain cross-sections falling within that range, and at least a second cross-section—orthogonal to the first cross-section—intersecting the geometric center of the metal alloy and having an average aspect ratio of grain cross-sections falling within that range. For example, according to certain embodiments, a metal alloy having a cross-sectional average grain aspect ratio of less than 2 includes a cross-section that intersects the geometric center of the metal alloy having an average aspect ratio of grain cross-sections of less than 2 and at least a second cross-section—orthogonal to the first cross-section—intersecting the geometric center of the metal alloy and having an average aspect ratio of grain cross-sections of less than 2.

[0090] According to certain embodiments, a metal alloy having a cross-sectional average grain aspect ratio falling within a particular range (e.g., any of the ranges described elsewhere herein) has a first cross-section intersecting the geometric center of the metal alloy and having an average aspect ratio of grain cross-sections falling within that range; a second cross-section—orthogonal to the first cross-section—intersecting the geometric center of the metal alloy and having an average aspect ratio of grain cross-sections falling within that range; and at least a third cross-section—orthogonal to the first cross-section and the second cross-section—intersecting the geometric center of the metal alloy and having an average aspect ratio of grain cross-sections falling within that range. For example, according to certain embodiments, a metal alloy having a cross-sectional average grain aspect ratio of less than 2 includes a first cross-section that intersects the geometric center of the metal alloy having an average aspect ratio of grain cross-sections of less than 2, a second cross-section—orthogonal to the first cross-section—intersecting the geometric center of the metal alloy and having an average aspect ratio of grain cross-sections of less than 2, and at least a third cross-section—orthogonal to the first cross-section and the second cross-section—intersecting the geometric center of the metal alloy and having an average aspect ratio of grain cross-sections of less than 2.

[0091] According to certain embodiments, the grains within the metal alloy can be both relatively small and relatively equiaxed. For example, according to certain embodiments, at least one cross-section (and, in some embodiments, at least a second cross-section that is orthogonal to the first cross-section and/or at least a third cross-section that is orthogonal to the first and second cross-sections) can have a volume-average cross-sectional grain size and an average aspect ratio of grain cross-sections falling within any of the ranges outlined above or elsewhere herein.

[0092] The metal alloy can, according to certain embodiments, be a bulk metal alloy (e.g., a bulk nanocrystalline metal alloy). A “bulk metal alloy” is a metal alloy that is not

in the form of a thin film. In certain embodiments, the bulk metal alloy has a smallest dimension of at least 1 micron. In some embodiments, the bulk metal alloy has a smallest dimension of at least 5 microns, at least 10 microns, at least 25 microns, at least 50 microns, at least 100 microns, at least 500 microns, at least 1 millimeter, at least 1 centimeter, at least 10 centimeters, at least 100 centimeters, or at least 1 meter. Other values are also possible. According to certain embodiments, the metal alloy is not in the form of a coating.

[0093] In certain embodiments, the metal alloy occupies a volume of at least 0.01 mm³, at least 0.1 mm³, at least 1 mm³, at least 5 mm³, at least 10 mm³, at least 0.1 cm³, at least cm³, at least 1 cm³, at least 10 cm³, at least 100 cm³, or at least 1 m³. Other values are also possible.

[0094] According to certain embodiments, the metal alloy comprises multiple phases. For example, in some embodiments, the metal alloy is a dual-phase metal alloy.

[0095] In some embodiments, the metal alloy has a high relative density. The term “relative density” refers to the ratio of the experimentally measured density of the metal alloy and the maximum theoretical density of the metal alloy. The “relative density” (ρ_{rel}) is expressed as a percentage, and is calculated as:

$$\rho_{rel} = \frac{\rho_{measured}}{\rho_{maximum}} \times 100\%$$

wherein $\rho_{measured}$ is the experimentally measured density of the metal alloy and $\rho_{maximum}$ is the maximum theoretical density of an alloy having the same composition as the metal alloy.

[0096] In some embodiments, the metal alloy (e.g., a sintered metal alloy, a nanocrystalline metal alloy, and/or a bulk metal alloy) has a relative density of at least 80%, at least 85%, at least 90%, at least 92%, at least 95%, at least 96%, at least 97%, at least 98%, or at least 99% (and/or, in certain embodiments, up to 99.8%, up to 99.9%, or more). In some embodiments, the nanocrystalline alloy has a relative density of 100%. Other values are also possible.

[0097] According to certain embodiments, the metal alloy is fully dense. As utilized herein, the term “fully dense” (or “full density”) refers to a material with a relative density of at least 98%. According to certain embodiments, the relative density of the metal alloy may impact other material properties of the metal alloy. Thus, by controlling the relative density of the metal alloy, other material properties of the metal alloy may be controlled.

[0098] According to certain embodiments, metal alloys described herein can be substantially stable at relatively high temperatures. A metal alloy is said to be “substantially stable” at a particular temperature when the metal alloy includes at least one cross-section intersecting the geometric center of the alloy in which the volume-average cross-sectional grain size (described above) of the cross-section does not increase by more than 20% (relative to the original volume-average cross-sectional grain size) when the metal alloy is heated to that temperature for 24 hours in an argon atmosphere. One of ordinary skill in the art would be capable of determining whether a metal alloy is substantially stable at a particular temperature by taking a cross-section of the article, determining the volume-average cross-sectional grain size of the cross-section at 25° C., heating the cross-section to the particular temperature for 24 hours in an argon

atmosphere, allowing the cross-section to cool back to 25° C., and determining—post-heating—the volume-average cross-sectional grain size of the cross-section. The metal alloy would be said to be substantially stable if the volume-average cross-sectional grain size of the cross-section after the heating step is less than 120% of the volume-average cross-sectional grain size of the cross-section prior to the heating step. According to certain embodiments, a metal alloy that is substantially stable at a particular temperature includes at least one cross-section intersecting the geometric center of the metal alloy in which the volume-average cross-sectional grain size of the cross-section does not increase by more than 15%, more than 10%, more than 5%, or more than 2% (relative to the original volume-average grain size) when the object is heated to that temperature for 24 hours in an argon atmosphere.

[0099] In some embodiments, the metal alloy is substantially stable at at least one temperature that is greater than or equal to 100 degrees Celsius (° C.). In certain embodiments, the metal alloy is substantially stable at at least one temperature that is greater than or equal to 200° C., greater than or equal to 300° C., greater than or equal to 400° C., greater than or equal to 500° C., greater than or equal to 600° C., greater than or equal to 700° C., greater than or equal to 800° C., greater than or equal to 900° C., greater than or equal to 1000° C., greater than or equal to 1100° C., greater than or equal to 1200° C., greater than or equal to 1300° C., or greater than or equal to 1400° C. Other ranges are also possible.

[0100] Certain of the metal alloys described herein are sintered metal alloys. Exemplary sintering methods that may be used to produce metal alloys according to the present disclosure are described in more detail below.

[0101] Also described herein are inventive methods of forming metal alloys (e.g., sintered metal alloys, bulk metal alloys, and/or nanocrystalline metal alloys). Certain of the inventive methods described herein can be used to form the inventive metal alloys described above and elsewhere herein. For example, certain of the methods described herein can be used to form nanocrystalline metal alloys, for example, including any of the grain sizes and/or grain size distributions described above or elsewhere herein. Certain of the methods described herein can be used to form metal alloys having high relative densities, including any of the relative densities described above or elsewhere herein. Certain of the methods described herein can be used to form bulk nanocrystalline metal alloys, for example, having any of the sizes described above or elsewhere herein. Certain of the methods described herein can be used to form metal alloys that are stable, for example, having any of the stabilities (e.g., against grain growth) described above or elsewhere herein.

[0102] In some embodiments, a metal alloy is formed by sintering a plurality of particulates. The shape of the particulates may be, for example, spherical, cubical, conical, cylindrical, needle-like, irregular, or any other suitable geometry. In some embodiments, at least some (e.g., at least 50%, at least 75%, at least 90%, or at least 95%) of the particulates are single crystals. In certain embodiments, at least some (e.g., at least 50%, at least 75%, at least 90%, or at least 95%) of the particulates are polycrystalline.

[0103] The particulates that are sintered can be, according to certain embodiments, nanocrystalline particulates. The nanocrystalline particulates can comprise, according to cer-

tain embodiments, grains with a grain size smaller than or equal to 1000 nm, smaller than or equal to 900 nm, smaller than or equal to 800 nm, smaller than or equal to 700 nm, smaller than or equal to 600 nm, smaller than or equal to 500 nm, smaller than or equal to 400 nm, smaller than or equal to 300 nm, smaller than or equal to 200 nm, smaller than or equal to 150 nm, smaller than or equal to 125 nm, smaller than or equal to 100 nm, smaller than or equal to 50 nm, smaller than or equal to 40 nm, smaller than or equal to 30 nm, or smaller than or equal to 20 nm. According to certain embodiments, at least some of the nanocrystalline particulates have a grain size of smaller than or equal to 50 nm. In some embodiments, at least some of the nanocrystalline particulates have a grain size of greater than or equal to 5 nm and smaller than or equal to 25 nm. In some embodiments, at least some of the nanocrystalline particulates have a grain size of greater than or equal to 10 nm and smaller than or equal to 20 nm.

[0104] According to certain embodiments, at least some of the nanocrystalline particulates comprise Fe and/or a second element (e.g., a second metal). In some embodiments, one portion of the nanocrystalline particulates is made up of Fe while another portion of the nanocrystalline particulates are made up of the second element (e.g., a second metal). In certain embodiments, at least some of the nanocrystalline particulates comprise both Fe and the second element (e.g., second metal).

[0105] According to certain embodiments, at least some of the nanocrystalline particulates comprise Fe, a second element (e.g., a second metal), and/or a third element (e.g., a third metal). In some embodiments, one portion of the nanocrystalline particulates is made up of Fe, while another portion of the nanocrystalline particulates are made up of the second element, while yet another portion of the nanocrystalline particulates are made up of the third element. In certain embodiments, at least some of the nanocrystalline particulates comprise both Fe and the second element. In certain embodiments, at least some of the nanocrystalline particulates comprise both Fe and the third element. In certain embodiments, at least some of the nanocrystalline particulates comprise Fe, the second element, and the third element.

[0106] In some embodiments, Fe is the most abundant element by atomic percentage in at least some of the nanocrystalline particulates. In some embodiments, Fe is the most abundant metal or metalloid element by atomic percentage in at least some of the nanocrystalline particulates. In some embodiments, Fe is the most abundant metal element by atomic percentage in at least some of the nanocrystalline particulates. In some embodiments, at least some of the particulates contain Fe in an amount of at least 50 at %, at least 55 at %, at least 60 at %, at least 70 at %, at least 80 at %, at least 90 at %, or at least 95 at %. In some embodiments, at least some of the particulates contain Fe in an amount of up to 96 at %, up to 97 at %, up to 98 at %, or more. Combinations of these ranges are also possible. Other values are also possible.

[0107] In some embodiments, Fe is the most abundant element by atomic percentage in the particulate material. In some embodiments, Fe is the most abundant metal or metalloid element by atomic percentage in the particulate material. In some embodiments, Fe is the most abundant metal element by atomic percentage in the particulate material. According to certain embodiments, the total amount of

Fe present in the particulate material is at least 50 at %, at least 55 at %, at least 60 at %, at least 70 at %, at least 80 at %, at least 90 at %, or at least 95 at % of the particulate material. In some embodiments, the total amount of Fe present in the particulate material is up to 96 at %, up to 97 at %, up to 98 at %, up to 99 at %, up to 99.5 at %, or more of the particulate material. Combinations of these ranges are also possible. Other values are also possible.

[0108] The second element (which can be a second metal) can be, for example, any of the second elements described above.

[0109] The third element (which can be a third metal) can be, for example, any of the third elements described above.

[0110] In some embodiments, at least a portion of the particulates include the second element (e.g., a second metal) in an amount of less than or equal to 40 at %, less than or equal to 35 at %, less than or equal to 32 at %, less than or equal to 30 at %, less than or equal to 25 at %, less than or equal to 22 at %, less than or equal to 20 at %, less than or equal to 15 at %, or less than or equal to 12 at %. In some embodiments, at least a portion of the particulates include the second element (e.g., a second metal) in an amount of at least 0.5 at %, at least 1 at %, at least 2 at %, at least 3 at %, at least 4 at %, at least 5 at %, at least 6 at %, at least 7 at %, at least 8 at %, at least 9 at %, at least 10 at %, or more. Combinations of these ranges are also possible. For example, in some embodiments, at least a portion of the particulates include the second element in an amount of from 0.5 at % to 40 at % of the particulate material. In some embodiments, at least a portion of the particulates include the second element in an amount of from 1 at % to 40 at % of the particulate material. In some embodiments, at least a portion of the particulates include the second element in an amount of from 8 at % to 32 at % of the particulate material. Other values are also possible.

[0111] In some embodiments, the total amount of the second element in the particulate material is less than or equal to 40 at %, less than or equal to 35 at %, less than or equal to 32 at %, less than or equal to 30 at %, less than or equal to 25 at %, less than or equal to 22 at %, less than or equal to 20 at %, less than or equal to 15 at %, or less than or equal to 12 at % of the particulate material. In some embodiments, the total amount of the second element in the particulate material is at least 0.5 at %, at least 1 at %, at least 2 at %, at least 3 at %, at least 4 at %, at least 5 at %, at least 6 at %, at least 7 at %, at least 8 at %, at least 9 at %, at least 10 at %, or more of the particulate material. Combinations of these ranges are also possible. For example, in some embodiments, the total amount of the second element present in the particulate material is from 0.5 at % to 40 at % of the particulate material. In some embodiments, the total amount of the second element present in the particulate material is from 1 at % to 40 at % of the particulate material. In some embodiments, the total amount of the second element present in the particulate material is from 8 at % to 32 at % of the particulate material. Other values are also possible.

[0112] In some embodiments, at least a portion of the particulates include the third element in an amount of less than or equal to 40 at %, less than or equal to 35 at %, less than or equal to 30 at %, less than or equal to 25 at %, less than or equal to 22 at %, less than or equal to 20 at %, less than or equal to 15 at %, or less than or equal to 12 at %. In some embodiments, at least a portion of the particulates

include the third element in an amount of at least 0.5 at %, at least 1 at %, at least 2 at %, at least 3 at %, at least 4 at %, at least 5 at %, at least 6 at %, at least 7 at %, at least 8 at %, at least 9 at %, at least 10 at %, or more. Combinations of these ranges are also possible. For example, in some embodiments, at least a portion of the particulates include the third element in an amount of from 0.5 at % to 30 at %, or from 1 at % to 30 at % of the particulate material. In some embodiments, at least a portion of the particulates include the third element in an amount of from 0.5 at % to 30 at %, or from 1 at % to 30 at % of the particulate material. Other values are also possible.

[0113] In some embodiments, the total amount of the third element in the particulate material is less than or equal to 40 at %, less than or equal to 35 at %, less than or equal to 30 at %, less than or equal to 25 at %, less than or equal to 22 at %, less than or equal to 20 at %, less than or equal to 15 at %, or less than or equal to 12 at %. In some embodiments, the total amount of the third element in the particulate material is at least 0.5 at %, at least 1 at %, at least 2 at %, at least 3 at %, at least 4 at %, at least 5 at %, at least 6 at %, at least 7 at %, at least 8 at %, at least 9 at %, at least 10 at %, or more. Combinations of these ranges are also possible. For example, in some embodiments, the total amount of the third element present in the particulate material is from 1 at % to 30 at % of the particulate material. In some embodiments, the total amount of the third element present in the particulate material is from 1 at % to 30 at % of the particulate material. Other values are also possible.

[0114] According to certain embodiments, at least some of the nanocrystalline particulates are formed by mechanically working a powder comprising the Fe and the second element. For example, certain embodiments comprise making nanocrystalline particulates, at least in part, by mechanically working a powder including a plurality of Fe particulates and a plurality of second element particulates (e.g., particulates comprising Mg). Certain embodiments comprise making nanocrystalline particulates, at least in part, by mechanically working particulates that include both Fe and the second element.

[0115] According to certain embodiments, at least some of the nanocrystalline particulates are formed by mechanically working a powder comprising the Fe, the second element, and the third element. For example, certain embodiments comprise making nanocrystalline particulates, at least in part, by mechanically working a powder including a plurality of Fe particulates, a plurality of second element particulates (e.g., particulates comprising Mg), and a plurality of third element particulates (e.g., particulates comprising Cr). Certain embodiments comprise making nanocrystalline particulates, at least in part, by mechanically working particulates that include both Fe and the second element; both Fe and the third element; both the second element and the third element; and/or all of Fe, the second element, and the third element.

[0116] In embodiments that make use of mechanical working, any appropriate method of mechanical working may be employed to mechanically work a powder and form nanocrystalline particulates. According to certain embodiments, at least some of the nanocrystalline particulates are formed by ball milling a powder comprising the Fe and the second element (and/or, when present, the third element). The ball milling process may be, for example, a high energy ball milling process. In a non-limiting exemplary ball milling

process, a tungsten carbide or steel milling vial may be employed, with a ball-to-powder ratio of 2:1 to 20:1 (e.g., from 5:1 to 12:1, such as 10:1), and an ethanol process control agent content of 0.01 to 3 mg/g of powder. According to certain other embodiments, the mechanical working is carried out in the absence of a process control agent. Other types of mechanical working may also be employed, including but not limited to, shaker milling and planetary milling. In some embodiments, the mechanical working (e.g., via ball milling or another process) may be performed under conditions sufficient to produce a nanocrystalline particulate comprising a supersaturated phase. Supersaturated phases are described in more detail below.

[0117] According to certain embodiments, the mechanical working (e.g., ball milling) is performed at a relatively low temperature. For example, in some embodiments, the mechanical working (e.g., ball milling) is performed while the particulates are at a temperature of less than or equal to 150° C., less than or equal to 100° C., less than or equal to 75° C., less than or equal to 50° C., less than or equal to 40° C., less than or equal to 35° C., less than or equal to 30° C., less than or equal to 25° C., or less than or equal to 20° C. In some embodiments, the mechanical working (e.g., ball milling) is performed while the particulates are at a temperature of at least 0° C. In some embodiments, the mechanical working (e.g., ball milling) is performed at a temperature of the surrounding, ambient environment.

[0118] In certain embodiments, the mechanical working (e.g., ball milling) may be conducted for a time of greater than or equal to 6 hours (e.g., greater than or equal to 8 hours, greater than or equal to 10 hours, greater than or equal to 12 hours, or greater than or equal to 15 hours). In certain embodiments, the mechanical working (e.g., ball milling) may be conducted for a time of less than or equal to 18 hours. In some embodiments, the mechanical working (e.g., ball milling) may be conducted for a time of 6 hour to 18 hours. In some cases, if the mechanical working time is too long, the Fe and/or the second element (and/or the third element, if present) may be contaminated by the material used to perform the mechanical working (e.g., milling vial material). The amount of the second element (and/or the third element, if present) that is dissolved in the Fe may, in some cases, increase with increasing mechanical working (e.g., milling) time. In some embodiments, after the mechanical working step (e.g., ball milling step), a phase rich in the second element material may be present.

[0119] According to certain embodiments, the Fe and the second element (and/or the third element, if present) are present in the particulates in a non-equilibrium phase. The particulates may, according to certain embodiments, include a non-equilibrium phase in which the second element (and/or the third element, if present) is dissolved in the Fe. In some embodiments, the non-equilibrium phase comprises a solid solution. According to some embodiments, the non-equilibrium phase may be a supersaturated phase comprising the second element (and/or the third element, if present) dissolved in the Fe. A “supersaturated phase,” as used herein, refers to a phase in which a material is dissolved in another material in an amount that exceeds the solubility limit. The supersaturated phase can include, in some embodiments, an activator element and/or a stabilizer element forcibly dissolved in the Fe in an amount that exceeds the amount of the activator element and/or the stabilizer element that could be otherwise dissolved in an equilibrium

phase of the Fe. For example, in one set of embodiments, the supersaturated phase is a phase that includes an activator element forcibly dissolved in Fe in an amount that exceeds the amount of activator element that could be otherwise dissolved in an equilibrium Fe phase.

[0120] In some embodiments, the supersaturated phase may be the only phase present after the mechanical working (e.g., ball milling) process.

[0121] According to certain embodiments, the non-equilibrium phase may undergo decomposition during the sintering of the nanocrystalline particulates (which sintering is described in more detail below). The sintering of the nanocrystalline particulates may cause the formation of a phase rich in the third element at at least one of the surface and grain boundaries of the nanocrystalline particulates. In some such embodiments, the Fe is soluble in the phase rich in the third element. The formation of the phase rich in the third element may be the result of the decomposition of the non-equilibrium phase during the sintering. The phase rich in the third element may, according to certain embodiments, act as a fast diffusion path for the Fe, enhancing the sintering kinetics and accelerating the rate of sintering of the nanocrystalline particulates. According to some embodiments, the decomposition of the non-equilibrium phase during the sintering of the nanocrystalline particulates accelerates the rate of sintering of the nanocrystalline particulates.

[0122] Certain, although not necessarily all, embodiments comprise cold pressing the plurality of nanocrystalline particulates during at least one portion of time prior to the sintering. It has been found that, according to certain embodiments, metal alloys comprising Fe and a second element (e.g., Fe and Mg), and/or metal alloys comprising Fe, a second element, and a third element (e.g., Fe, Mg, and Cr) can be compressed such that high relative densities are achieved without the need for simultaneous heating. In some embodiments, the cold pressing comprises compressing of the plurality of nanocrystalline particulates at a force greater than or equal to 300 MPa, greater than or equal to 400 MPa, greater than or equal to 500 MPa, greater than or equal to 750 MPa, greater than or equal to 1000 MPa, or higher. In some embodiments, the cold compression comprises compressing the plurality of nanocrystalline particulates at a force of up to 1400 MPa, or greater. Combinations of these ranges are also possible (e.g., greater than or equal to 300 MPa and less than or equal to 1400 MPa). Other ranges are also possible.

[0123] According to certain embodiments, the cold compression is performed at a relatively low temperature. For example, in some embodiments, the cold compression is performed while the particulates are at a temperature of less than or equal to 150° C., less than or equal to 100° C., less than or equal to 75° C., less than or equal to 50° C., less than or equal to 40° C., less than or equal to 35° C., less than or equal to 30° C., less than or equal to 25° C., or less than or equal to 20° C. In some embodiments, the cold compression is performed at a temperature of the surrounding, ambient environment.

[0124] As noted above, certain embodiments comprise sintering a plurality of nanocrystalline particulates to form the nanocrystalline metal alloy. Those of ordinary skill in the art are familiar with the process of sintering, which involves applying heat to the material (e.g., particulates) that is to be sintered such that the material becomes a single solid mass.

[0125] FIGS. 1A-1C are exemplary schematic diagrams showing a sintering process, according to certain embodiments. In FIG. 1A, a plurality of particulates **100** are shown in the form of spheres (although, as mentioned elsewhere, other shapes could be used). As shown in FIG. 1B, particulates **100** can be arranged such that they contact each other. As shown in FIG. 1C, as the particulates are heated, they agglomerate to form a single solid material **110**. During the sintering process, according to certain embodiments, interstices **105** between particulates **100** (shown in FIG. 1B) can be greatly reduced or eliminated, such that a solid having a high relative density is formed (shown in FIG. 1C).

[0126] According to certain embodiments, the sintering can be performed when the metal particulates are at a relatively low temperature and/or for a relatively short period of time, while maintaining the ability to form metal alloys having high relative densities, small grain sizes, and/or equiaxed grains.

[0127] According to certain embodiments, sintering the plurality of nanocrystalline particulates involves heating the nanocrystalline particulates to a sintering temperature of less than or equal to 1200° C., less than or equal to 1100° C., less than or equal to 1000° C., less than or equal to 900° C., less than or equal to 850° C., less than or equal to 800° C., less than or equal to 750° C., less than or equal to 700° C., less than or equal to 650° C., less than or equal to 600° C., less than or equal to 550° C., less than or equal to 500° C., less than or equal to 450° C., less than or equal to 400° C., or less than or equal to 400° C. According to certain embodiments, sintering the plurality of nanocrystalline particulates involves heating the nanocrystalline particulates to a sintering temperature of greater than or equal to 300° C., greater than or equal to 350° C., greater than or equal to 400° C., greater than or equal to 500° C., greater than or equal to 600° C., greater than or equal to 700° C., or greater than or equal to 900° C. Combinations of these ranges are also possible. For example, in some embodiments, sintering the plurality of nanocrystalline particulates involves heating the nanocrystalline particulates to a sintering temperature that is greater than or equal to 600° C. and less than or equal to 1100° C. In some embodiments, the temperature of the sintered material is within these ranges for at least 10%, at least 25%, at least 50%, at least 75%, at least 90%, or at least 99% of the sintering time.

[0128] According to certain embodiments, sintering the plurality of nanocrystalline particulates involves maintaining the nanocrystalline particulates within the range of sintering temperatures for less than 72 hours, less than 48 hours, less than or equal to 24 hours, less than or equal to 12 hours, less than or equal to 6 hours, less than or equal to 4 hours, less than or equal to 3 hours, less than or equal to 2 hours, or less than or equal to 1 hour (and/or, in some embodiments, for at least 10 minutes, at least 20 minutes, at least 30 minutes, at least 50 minutes, at least 3 hours, or at least 6 hours). Combinations of these ranges are also possible. For example, in some embodiments, sintering the plurality of nanocrystalline particulates involves heating the nanocrystalline particulates to a first sintering temperature that is greater than or equal to 600° C. and less than or equal to 1100° C. for a sintering duration greater than or equal to 6 hours and less than or equal to 24 hours.

[0129] According to certain embodiments, sintering comprises heating the nanocrystalline particulates to a first sintering temperature that is lower than a second sintering

temperature needed for sintering Fe in the absence of the second element. To determine whether such conditions were met, one of ordinary skill in the art would compare the temperature necessary to achieve sintering in the sample containing the Fe and the second element to the temperature necessary to achieve sintering in a sample containing the Fe without the second element, but otherwise identical to the sample containing the Fe and the second element. In some embodiments, the first sintering temperature can be at least 25° C., at least 50° C., at least 100° C., or at least 200° C. lower than the second sintering temperature. In some embodiments, the first sintering step is performed at a temperature of at least 500° C. (or at least 600° C.). In some embodiments, the second sintering step is performed at a temperature of at least 900° C. (or at least 1100° C.).

[0130] According to certain embodiments, a non-equilibrium phase present in the nanocrystalline particulates (e.g., any of the non-equilibrium phases described above or elsewhere herein) undergoes decomposition during the sintering. In some such embodiments, the decomposition of the non-equilibrium phase accelerates a rate of sintering of the nanocrystalline particulates.

[0131] In some embodiments, the sintering further comprises forming a second phase at at least one of a surface and a grain boundary of the nanocrystalline particulates during the sintering. In some such embodiments, the second phase is rich in the second element. The term “rich” with respect to the content of an element in a phase refers to a content of the element in the phase of at least 50 at % (e.g., at least 60 at %, at least 70 at %, at least 80 at %, at least 90 at %, at least 99 at %, or higher). The term “phase” is generally used herein to refer to a state of matter. For example, the phase can refer to a phase shown on a phase diagram.

[0132] The sintering may be conducted in a variety of suitable environments. In certain embodiments, the nanocrystalline particulates are in an inert atmosphere during the sintering process. The use of an inert atmosphere can be useful, for example, when reactive metals are employed in the nanocrystalline particulates. For example, Fe and Mg are reactive (separately and/or together) with oxygen.

[0133] In some embodiments, the sintering is performed in an atmosphere in which at least 90 vol. %, at least 95 vol. %, at least 99 vol. %, or substantially all of the atmosphere is made up of an inert gas. The inert gas can be or comprise, for example, helium, argon, xenon, neon, krypton, combinations of two or more of these, or other inert gas(es).

[0134] In certain embodiments, oxygen scavengers (e.g., getters) may be included in the sintering environment. The use of oxygen scavengers can reduce the degree to which the metals are oxidized during the sintering process, which may be advantageous according to certain embodiments. In some embodiments, the sintering environment can be controlled such that oxygen is present in an amount of less than 1 vol. %, less than 0.1 vol. %, less than 100 parts per million (ppm), less than 10 ppm, or less than 1 ppm.

[0135] In certain embodiments, the sintering is performed in an atmosphere containing a gas that, when exposed to oxygen gas (i.e., O₂) under the sintering conditions, will react with the oxygen gas. In some embodiments, the sintering is performed in an atmosphere comprising hydrogen gas (H₂). In some embodiments, the combination of hydrogen gas and inert gas makes up at least 90 vol. %, at least 95 vol. %, at least 99 vol. %, or substantially all of the atmosphere in which the sintering is performed. In some

embodiments, the combination of hydrogen gas and argon gas makes up at least vol. %, at least 95 vol. %, at least 99 vol. %, or substantially all of the atmosphere in which the sintering is performed.

[0136] According to certain embodiments, the sintering is conducted essentially free of external applied stress. For example, in some embodiments, for at least 20%, at least 50%, at least 75%, at least 90%, or at least 98% of the time during which sintering is performed, the maximum external pressure applied to the nanocrystalline particulates is less than or equal to 2 MPa, less than or equal to 1 MPa, less than or equal to 0.5 MPa, or less than or equal to 0.1 MPa. The maximum external pressure applied to the nanocrystalline particulates refers to the maximum pressure applied as a result of the application of a force external to the nanocrystalline particulates, and excludes the pressure caused by gravity and arising between the nanocrystalline particulates and the surface on which the nanocrystalline particulates are positioned during the sintering process. Certain of the sintering processes described herein can allow for the production of relatively highly dense sintered ultra-fine and nanocrystalline materials even in the absence or substantial absence of external pressure applied during the sintering process. According to certain embodiments, the sintering may be a pressureless sintering process.

[0137] According to certain embodiments, at least one activator element may be present during the sintering process. The activator element may enhance the sintering kinetics of Fe. According to certain embodiments, the activator element may provide a high diffusion path for the Fe atoms. For example, in some embodiments, the activator element atoms may surround the Fe atoms and provide a relatively high transport diffusion path for the Fe atoms, thereby reducing the activation energy of diffusion of the Fe. In some embodiments, this technique is referred to as activated sintering. The activator element may, in some embodiments, lower the temperature required to sinter the nanocrystalline particulates, relative to the temperature that would be required to sinter the nanocrystalline particulates in the absence of the activator element but under otherwise identical conditions. Thus, the sintering may involve, according to certain embodiments, a first sintering temperature, and the first sintering temperature may be lower than a second sintering temperature needed for sintering the Fe in the absence of the third element. To determine the sintering temperature needed for sintering the Fe in the absence of the third element, one would prepare a sample of the Fe material that does not contain the third element but is otherwise identical to the nanocrystalline particulate material. One would then determine the minimum temperature needed to sinter the sample that does not include the third element. In some embodiments, the presence of the third element lowers the sintering temperature by at least 25° C., at least 50° C., at least 100° C., at least 200° C., or more.

[0138] According to certain embodiments, at least one stabilizer element may be present during the sintering process. The stabilizer element may be any element capable of reducing the amount of grain growth that occurs, relative to the amount that would occur in the absence of the stabilizer element but under otherwise identical conditions. In some embodiments, the stabilizer element reduces grain growth by reducing the grain boundary energy of the sintered material, and/or by reducing the driving force for grain growth. The stabilizer element may, according to certain

embodiments, exhibit a positive heat of mixing with the sintered material. The stabilizer element may stabilize nanocrystalline Fe by segregation in the grain boundaries. This segregation may reduce the grain boundary energy, and/or may reduce the driving force against grain growth in the alloy.

[0139] In some embodiments, the stabilizer element may also be the activator element. The use of a single element both as the stabilizer and activator elements has the added benefit, according to certain embodiments, of removing the need to consider the interaction between the activator and the stabilizer. In some embodiments, the element that may be utilized as both the activator and stabilizer element may be a metal or metalloid element, which may be any of the aforescribed metal or metalloid elements.

[0140] According to certain embodiments, when one element cannot act as both the stabilizer and the activator, two elements may be employed. The interaction between the two elements may be accounted for, according to some embodiments, to ensure that the activator and stabilizer roles are properly fulfilled. For example, when the activator and the stabilizer form an intermetallic compound each of the elements may be prevented from fulfilling their designated role, in some cases. As a result, activator and stabilizer combinations with the ability to form intermetallic compounds at the expected sintering temperatures should be avoided, at least in some instances. The potential for the formation of intermetallic compounds between two elements may be analyzed with phase diagrams.

[0141] According to one set of embodiments, iron powders and magnesium powders (e.g., 10, 20, or 30 at % Mg with the balance being iron) can be mechanically alloyed via ball milling, cold compressed, and subsequently annealed (e.g., in a thermomechanical analyzer for several hours). In some embodiments, the Fe—Mg—Cr alloy system exhibits nanocrystalline grain size stabilization by Mg segregation to Fe grain boundaries, and by formation of Mg-rich precipitates which pin grain boundaries and further prevent grain growth.

[0142] According to certain embodiments, powders of elemental Fe, Mg and Cr are mixed and milled to achieve supersaturation and a decrease of the grain size to the nanometer scale. In some embodiments, annealing of compressed powders leads to the development of a nano-duplex structure consisting of Fe-rich grains and Cr-rich precipitates. In some embodiments, a nanocrystalline structure with grain sizes of around 100 nm can be maintained even after 18 hours at 900° C. (which is 65% of the melting temperature for Fe). In some embodiments, high relative densities can be achieved for Fe-29 at % Cr-1 at % Mg. It is believed that this may indicate that accelerated densification is possible.

[0143] Certain embodiments are related to a metallic alloy based on iron with a nanocrystalline microstructure, which is thermally stable. This alloy can be prepared from metallic powders by mechanical alloying, and then consolidated at high temperatures into a fully dense material, while retaining its nano-scale grain size. In accordance with certain embodiments, the dense nanocrystalline alloy is significantly stronger than a similar alloy which is not nanocrystalline.

[0144] According to certain embodiments, the alloys are based on iron (Fe) and typically contain magnesium (Mg) and chromium (Cr) of varying compositions. They are

prepared, according to some embodiments, by high-energy ball milling of elemental powders, which results in mechanical alloying (creating the alloy) and grain refinement (forming a nanocrystalline structure). In some embodiments, the alloy powders are then cold-compressed, and annealed in an inert atmosphere without any applied pressure. It is believed that, in accordance with certain embodiments, the addition of Mg stabilizes the grain boundaries so that the nanocrystalline structure is maintained during the annealing process. It is also believed that, in accordance with some embodiments, the addition of Cr helps accelerate the sintering (densification) process by forming a second phase during annealing.

[0145] Certain, although not necessarily all, of the embodiments described herein may have one or more advantages and/or improvements over existing methods, devices, and/or materials.

[0146] According to some embodiments, methods described herein allow for creating fully dense bulk nanocrystalline parts with potentially complex shapes, in a scalable way. Alternative methods, such as severe plastic deformation methods (SPD) of dense, coarse-grained material, are believed to be generally not as scalable and are believed to be generally limited to simple part shapes. Additionally, certain of the methods described herein allow for sintering the powder without applied pressure during heating which greatly simplifies the processing route.

[0147] Certain of the articles, systems, and/or methods described herein can have any of a variety of commercial applications and/or may be particularly economically attractive. For example, in accordance with certain embodiments, bulk nanocrystalline metal parts can substitute any structural metallic parts in commercial applications, as they may provide significantly improved mechanical properties. These nanocrystalline iron alloys, in accordance with some embodiments, can then replace conventional iron alloy parts in construction, the auto and aerospace industries, and the like. In some embodiments, if their increased strength is not required, they can be used to reduce weight. For example, in accordance with certain embodiments, a thinner panel may provide the same engineering properties as a thicker one made of a conventional alloy. In some embodiments, alloys described herein can be used to provide both increased strength and weight reduction.

[0148] U.S. Provisional Application No. 62/501,240, filed May 4, 2017, and entitled “Thermally Stable Nanocrystalline Iron Alloys”; U.S. Provisional Application No. 62/646,282, filed Mar. 21, 2018, and entitled “Thermally Stable Nanocrystalline Iron Alloys and Associated Systems and Methods”; and U.S. Provisional Application No. 62/649,178, filed Mar. 28, 2018, and entitled “Thermally Stable Nanocrystalline Iron Alloys and Associated Systems and Methods”; are each incorporated herein by reference in their entireties for all purposes.

[0149] The following example is intended to illustrate certain embodiments of the present invention, but does not exemplify the full scope of the invention.

Example 1

[0150] This example describes the use of low-temperature, accelerated sintering methods to produce nanocrystalline iron-magnesium-chromium (Fe—Mg—Cr) alloys with thermal stability and high relative density.

[0151] Iron powders with different additions of magnesium powders (1, 5, 10, 15, 20, 25, 30, and 35 at % Mg) were mechanically alloyed via high-energy ball milling in a hardened steel vial with hardened steel media. With this process, supersaturated powders with microcrystalline particles and nanocrystalline grain sizes were produced after milling times of around 15 hours. The thermal stability of the resulting nanocrystalline grains was examined in powder form, where the grain size was tracked in-situ at a temperature range of 600-900° C. by x-ray diffraction (XRD), and the resulting microstructures were examined by high resolution electron microscopy and atom probe tomography (APT).

[0152] FIG. 2A shows an XRD pattern taken from an as-milled Fe-15Mg powder, with all reflections belonging to the α -Fe solid solution phase. FIG. 2B and FIG. 2C show transmission electron microscopy (TEM) micrographs of that alloy, with some nanocrystalline grains indicated in dark contrast, marked by dashed circles.

[0153] FIGS. 3A-3B show the grain sizes obtained from the in-situ XRD data as a function of composition (FIG. 3A), showing two annealing temperatures (600 and 900° C.) and temperature (FIG. 3B), showing one composition (5 at % Mg). Interpolated data averaged over all temperatures and all compositions are shown in solid lines.

[0154] From these powders two magnesium compositions were identified as yielding the highest thermal stability (smallest grain size)—1 and 20 at % Mg, based on FIG. 3A. To minimize the effect of oxidation, a composition of 1 at % Mg was chosen for further investigation. Next, a ternary alloy, Fe—Mg—Cr was prepared in the same fashion employing 1 at % Mg and different additions of chromium (9, 19, 29 at % Cr). The thermal stability was again studied in-situ to demonstrate the powders retain their nanocrystallinity upon the same thermal exposure.

[0155] The powders were then cold compressed and subsequently sintered in a forming gas atmosphere (Ar/H_2). The microstructure of the milled powders consisted of supersaturated titanium grains with sizes of around 10 to 20 nm. After sintering (also referred to herein as “annealing”) to 600° C., the grain size increased to around 30 nm and separated into iron-rich and chromium-rich grains. Increasing the sintering temperature to 900° C. resulted in a homogenization of the microstructure into a single iron-rich phase with a grain size of around 60 nm. Even after prolonged sintering times, the structure remained stable.

[0156] Accelerated sintering (pressureless) of nanocrystalline alloys was conducted. Production of supersaturated powders was accomplished via high-energy ball milling. It is believed that the sintering involved precipitation and neck formation of solute on solvent. The effect of necks may have involved fast solute diffusion due to excess vacancies, and diffusion of solvent within necks due to solubility of solvent in solute, that resulted in enhanced densification.

[0157] FIGS. 4A-4B show the grain size obtained by XRD as a function of annealing temperature and time. The temperature profile is shown in FIG. 4A, and the short and long data bars indicate a short or a long XRD scan, respectively. The grain sizes of Fe-19Cr-1Mg and of Fe-1Mg (all at %) are shown in FIG. 4B. For Fe-19Cr-1Mg, annealing to 900° C. resulted in a partial phase transformation ($\alpha\gamma$) and the grain sizes of both phases are indicated. The final two data points indicate the grain size upon cooling back to room temperature.

[0158] FIG. 5A shows a TEM micrograph of a sintered Fe-19Cr-1Mg alloy. The Fe-rich grains can be identified by the diffraction contrast and were under 100 nm, in agreement with the XRD results in FIG. 4B. FIG. 5B is an elemental map showing the distribution of Fe, Cr and Mg (as MgO precipitates) in the same field of view as FIG. 5A. There, Cr-rich grains can be identified separately from the Fe-rich matrix, and these were also mostly under 100 nm in size. Mg was present in the alloy as a segregant in Fe grain boundaries and Fe/Cr interphase boundaries. It was also present in its oxidized form, MgO, forming nanoprecipitates which further helped limit grain growth.

[0159] FIG. 6A and FIG. 6B show scanning electron microscopy (SEM) micrographs of Fe-19Cr-1Mg and Fe-1Mg alloys, respectively, sintered under the same conditions. The porosity of the ternary alloy (5% measured as surface porosity) was significantly lower than that of the binary alloy (20%), which was itself relatively high.

Example 2

[0160] This example describes the impact of the annealing environment, annealing temperature, and alloy composition on alloy properties for Fe alloys containing various amounts of Mg.

[0161] Iron powders with different additions of magnesium (0 at % Mg and 15 at % Mg) were mechanically alloyed via high-energy ball milling in a hardened steel vial with hardened steel media. With this process, microcrystalline particles with nanocrystalline grain sizes were produced after milling times of around 15 hours. The thermal stability of the resulting nanocrystalline grains was examined in powder form, where the grain size was tracked in-situ at a temperature range of 600-900° C. by x-ray diffraction (XRD), and the resulting microstructures were examined by high resolution electron microscopy and atom probe tomography.

[0162] FIG. 7 is a plot showing grain size and the first derivative of grain size as a function of heating time for the pure Fe sample, an Fe-15Mg sample heated in a pure Ar environment, and an Fe-15Mg sample heated in an environment of 90% Ar/10% H_2 environment. FIG. 8A shows a Bright Field (BF) Scanning TEM (STEM) micrograph of the Fe powder in FIG. 7A after annealing, showing a grain size of about 500-1000 nm in size. FIG. 8B shows a BF STEM micrograph of the Fe-15Mg powder in FIG. 7A after annealing in Ar, with Mg-rich precipitates and a grain size of about 100-200 nm in size. FIG. 8C shows a Dark Field (DF) TEM micrograph of the Fe-15Mg powder in FIG. 7A after annealing in Ar with 10% H_2 with grains of about 50 nm in size.

[0163] As shown in FIG. 7, the pure Fe sample reached the resolution limit, and was relatively coarse-grained after cooling. A substantial improvement in thermal stability was realized when Mg was added. In addition, annealing in $\text{Ar}-\text{H}_2$ yielded much less oxide and smaller grains. In fact, the Fe-15Mg sample had a final grain size of around 50 nm after being heated for 12 hours between 600 and 900° C. In summary, the presence of Mg led to substantially smaller grain sizes, relative to the pure Fe sample. In addition, the presence of H_2 in the ambient environment led to even smaller grain sizes.

[0164] Additional Fe—Mg alloys were made, with percentages of Mg ranging from 0 at % to 35 at %. Powders having these compositions were annealed under different environments: one being pure Ar, and the other being 90%

Ar/10% H₂. FIG. 9 is a plot of grain size as a function of composition (at % Mg) for the two different annealing environments. FIG. 10A shows a BF TEM micrograph of the Fe-20Mg powder after annealing in Ar. FIG. 10B shows a DF TEM micrograph of the Fe-20Mg powder after annealing in Ar with 10% H₂. As seen from FIG. 9, annealing under pure Ar resulted in consistently higher grain sizes and more oxide, grain size values that reached the resolution limit, and relatively coarse-grained after cooling in most cases. In contrast, the presence of H₂ led to substantially smaller grain sizes.

[0165] FIG. 11 shows an exemplary contour plot of a surface of grain size over composition and temperature space, obtained from in-situ XRD data, and interpolated with composition and temperature steps of 0.1 at. % and 0.5° C., respectively. Grain size (nm) increases in a direction normal to the number-labeled contour lines (labeled with grain size (nm)) and towards higher numbered contour lines, with labeled iso-(grain size) lines. The top and right plots each represent the dependence of grain size on composition and temperature, for specific temperature or composition value(s) and averaged over all temperatures or compositions values, respectively. From FIG. 11, it can be seen that grain size surfaces had a plateau value at each composition and temperature. Generally, grain sizes consistently increased with temperature. There were extrema for each composition, which were shallower at higher temperatures.

[0166] FIG. 12 shows the ratio between limiting grain size and pinning particle size as a function of pinning particle volume fraction for different material systems ("Zener plot"). The full, small black circles at the bottom right are data for Fe—Mg alloys indicating improved stability than what is traditionally expected from Zener pinning (retardation of grain growth via precipitates which impede grain boundary motion) alone.

[0167] In summary, thermal stability and oxide evolution in Fe—Mg alloys were investigated in-situ. Grain size exhibited extrema as a function of composition and sintering temperature. Using a reducing ambient (e.g., including H₂) resulted in less oxide formation and smaller grains. Without wishing to be bound by any particular theory, it is believed that there is a complex interplay between thermodynamic and kinetic mechanisms. Zener pinning alone did not lead to stability. Grain boundary segregation was observed in TEM and APT images. Alloy composition and annealing environment can be used to tune grain size and oxide content. In addition, alloy composition and annealing environment can be used to improve creep resistance.

[0168] While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodi-

ments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, and/or methods, if such features, systems, articles, materials, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

[0169] The indefinite articles "a" and "an," as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean "at least one."

[0170] The phrase "and/or," as used herein in the specification and in the claims, should be understood to mean "either or both" of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Other elements may optionally be present other than the elements specifically identified by the "and/or" clause, whether related or unrelated to those elements specifically identified unless clearly indicated to the contrary. Thus, as a non-limiting example, a reference to "A and/or B," when used in conjunction with open-ended language such as "comprising" can refer, in one embodiment, to A without B (optionally including elements other than B); in another embodiment, to B without A (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

[0171] As used herein in the specification and in the claims, "or" should be understood to have the same meaning as "and/or" as defined above. For example, when separating items in a list, "or" or "and/or" shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as "only one of" or "exactly one of," or, when used in the claims, "consisting of," will refer to the inclusion of exactly one element of a number or list of elements. In general, the term "or" as used herein shall only be interpreted as indicating exclusive alternatives (i.e. "one or the other but not both") when preceded by terms of exclusivity, such as "either," "one of," "only one of," or "exactly one of." "Consisting essentially of," when used in the claims, shall have its ordinary meaning as used in the field of patent law.

[0172] As used herein in the specification and in the claims, the phrase "at least one," in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase "at least one" refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A or B," or, equivalently "at least one of A and/or B") can refer, in one embodiment, to at least one, optionally

including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

[0173] In the claims, as well as in the specification above, all transitional phrases such as “comprising,” “including,” “carrying,” “having,” “containing,” “involving,” “holding,” and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of” shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

What is claimed is:

1-51. (canceled)

52. A method of forming a nanocrystalline metal alloy, comprising:

sintering a plurality of nanocrystalline particulates to form the nanocrystalline metal alloy;

wherein at least some of the nanocrystalline particulates comprise Fe and a second element, and wherein:

Fe is the most abundant element by atomic percentage in at least some of the nanocrystalline particulates; and/or

sintering the plurality of nanocrystalline particulates involves heating the nanocrystalline particulates to a first sintering temperature that is greater than or equal to 500° C. and less than or equal to 1100° C. for a sintering duration greater than or equal to 6 hours and less than or equal to 24 hours; and/or

sintering the plurality of nanocrystalline particulates involves heating the nanocrystalline particulates such that the nanocrystalline particulates are not at a temperature of greater than or equal to 1100° C. for more than 24 hours; and/or

the second element and Fe exhibit a miscibility gap.

53-57. (canceled)

58. A method of forming a metal alloy, comprising:

sintering powder comprising Fe and Mg to produce the metal alloy, wherein the metal alloy has a relative density of greater than or equal to 80%.

59. The method of claim 52, wherein the second element is a second metal.

60. (canceled)

61. The method of claim 52, wherein the Fe and the second element are present in a non-equilibrium phase.

62. The method of claim 52, wherein the non-equilibrium phase undergoes decomposition during the sintering.

63. The method of claim 52, wherein the non-equilibrium phase undergoes decomposition during the sintering, and the decomposition of the non-equilibrium phase accelerates a rate of sintering of the nanocrystalline particulates.

64. The method of claim 52, wherein the non-equilibrium phase comprises a supersaturated phase comprising the second element dissolved in Fe.

65. The method of claim 52, wherein the second element is selected from the group consisting of magnesium (Mg), boron (B), zirconium (Zr), gold (Au), chromium (Cr), nickel (Ni), vanadium (V), platinum (Pt), lead (Pb), copper (Cu), cobalt (Co), and tin (Sn).

66. The method of claim 52, wherein the second element is Mg.

67. The method of claim 52, further comprising cold pressing the plurality of nanocrystalline particulates during at least one portion of time prior to the sintering.

68. (canceled)

69. The method of claim 52, wherein the cold pressing comprises cold compression of the plurality of nanocrystalline particulates at a force greater than or equal to 300 MPa and less than or equal to 1400 MPa.

70. The method of claim 52, wherein the sintering comprises heating the nanocrystalline particulates to a first sintering temperature lower than a second sintering temperature needed for sintering Fe in the absence of the second element.

71. The method of claim 52, wherein the sintering comprises heating the nanocrystalline particulates to a temperature greater than or equal to 600° C. and less than or equal to 1100° C. for a duration greater than or equal to 6 hours and less than or equal to 24 hours.

72. (canceled)

73. The method of claim 52, wherein the non-equilibrium phase comprises a solid solution.

74. The method of claim 52, further comprising forming at least some of the nanocrystalline particulates by mechanically working a powder comprising Fe and the second element.

75. The method of claim 52, further comprising forming at least some of the nanocrystalline particulates by ball milling a powder comprising Fe and the second element.

76. The method of claim 52, wherein at least some of the nanocrystalline particulates have a grain size of smaller than or equal to 50 nm.

77-78. (canceled)

79. The method of claim 52, wherein the second element is present in the nanocrystalline particulates in an amount of less than or equal to 30 at % of the nanocrystalline particulates.

80-84. (canceled)

85. The method of claim 52, wherein the nanocrystalline metal alloy has a relative density of at least 90%.

86. The method of claim 52, wherein the sintering further comprises forming a second phase at at least one of a surface and a grain boundary of the nanocrystalline particulates during the sintering.

87. The method of claim 52, wherein the sintering further comprises forming a second phase at at least one of a surface and a grain boundary of the nanocrystalline particulates during the sintering; and the second phase is rich in the second element.

88. The method of claim 52, wherein the nanocrystalline metal alloy has a first grain size and a sintered material comprising Fe in the absence of the second element has a second grain size, the first grain size being smaller than the second grain size.

89. (canceled)

90. The method of claim 52, wherein the sintering is conducted essentially free of external applied stress.

91. (canceled)

92. A nanocrystalline metal alloy produced by the method of claim 52.

93. (canceled)

94. The method of claim 52, wherein for at least 20% of the time during which sintering is performed, the maximum

external pressure applied to the nanocrystalline particulates is less than or equal to 2 MPa.

95. The method of claim **52**, wherein the sintering is pressureless sintering.

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