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(54) PRECIPITATION HARDENING HIGH ENTROPY ALLOY AND METHOD OF MANUFACTURING THE SAME

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(57) ABSTRACT

High-entropy alloy, particularly a precipitation hardening high entropy alloy, is provided as a component material used in electromagnetic, chemical, shipbuilding, mechanical, and other applications, a component material used in extreme environments requiring high strength and good corrosion resistance, and the like.

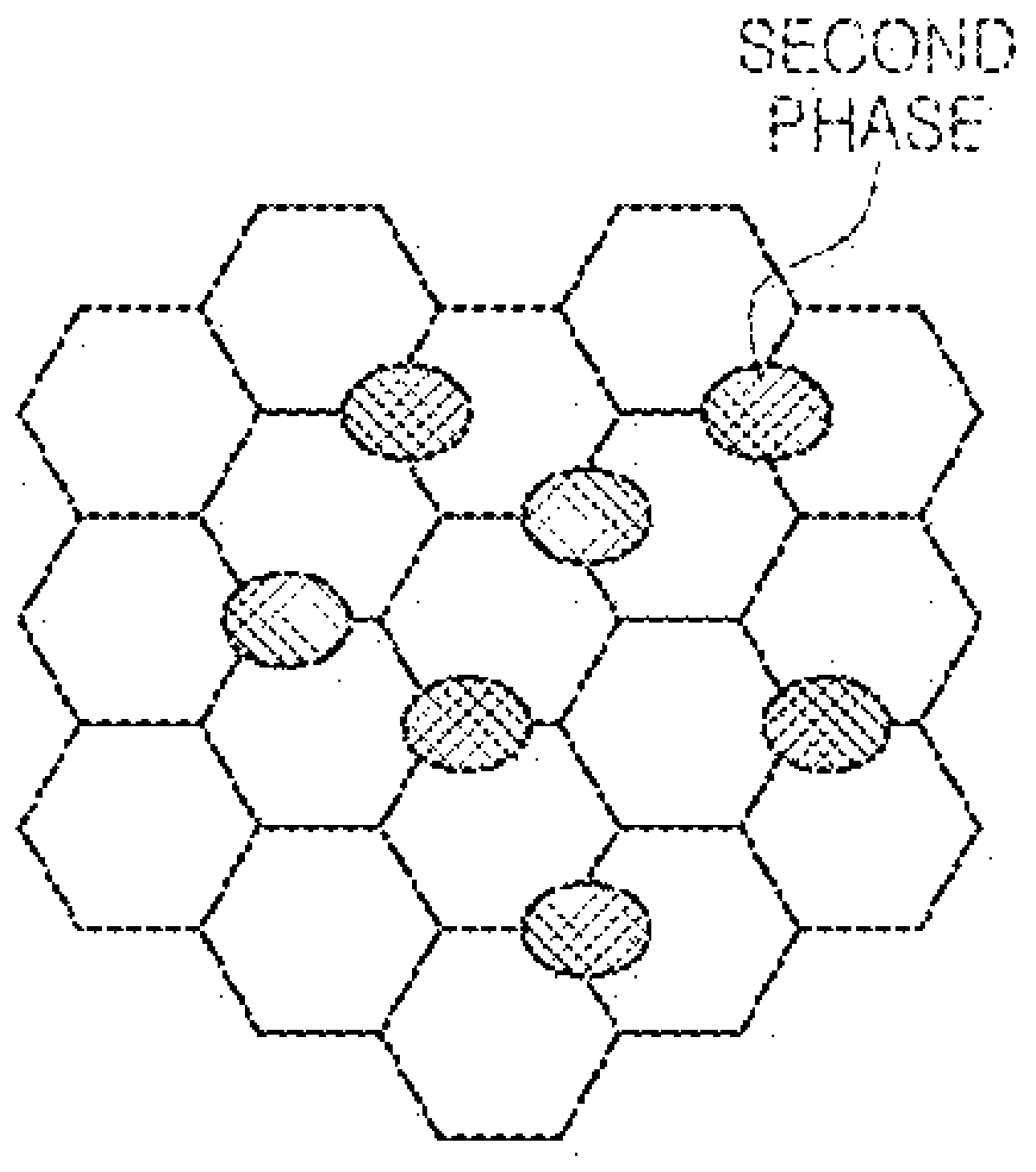

FIG. 1A

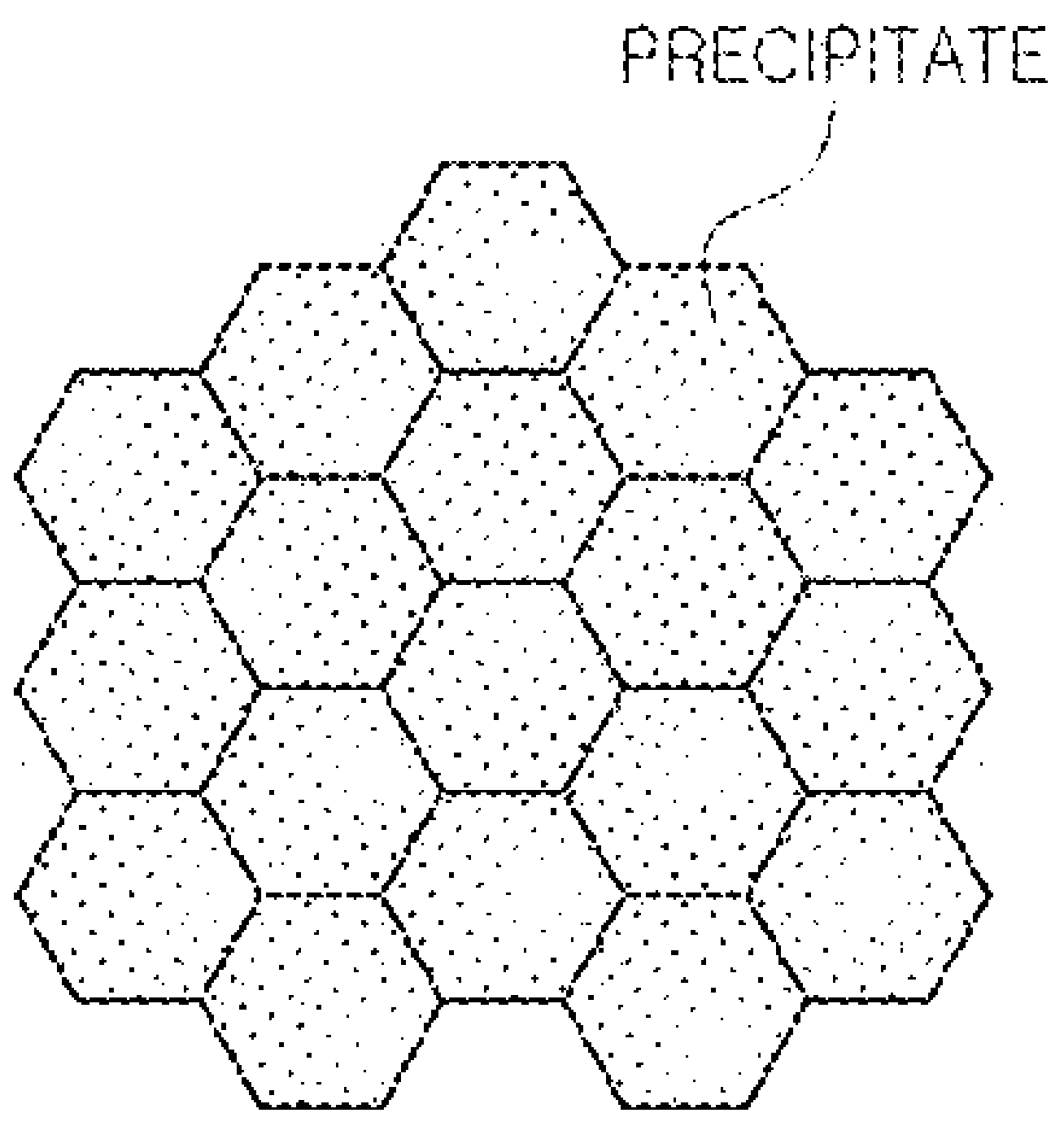

FIG. 1B

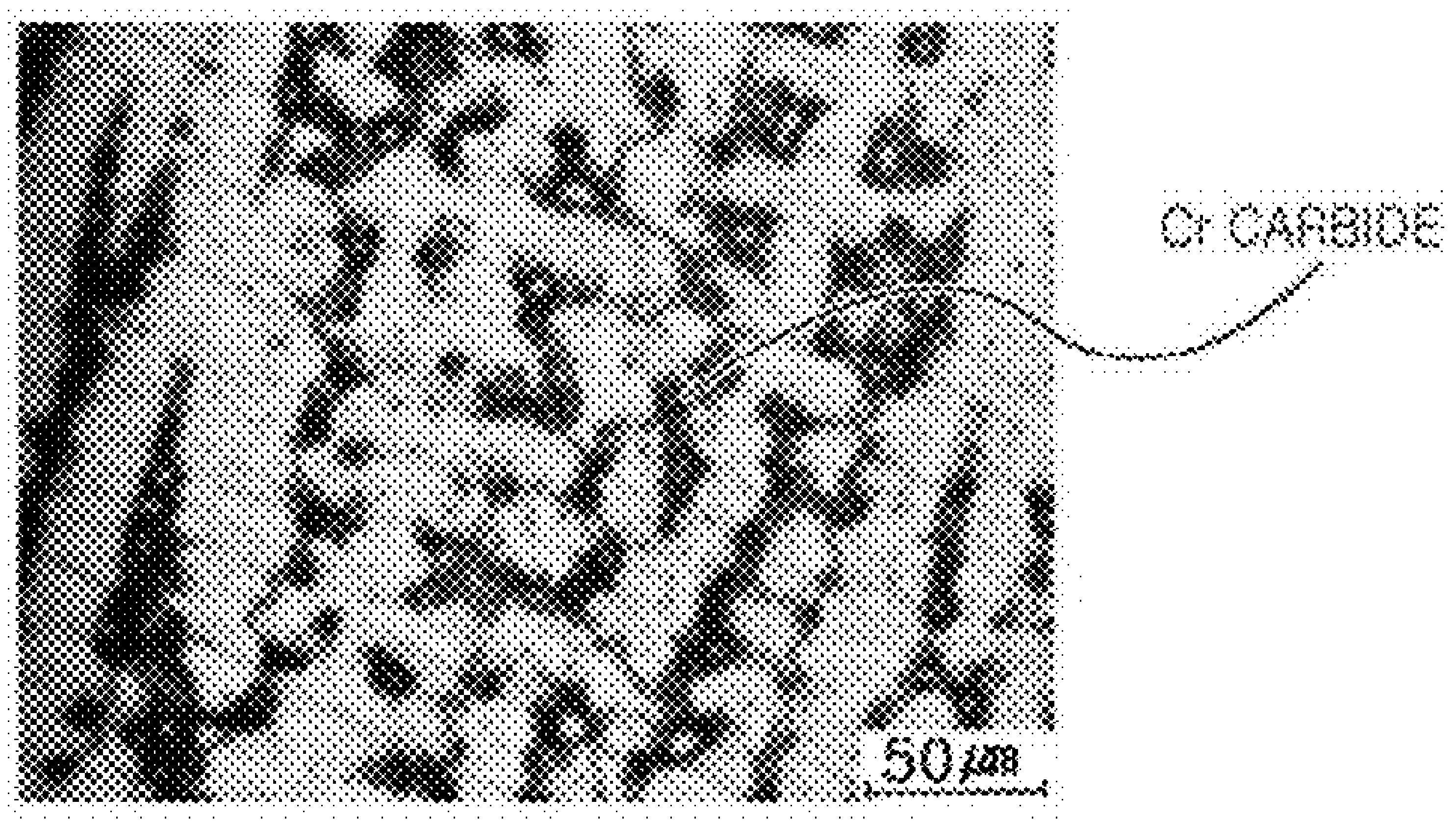

FIG. 2A

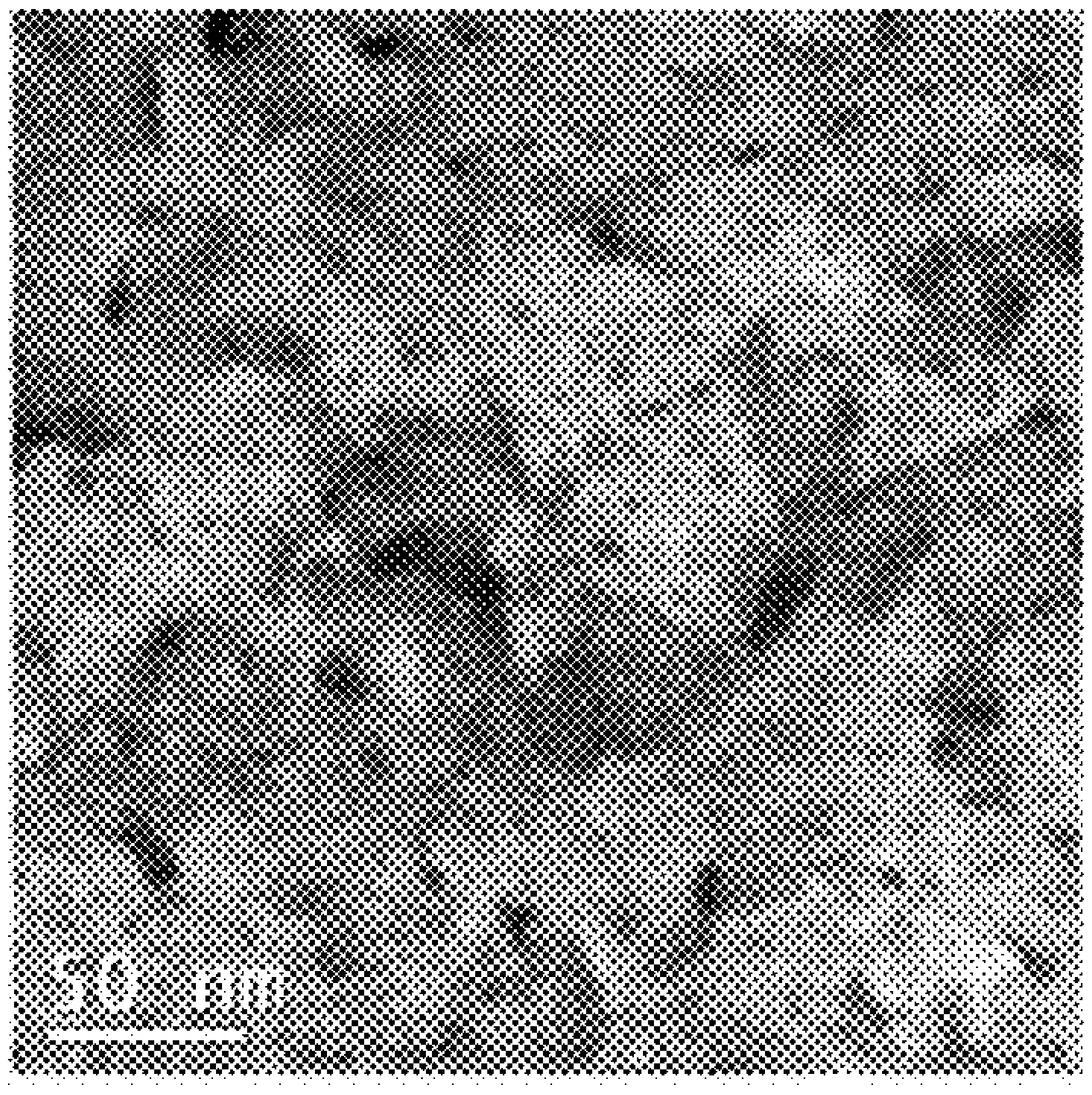

FIG. 2B

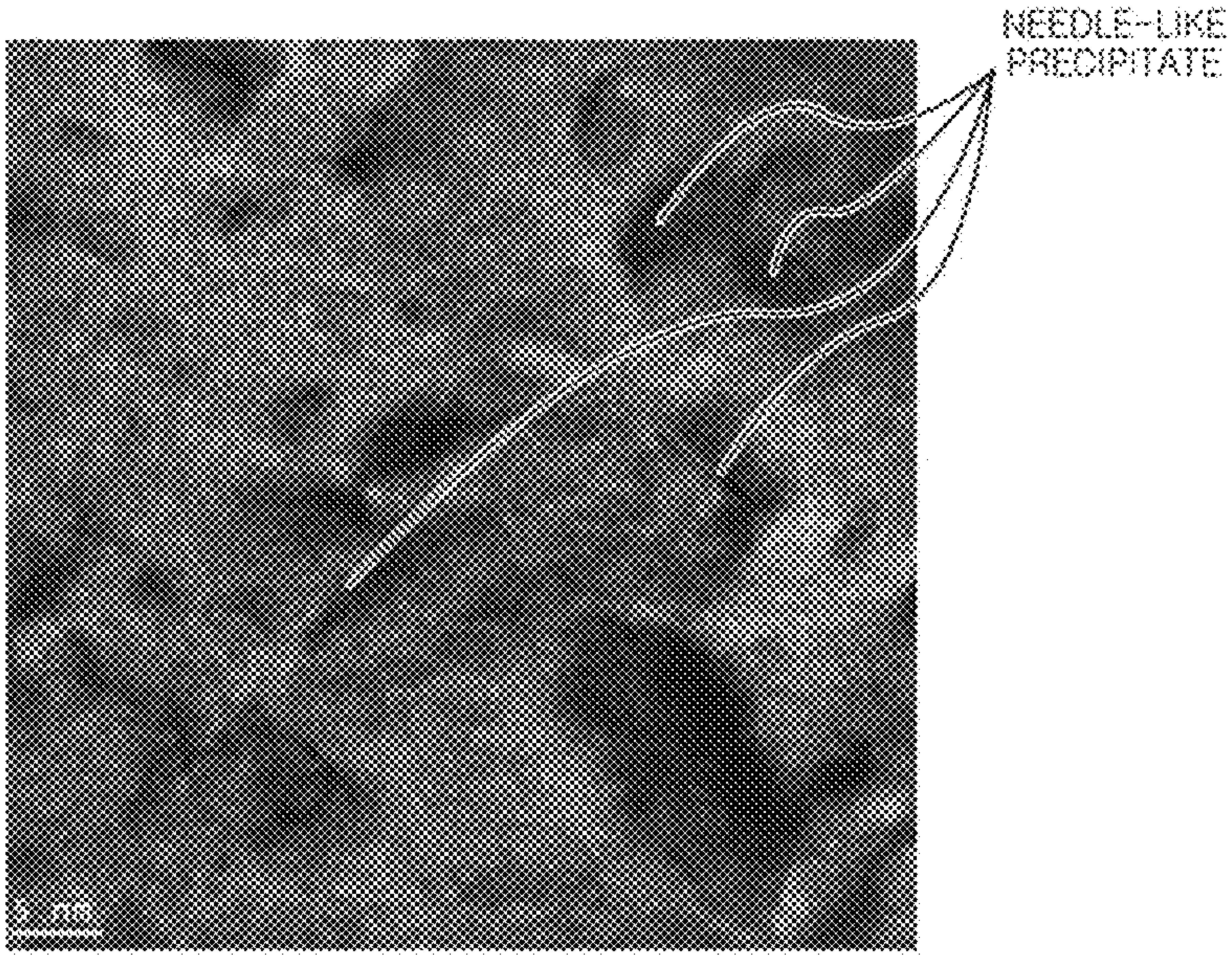

FIG. 3

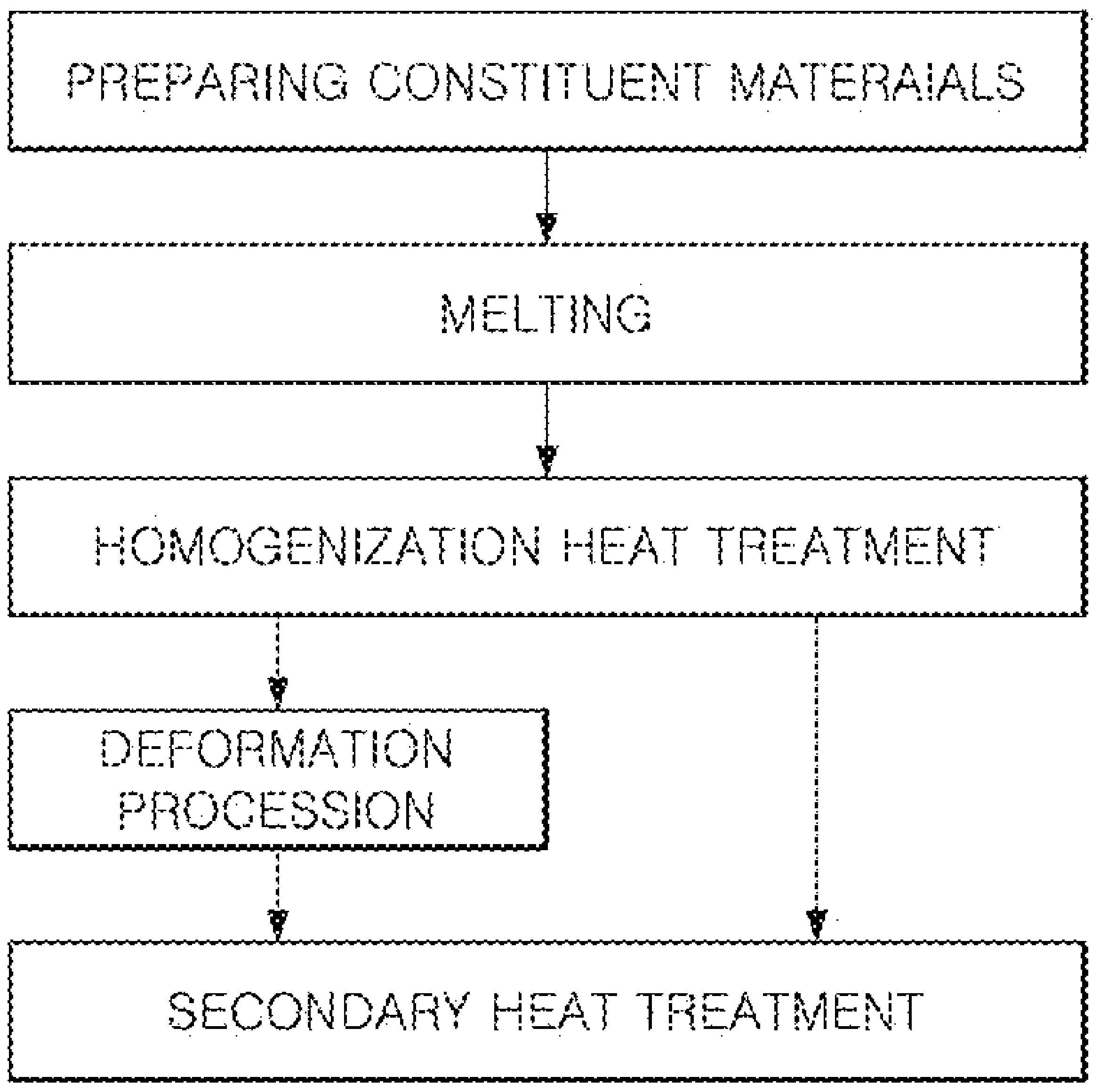
PREPARING CONSTITUENT MATERAIALS
MELTING
HOMOGENIZATION HEAT TREATMENT
DEFORMATION PROCESSION
SECONDARY HEAT TREATMENT

FIG. 4

PRECIPITATION HARDENING HIGH ENTROPY ALLOY AND METHOD OF MANUFACTURING THE SAME

BACKGROUND

1. Field

[0001] The present disclosure relates to a metal alloy, in detail, a high-entropy alloy, used as a component material in a device having electromagnetic, chemical, shipbuilding, mechanical, and other applications, a component material used in extreme environments requiring high strength and good corrosion resistance, and the like.

2. Description of Related Art

[0002] Due to technological breakthroughs in industrial technology, conventional metals and alloys according to the related art have limitations in satisfying performance required for various applications. To satisfy requirements for enhanced properties and multifunctionality, a new type of material referred to as a high-entropy alloy has recently been proposed and developed.

[0003] A high-entropy alloy typically refers to a multi-component single phase alloy formed by the reduction of total free energy of the solid solution single phase due to a significant increase in configuration entropy of the multi-component system, prohibiting the formation of intermetallic compounds. In other words, a high-entropy alloy refers not to an intermetallic compound or an amorphous alloy, but to a stable single phase multi-component alloy.

[0004] A high-entropy alloy is disclosed in Non-Patent Document 1 (Materials Science and Engineering A, Vol. 0.375-377, 2004, page 213-218). In Non-Patent Document 1, a multi-element alloy, $Fe_{20}Cr_{20}Mn_{20}Ni_{20}Co_{20}$, expected to be formed as an amorphous alloy or complex intermetallic compound, is unexpectedly formed as a crystalline face-centered cubic (FCC) solid solution, thereby raising interest. High-entropy alloys have unusual characteristics in which a single phase is formed, even when alloying elements are mixed in similar amounts in a quartenary, quinary, or higher system, as compared to the case in which an alloy according to the related art is formed by adding additional alloying elements to a main alloying element present in an amount of 60 weight % to 90 weight %, the unusual characteristics being found in an alloy system in which a degree of configuration entropy is high due to mixing.

[0005] A high-entropy alloy is an alloy system containing four or more types of metal having an atomic concentration between 5 at % and 35 at %, and in which all alloying elements, having been added, act as a main element. If a high configurational entropy is induced due to a similar atomic fraction of elements in an alloy, a solid solution, which is stable at high temperature, is formed instead of intermetallic compounds.

[0006] As prior art related to high-entropy alloys, there are provided Patent Document 1 (U.S. Laid-Open Patent No. US 2013/0108502 A1) and Patent Document 2 (U.S. Laid-Open Patent No. 2009/0074604 A1). In Patent Document 1, disclosed is a high-entropy alloy having high hardness and elasticity (an elastic modulus), and formed as a single phase solid solution having a face-centered cubic and/or body-centered cubic structure. In addition, the high-entropy alloy is provided as an alloy system containing five or more elements, in which each element such as vanadium (V), niobium (Nb), tantalum (Ta), molybdenum (Mo), titanium (Ti), or the like is included with a deviation of ±15 atomic % or less, as various metals, and in which all elements, having been added, act as a main element. However, in Patent Document 1, different types of relatively expensive and heavy alloying elements are added, so there may be a difficulty in a manufacturing process due to a wide difference of melting points among the alloying elements having been added.

[0007] Meanwhile, in Patent Document 2, disclosed is a high-entropy alloy having a high hardness, manufactured in a powder metallurgy process using a ceramic powders (representatively, a tungsten carbide) and multi-component high-entropy alloy powders. The high-entropy alloy is formed as a single phase solid solution having a face-centered cubic and/or body-centered cubic structure, and thus having excellent mechanical properties. However, in Patent Document 2, since a high temperature process is required when a ceramic material is used to manufacture an alloy, a problem in which limitations on manufacturing are present may occur.

[0008] In recent years, while breaking a method of manufacturing a high-entropy alloy using a solid solution single-phase, there has been growing interest in a high-entropy alloy in which a single phase and a second phase are mixed. In addition, research into strengthening mechanisms such as solid solution strengthening, precipitation strengthening, composite materials, and the like, has been extensively undertaken. In Patent Document 3 (CN Laid-Open Patent No. 104694808 A), a technique is provided in which a $Ni_3(Ti, Al)$ intermetallic compound is dispersed in a high-entropy alloy matrix, so excellent mechanical properties are implemented.

SUMMARY OF THE INVENTION

[0009] An aspect of the present disclosure provides a high-entropy alloy, in detail, a high-entropy alloy with excellent strength and ductility by forming a nanoscale and/or sub-micron precipitate by adding alloying elements with no or limited solubility, nitride or carbide forming elements, or the like, while a matrix maintains high configurational entropy due to formation of the solid solution phase of various major alloying elements comprising the matrix; and a method of manufacturing the same.

[0010] According to an aspect of the present disclosure, a precipitation hardening high-entropy alloy includes:

[0011] four or more selected from the group consisting of more than 5 wt % to 35 wt % or less of iron (Fe), more than 5 wt % to 35 wt % or less of chromium (Cr), more than 5 wt % to 35 wt % or less of nickel (Ni), more than 5 wt % to 35 wt % or less of manganese (Mn), more than 5 wt % to 35 wt % or less of cobalt (Co), more than 5 wt % to 35 wt % or less of copper (Cu);

[0012] one or more of 1) and 2):

[0013] 1) one or more of interstitial atoms such as; 0.01 wt % to 1.5 wt % of carbon (C), 0.01 wt % to 1.5 wt % of nitrogen (N), and 0.01 wt % to 1.5 wt % of boron (B),

[0014] 2) one or more of substitutional atoms such as; 0.01 wt % to 5 wt % of titanium (Ti), 0.01 wt % to 5 wt % of zirconium (Zr), 0.01 wt % to 5 wt % of hafnium (Hf), 0.01 wt % to 5 wt % of molybdenum (Mo), 0.01 wt % to 5 wt % of tungsten (W), 0.01 wt % to 5 wt % of niobium (Nb), 0.01 wt % to 5 wt % of vanadium (V), 0.01 wt % to 5 wt % of tantalum (Ta), 0.01 wt % to 5 wt % of silver (Ag), 0.01 wt % to 5 wt % of silicon (Si), 0.01 wt % to 5 wt % of copper (Cu), and 0.01 wt % to 5 wt % of germanium (Ge); and

[0015] inevitable residual impurities,

wherein the high-entropy alloy is provided with a high entropy matrix in which precipitates are dispersed.

[0016] According to another aspect of the present disclosure, a method of manufacturing a precipitation hardening high-entropy alloy includes: preparing a metal including

[0017] four or more selected from the group consisting of more than 5 wt % to 35 wt % or less of Fe, more than 5 wt % to 35 wt % or less of Cr, more than 5 wt % to 35 wt % or less of Ni, more than 5 wt % to 35 wt % or less of Mn, more than 5 wt % to 35 wt % or less of Co, and more than 5 wt % to 35 wt % or less of Cu, and

[0018] one or more of 1) and 2):

[0019] 1) one or more of interstitial atoms such as; 0.01 wt % to 1.5 wt % of carbon (C), 0.01 wt % to 1.5 wt % of nitrogen (N), and 0.01 wt % to 1.5 wt % of boron (B),

[0020] 2) one or more of substitutional atoms such as; 0.01 wt % to 5 wt % of Ti, 0.01 wt % to 3 wt % of Zr, 0.01 wt % to 5 wt % of Hf, 0.01 wt % to 5 wt % of Mo, 0.01 wt % to 5 wt % of W, 0.01 wt % to 5 wt % of Nb, 0.01 wt % to 5 wt % of V, 0.01 wt % to 5 wt % of Ta, 0.01 wt % to 5 wt % of Ag, 0.01 wt % to 5 wt % of Si, 0.01 wt % to 5 wt % of Cu, and 0.01 wt % to 5 wt % of Ge, and

[0021] inevitable residual impurities; manufacturing an alloy by melting the constituent metals, having been prepared; homogenization heat treating the alloy, having been manufactured, at a temperature within a range of 600° C. to 1200° C.; cooling the alloy after the homogenization heat treating; and secondary heat treating the alloy by maintaining the alloy at a temperature within a range of 350° C. to 1000° C. for a certain period of time after cooling and cooling the alloy.

BRIEF DESCRIPTION OF DRAWINGS

[0022] The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawings will be provided by the Office upon request and payment of the necessary fee.

[0023] The above and other aspects, features, and advantages of the present disclosure will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

[0024] FIGS. **1**A and **1**B are schematic diagrams illustrating a microstructure of a high-entropy alloy according to the present disclosure, FIG. **1**A illustrates a microstructure before secondary heat treatment, and FIG. **1**B illustrates a microstructure after secondary heat treatment;

[0025] FIGS. **2**A and **2**B are electron micrographs illustrating a microstructure according to Inventive Example 7 of Example of the present disclosure, FIG. **2**A illustrates in color a microstructure before secondary heat treatment, and FIG. **2**B illustrates a microstructure after secondary heat treatment;

[0026] FIG. **3** is an image of a microstructure according to Inventive Example 2 of Example of the present disclosure; and

[0027] FIG. **4** is a flowchart illustrating an example of a manufacturing method according to the present disclosure.

DETAILED DESCRIPTION

[0028] The inventors of the present disclosure conducted research into a method for improving mechanical/physical properties such as strength, ductility, and the like of a high-entropy alloy. As a result, unlike the case in which various alloying elements form a single-phase solid solution, it can be confirmed that when nanoscale and/or sub-micron precipitates are formed in a high-entropy alloy matrix, high ductility and high strength characteristics can be secured at the same time. In detail, a non-metallic alloying element, such as carbon (C), nitrogen (N), boron (B), or the like is added to a high-entropy alloy over a solubility limit to precipitate a carbonitride, a nitride, a boride, or the like. Alternatively, a metallic element, such as titanium (Ti), zirconium (Zr), molybdenum (Mo), tungsten (W), silver (Ag), silicon (Si), copper (Cu), niobium (Nb), hafnium (Hf), vanadium (V), tantalum (Ta), germanium (Ge), or the like is added thereto to form precipitates. Thus, it can be confirmed that a high-entropy alloy with excellent strength and ductility is provided, leading to the present disclosure.

[0029] Hereinafter, a high-entropy alloy according to the present disclosure will be described in detail. First, a composition of a high-entropy alloy according to the present disclosure will be described in detail.

[0030] A high-entropy alloy according to the present disclosure includes

[0031] four or more selected from the group consisting of more than 5 wt % to 35 wt % or less of iron (Fe), more than 5 wt % to 35 wt % or less of chromium (Cr), more than 5 wt % to 35 wt % or less of Nickel (Ni), more than 5 wt % to 35 wt % or less of manganese (Mn), more than 5 wt % to 35 wt % or less of cobalt (Co), and more than 5 wt % to 35 wt % or less of copper (Cu),

[0032] one or more of 1) and 2):

[0033] 1) one or more of interstitial atoms such as; 0.01 wt % to 1.5 wt % of C, 0.01 wt % to 1.5 wt % of N, and 0.01 at % to 1.5 wt % of B

[0034] 2) one or more of substitutional atoms such as; 0.01 wt % to 5 wt % of Ti, 0.01 wt % to 3 wt % of Zr, 0.01 wt % to 5 wt % of Hf, 0.01 wt % to 5 wt % of Mo, 0.01 wt % to 5 wt % of W, 0.01 wt % to 5 wt % of Nb, 0.01 wt % to 5 wt % of V, 0.01 wt % to 5 wt % of Ta, 0.01 wt % to 5 wt % of Ag, 0.01 wt % to 5 wt % of Si, 0.01 wt % to 5 wt % of Cu, and 0.01 wt % to 5 wt % of Ge, and inevitable residual impurities.

[0035] Each of Fe, Cr, Ni, Mn, Co, and Cu, an element forming a high-entropy alloy matrix, is a fourth period transition element, and the difference in the atomic radius is small, thereby favoring the formation of a solid solution, or the like. Each of Mn and Ni is an element promoting formation of a face-centered cubic (FCC) solid solution, Co promotes refinement of a structure, Cr improves corrosion resistance, and Fe is an element promoting formation of a face-centered cubic (FCC) structure at intermediate temperatures and improves the strength. Here, the content of the elements is more than 5% to 35% or less, for the reason to induce the increase of configurational entropy as much as possible in a uniform mixture, while not being outside of a range of entropy, for formation of a solid solution.

[0036] Meanwhile, C, B, and N are combined with Ti, Zr, Mo, W, Nb, V, Ta, Mn, Cr, or the like, in a high-entropy alloy to form a carbide, a nitride, a boride, or the like, and are precipitated in a matrix of a high-entropy alloy matrix, so the matrix may be strengthened and work hardenability may be improved. Here, the content of each of C, N, and B is 0.01 wt % to 1.5 wt %. If the content of the element is insignificant, such as an amount of less than 0.01 wt %, precipitation hardenability may be insignificant. If the content of the element exceeds 1.5 wt %, work hardenability may be reduced, so brittleness may occur.

[0037] In the case of Ti, Zr, Mo, W, Ag, Si, Cu, Nb, Hf, V, Ta, and Ge, a difference in the atomic radius from Fe, Cr, Ni, Mn, Co, and Cu, which are main elements forming a matrix of a high-entropy alloy, is large, and a difference in the valency therefrom is also large. Thus, as solubility in a matrix of a high-entropy alloy is small, precipitation is favored, so the matrix may be strengthened by precipitation hardening. Thereamong, in the case in which Ti, Zr, Mo, W, Nb, V, Ta, or the like is added with C, N, B, or the like, at the same time, a carbide, a nitride, or a boride may also be formed, so the matrix may be strengthened. In the case in which one thereamong is added alone, elemental precipitates or intermetallic compounds are formed, so the matrix may be strengthened. Here, the content of each of Ti, Zr, Mo, W, Ag, Si, Cu, Hf, Nb, V, Ta, and Ge is 0.01 wt % to 5 wt %. If the content thereof is less than 0.01 wt %, precipitation hardening effect is insignificant. If the content thereof exceeds 5 wt %, the volume fraction and the size of precipitates exceed the limits, so work hardenability may be reduced and brittleness may be caused.

[0038] In the case of Ag, Si, Cu, Ge, and Hf, a difference in an atomic radius from that of Fe, Cr, Ni, Mn, Co, and Cu, which are main elements forming a matrix of a high-entropy alloy, is large, and a difference in a valency, or the like therefrom is also large. Thus, solubility in a high-entropy alloy matrix is low, precipitation occurs, so a matrix may be strengthened. Here, the content of each of Ag, Si, Cu, Ge, and Hf is 0.01 wt % to 5 wt %. If the content thereof is lower than 0.01 wt %, an amount of a precipitation is insignificant. If the content thereof exceeds 5 wt %, the volume fraction and the size of precipitates exceed the limits, so work hardenability may be reduced and brittleness may be caused.

[0039] Hereinafter, a microstructure of a high-entropy alloy according to the present disclosure will be described in detail. FIGS. **1**A and **1**B are schematic diagrams illustrating a microstructure of a high-entropy alloy. FIG. **1**A illustrates a schematic microstructure (with coarse second phase particles) in which some elements, not dissolved but separated from the matrix, are segregated as coarse particles in the matrix or at grain boundaries, before secondary heat treatment, in a process in which a high-entropy alloy according to the present disclosure is manufactured. FIG. **1**B illustrates a schematic microstructure of precipitation hardened high-entropy alloy according to the present disclosure in which a precipitate is uniformly dispersed throughout a matrix, as the form illustrated in FIG. **1**A processed by secondary heat treatment.

[0040] The precipitate may be carbides, nitrides, borides, or the like, as Ti, Zr, Mo, W, Nb, V, Ta, or the like is combined with C, N, or B, interstitial alloying elements. Alternatively, in the case in which one or more substitutional elements are added, without adding C, N, or B, the precipitates may be of the type that include one or more of Ti, Zr, Mo, W, Nb, V, Ta, Hf, Ag, Si, Cu, or Ge, and intermetallic compounds thereof. In a precipitate hardened high-entropy alloy according to the present disclosure, nanoscale and sub-micron precipitates described above are precipitated in the matrix with high configurational entropy, so that excellent strength and ductility may be secured.

[0041] The precipitates in a high entropy alloy matrix block dislocation movement or prevent annihilation of dislocations, so the density of dislocation is increased, thereby enhancing the work hardening rate and strength. It is preferable that the size of the precipitate has a diameter (or a length) of 0.5 nm to 50 nm and the spacing between precipitates is 1 nm to 500 nm.

[0042] Hereinafter, a method of manufacturing a precipitation hardening high-entropy alloy according to the present disclosure will be described in detail. FIG. **4** illustrates a schematic sequence of a manufacturing method according to the present disclosure. Hereinafter, the manufacturing method according to the present disclosure will be described with reference to FIG. **4**.

[0043] To manufacture a high-entropy alloy according to the present disclosure, constituent materials are prepared, including four or more selected from the group consisting of more than 5 wt % to 35 wt % or less of Fe, more than 5 wt % to 35 wt % or less of Cr, more than 5 wt % to 35 wt % or less of Ni, more than 5 wt % to 35 wt % or less of Mn, more than 5 wt % to 35 wt % or less of Co, and more than 5 wt % to 35 wt % or less of Cu,

[0044] 1) one or more of 0.01 wt % to 1.5 wt % of C, 0.01 wt % to 1.5 wt % of N, and 0.01 at % to 1.5 wt % of B,

[0045] 2) one or more of 0.01 wt % to 5 wt % of Ti, 0.01 wt % to 3 wt % of Zr, 0.01 wt % to 5 wt % of Hf, 0.01 wt % to 5 wt % of Mo, 0.01 wt % to 5 wt % of W, 0.01 wt % to 5 wt % of Nb, 0.01 wt % to 5 wt % of V, 0.01 wt % to 5 wt % of Ta, 0.01 wt % to 5 wt % of Ag, 0.01 wt % to 5 wt % of Si, 0.01 wt % to 5 wt % of Cu, and 0.01 wt % to 5 wt % of Ge, and inevitable residual impurities. Thereafter, melting, homogenization heat treatment, cooling, deformation processing and solution treatment if necessary, and secondary heat treatment are performed to manufacture the precipitation hardening high-entropy alloy.

[0046] The melting is provided to allow the metal, having been manufactured, to be alloyed, a method thereof is not particularly limited, and a method commonly performed in a technical field of the present disclosure is used. For example, the alloy is manufactured through casting, arc melting, powder metallurgy, or the like.

[0047] Next, the alloy, having been manufactured, is homogenization heat treated. In a high-entropy alloy, various elements are mixed, so homogenization heat treating is performed to induce sufficient diffusion. It is preferable to perform the homogenization heat treating at a temperature within a range of 600° C. to 1200° C. for 1 hour to 48 hours.

[0048] After the homogenization heat treating, cooling is performed. A method of the cooling is not particularly limited, and a method, such as water cooling, oil cooling, air cooling, or the like, may be performed. Through the homogenization and cooling, some microstructural inhomogeniety are removed.

[0049] In order to develop a microstructure in which nanoscale and sub-micron precipitates are present in a matrix, a single-phase solid solution, by forming the precipitate in the matrix after the cooling, secondary heat treatment is performed. The secondary heat treatment includes the solution treatment and aging treatment. The solution treatment is performed to allow an alloy to dissolve coarse second phase particles and form the microstructure with no or minimal second phase particles above a solubility limit temperature (typically >700° C.) and then is cooled. In this case, the cooling may be performed in a method such as water cooling, oil cooling, air cooling, furnace cooling, or the like.

[0050] The aging treatment is performed to allow an alloy to induce precipitation of nanoscale and sub-micron second phase particles below a solubility limit temperature (typically <800° C.) by making some supersaturated alloying elements in a thermodynamically unstable or metastable state and then is cooled and nanoscale and sub-micron second phase particles are uniformly precipitated in a matrix. The alloy is maintained at a temperature within a range of 300° C. to 800° C. for 0.5 hour to 72 hours, and then is cooled. In this case, the cooling may be performed in a method such as water cooling, oil cooling, air cooling, furnace cooling, or the like, as described above.

[0051] Hereinafter, Examples according to the present disclosure will be described in detail. The Examples are for the purpose of understanding the present disclosure and are not intended to limit the present disclosure.

Example

[0052] First, as illustrated in Table 1, a high-entropy alloy according to Comparative Examples 1 through 3 and Inventive Examples 1 through 13 is manufactured.

[0053] Pieces of constituent pure metals weighted to attain a composition (wt %) of Table 1 were prepared, and the mixed pieces were arc melted in a vacuum atmosphere to manufacture an alloy. Hereinafter, homogenization heat treating was performed at 1050° C. for 24 hours, and rapid cooling was performed.

[0054] The alloy, having been cooled after the homogenization heat treating, is rolled downed to the thickness of 1 mm, heat treated at 430° C. for 10 hours, so a precipitate was formed.

[0055] Meanwhile, regarding the high-entropy alloy having been manufactured as described above, a sheet having a thickness of 1 mm was tensile-tested, and mechanical properties were evaluated, which are illustrated in Table 1.

TABLE 1

Division	Alloy	Precipitate form	Tensile strength (MPa)	Yield strength (MPa)	Elongation (%)
Comparative Example 1	$Co_{20}Cr_{20}Fe_{20}Mn_{20}Ni_{20}$	—	620	480	40
Comparative Example 2	$Fe_{25}Ni_{25}Co_{25}Cr_{25}$	—	1000	870	35
Comparative Example 3	$Fe_{20}Mn_{20}Ni_{20}Co_{20}Cr_{20}$	—	760	640	15
Inventive Example 1	$Fe_{20}Cr_{20}Ni_{20}Mn_{19.2}Cu_{20}Si_{0.8}$	Precipitate (Si)	1300	1050	25
Inventive Example 2	$Fe_{20}Cr_{20}Ni_{20}Co_{20}Mn_{18}Nb_{2.0}$	Precipitate (Nb)	1320	1120	20
Inventive Example 3	$Fe_{20}Cr_{20}Ni_{20}Mn_{18}Cu_{20}Ag_{2.0}$	Precipitate (Ag)	1390	1180	22
Inventive Example 4	$Fe_{20}Cr_{19.2}Ni_{20}Co_{20}Cu_{20}Ti_{0.8}$	Precipitate (Ti)	1230	1010	23
Inventive Example 5	$Fe_{20}Cr_{20}Ni_{20}Mn_{19.2}Cu_{20}Mo_{0.8}$	Precipitate (Mo)	1320	1140	20
Inventive Example 6	$Fe_{20}Cr_{20}Ni_{20}Co_{20}Mn_{19.2}Ta_{0.8}$	Precipitate (Ta)	1250	1080	22
Inventive Example 7	$Fe_{20}Cr_{20}Ni_{20}Co_{20}Mn_{19.8}C_{0.2}$	Carbide (M_xC)	1330	1190	20
Inventive Example 8	$Fe_{20}Cr_{20}Ni_{20}Co_{20}Mn_{19.6}V_{0.2}C_{0.2}$	Carbide (M_xC)	1460	970	30
Inventive Example 9	$Fe_{20}Cr_{20}Ni_{20}Mn_{19.6}Cu_{20}Ti_{0.2}C_{0.2}$	Carbide (M_xC)	1490	990	28
Inventive Example 10	$Fe_{20}Cr_{19.8}Ni_{20}Co_{20}Mn_{20}N_{0.2}$	Nitride (M_xN)	1410	920	31
Inventive Example 11	$Fe_{20}Cr_{20}Ni_{20}Mn_{19.8}Cu_{20}N_{0.2}$	Nitride (M_xN)	1390	925	35
Inventive Example 12	$Fe_{20}Cr_{20}Ni_{20}Co_{20}Mn_{18.6}N_{0.2}C_{0.2}$	Carbonitride ($M_x(C, N)$)	1180	920	26
Inventive Example 13	$Fe_{20}Cr_{20}Ni_{20}Mn_{19.6}Cu_{20}Si_{0.2}B_{0.2}$	Precipitate (Si)	1350	940	24

[0056] As illustrated in Table 1, in the case of Inventive Examples 1 through 6 satisfying a composition according to the present disclosure and forming various alloying precipitates in a matrix, Inventive Examples 7 through 12 satisfying the composition and forming a carbide (M_xC, M=Ti, Zr, Mo, W, Nb, V, or Ta), a nitride (M_xN, M=Ti, Zr, Mo, W, Nb, V, or Ta), a carbonitride (M_xC,N, M=Ti, Zr, Mo, W, Nb, V, or Ta), or a boride (MB_x, M=Ti, Zr, Mo, W, Nb, V, or Ta), and Inventive Example 13 satisfying the composition and forming an alloying precipitate by adding an interstitial alloying element B, it is confirmed that excellent strength and ductility are secured in balance, compared to Comparative Example. In detail, in the case of Comparative Examples 1 through 3, precipitates are not particularly observed. However, in the case of Inventive Example according to the present disclosure, it is confirmed that needle-like, spherical, and various shaped precipitates are formed and excellent strength and ductility are secured.

[0057] Meanwhile, FIGS. **2**A and **2**B are images of a microstructure of Inventive Example 7. In FIG. **2**A, it is confirmed that coarse Cr carbides are formed in the matrix before secondary heat treatment. In FIG. **2**B, it is confirmed that nanoscale spherical carbides are formed after secondary heat treating, the spherical carbides block dislocation movement, so an alloy may be strengthened.

[0058] FIG. **3** is an image of a microstructure of Inventive Example 2. It is confirmed that a needle-like precipitate formed after secondary heat treatment are uniformly dispersed, the precipitates block dislocation movement in a matrix, so the matrix may be strengthened.

[0059] As set forth above, according to an exemplary embodiment, a matrix, as well as nanoscale nitride, carbide, or boride precipitates are formed in a high-entropy alloy matrix, so excellent strength and ductility may be implemented. Therethrough, a high-entropy alloy may be widely used.

[0060] While exemplary embodiments have been shown and described above, it will be apparent to those skilled in the art that modifications and variations could be made without departing from the scope of the present invention as defined by the appended claims.

What is claimed is:

1. Precipitation hardening high-entropy alloy, the high-entropy alloy comprising:

four or more elements selected from the group consisting of more than 5 wt % to 35 wt % or less of iron (Fe), more than 5 wt % to 35 wt % or less of chromium (Cr), more than 5 wt % to 35 wt % or less of nickel (Ni), more than 5 wt % to 35 wt % or less of manganese (Mn), more than 5 wt % to 35 wt % or less of cobalt (Co), more than 5 wt % to 35 wt % or less of copper (Cu);

one or more elements of 1) and 2):

1) one or more of 0.01 wt % to 1.5 wt % of C, 0.01 wt % to 1.5 wt % of N, and 0.01 at % to 1.5 wt % of B,

2) one or more of 0.01 wt % to 5 wt % of Ti, 0.01 wt % to 3 wt % of Zr, 0.01 wt % to 5 wt % of Hf, 0.01 wt % to 5 wt % of Mo, 0.01 wt % to 5 wt % of W, 0.01 wt % to 5 wt % of Nb, 0.01 wt % to 5 wt % of V, 0.01 wt % to 5 wt % of Ta, 0.01 wt % to 5 wt % of Ag, 0.01 wt % to 5 wt % of Si, 0.01 wt % to 5 wt % of Cu, and 0.01 wt % to 5 wt % of Ge, and inevitable residual impurities;

wherein the high-entropy alloy is provided with a matrix in which precipitates are dispersed.

2. The precipitation hardening high-entropy alloy of claim **1**, wherein the precipitate is one or more of 1) and 2):

1) one or more of carbides (M_xC), nitrides (M_xN), carbonitrides (M_xC,N), and borides (MBx); and

2) one or more of precipitates that include one or more of Ti, Zr, Hf, Mo, W, Nb, V, Ta, Ag, Si, Cu, or Ge, and intermetallic compounds thereof.

3. The precipitation hardening high-entropy alloy of claim **1**, wherein the precipitate has the diameter of 0.5 nm to 50 nm, and the spacing between dispersed precipitates is 1 nm to 500 nm.

4. A method of manufacturing a precipitation hardening high-entropy alloy, comprising the following steps:

(a) preparing constituent materials including

four or more elements selected from the group consisting of more than 5 wt % to 35 wt % or less of Fe, more than 5 wt % to 35 wt % or less of Cr, more than 5 wt % to 35 wt % or less of Ni, more than 5 wt % to 35 wt % or less of Mn, more than 5 wt % to 35 wt % or less of Co, and more than 5 wt % to 35 wt % or less of Cu,

one or more elements of 1) and 2):

1) one or more of 0.01 wt % to 1.5 wt % of C, 0.01 wt % to 1.5 wt % of N, and 0.01 at % to 1.5 wt % of B,

2) one or more of 0.01 wt % to 5 wt % of Ti, 0.01 wt % to 3 wt % of Zr, 0.01 wt % to 5 wt % of Hf, 0.01 wt % to 5 wt % of Mo, 0.01 wt % to 5 wt % of W, 0.01 wt % to 5 wt % of Nb, 0.01 wt % to 5 wt % of V, 0.01 wt % to 5 wt % of Ta, 0.01 wt % to 5 wt % of Ag, 0.01 wt % to 5 wt % of Si, 0.01 wt % to 5 wt % of Cu, and 0.01 wt % to 5 wt % of Ge, and inevitable residual impurities;

(b) manufacturing an alloy by melting the constituent materials of step (a), having been prepared, using casting, arc melting, or powder metallurgy;

(c) homogenization heat treating the alloy, having been manufactured, at a temperature within a range of 600° C. to 1200° C.;

(d) cooling the alloy after the homogenization heat treating; and

(e) secondary heat treating the alloy by maintaining the alloy at a temperature within a range of 300° C. to 800° C. for a certain period of time after cooling step (d) and subsequently cooling the alloy.

5. The method of claim **4**, wherein the homogenization heat treating step (c) is performed for 1 hour to 48 hours.

6. The method of claim **4**, wherein the secondary heat treating step (e) is performed by maintaining the alloy at for 0.5 hour to 72 hours at temperature and cooling the alloy.

7. The method of claim **4**, wherein the secondary heating treating of step (e) is performed by maintaining the alloy at a temperature within a range of 300° C. to 800° C. with a solution treatment above 700° C.

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