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(54) **CR FILAMENT-REINFORCED
CRMNFENICU(AG)-BASED HIGH-ENTROPY
ALLOY AND METHOD FOR
MANUFACTURING THE SAME**

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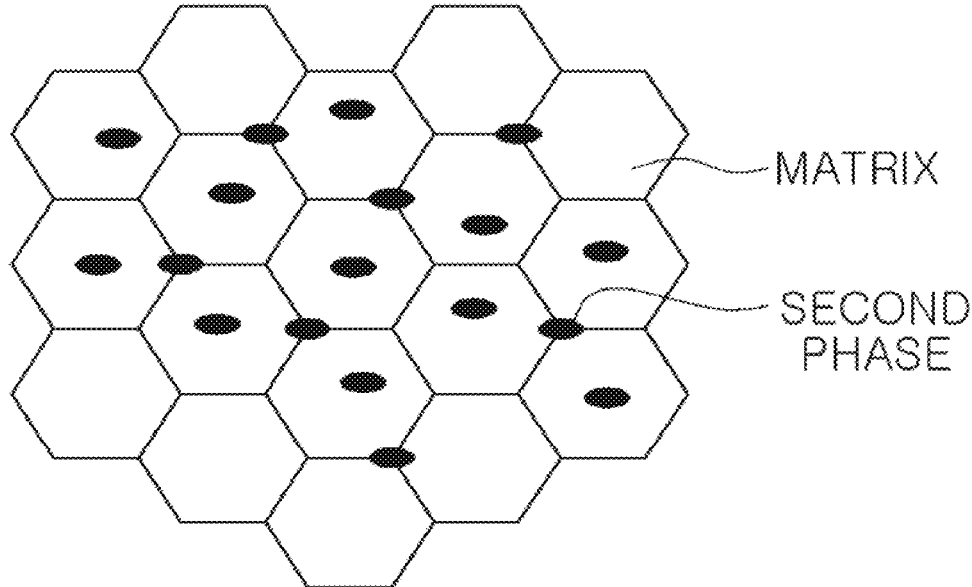
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ABSTRACT

A Cr filament-reinforced CrMnFeNiCu(Ag)-based high-entropy alloy and a method for manufacturing the same are provided. The high-entropy alloy, according to an exemplary embodiment in the present disclosure, includes, by at. %, Cr in an amount greater than 5% and less than 42%, Mn in an amount greater than 5% and less than 35%, Fe in an amount greater than 5% and less than 35%, Ni in an amount greater than 5% and less than 35%, and at least one of Cu in an amount greater than 3% and less than 35%, and Ag in an amount greater than 3% and less than 35%, and residual inevitable impurities. The high-entropy alloy has a dual phase in which a Cr or a Cr-rich phase is distributed within a matrix of the high-entropy alloy in filament or ribbon form.

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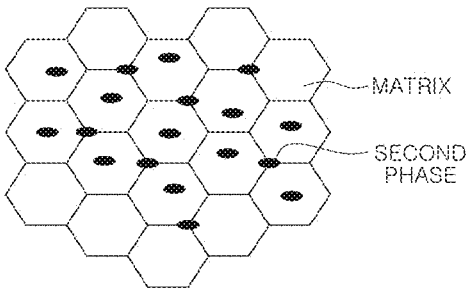


FIG. 1A

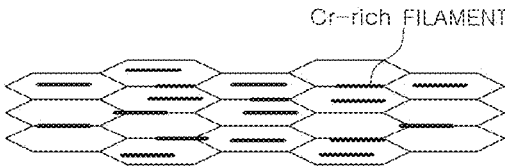


FIG. 1B

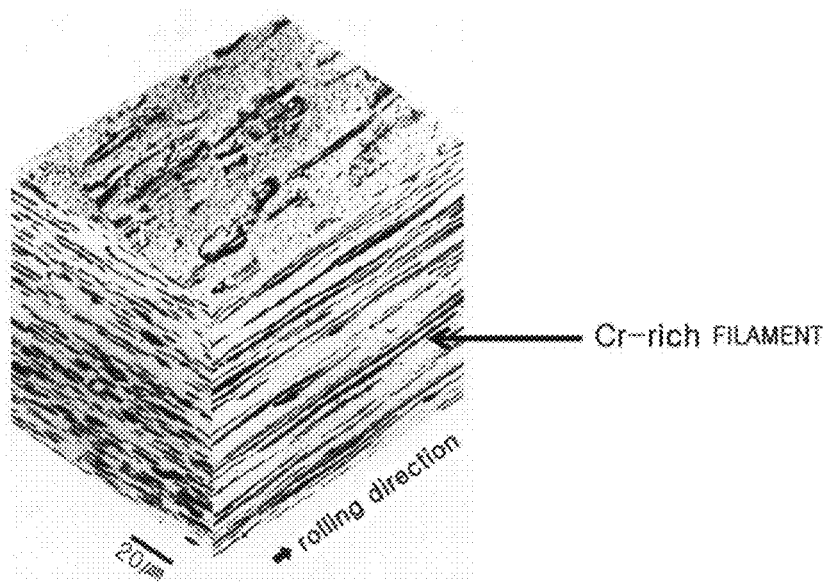


FIG. 2

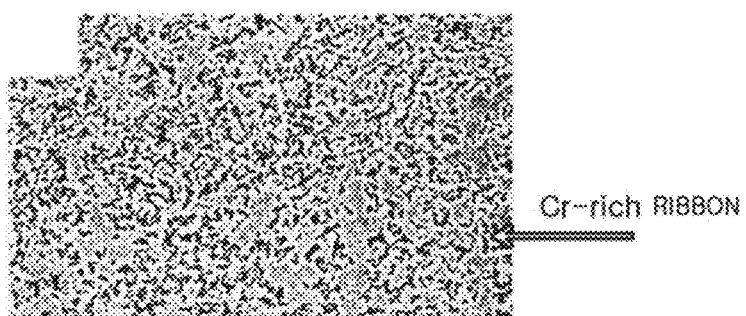


FIG. 3A

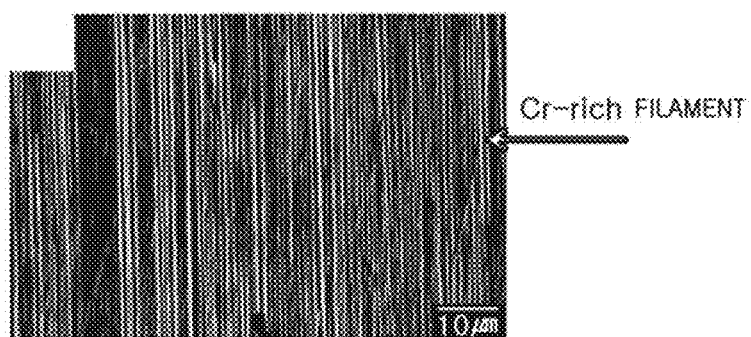


FIG. 3B

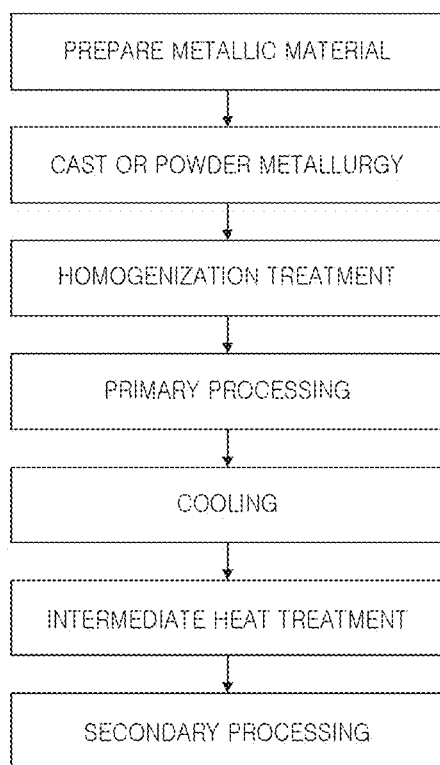


FIG. 4

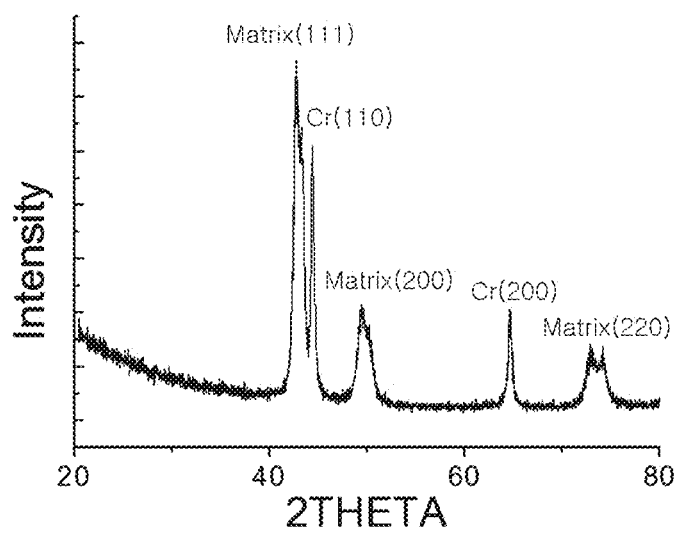


FIG. 5

**CR FILAMENT-REINFORCED
CRMNFENICU(AG)-BASED HIGH-ENTROPY
ALLOY AND METHOD FOR
MANUFACTURING THE SAME**

**CROSS-REFERENCE TO RELATED
APPLICATION**

[0001] This application claims priority to Korean Patent Application No. 10-2017-0089095 filed Jul. 13, 2017, the disclosure of which is hereby incorporated in its entirety by reference.

BACKGROUND

[0002] The present disclosure relates to a method for manufacturing a CrMnFeNiCu-, CrMnFeNiAg-, or CrMnFeNiCuAg-based high-entropy alloy that may be used in materials for parts in the electromagnetic, chemical, ship-building, and machinery, and in engineering components and structural materials employed in extreme and harsh environments, and more particularly, to a method for manufacturing a Cr filament-reinforced CrMnFeNiCu(Ag)-based high-entropy alloy that may provide a plate material, a rod material, or a wiring material, which may be a Cr filament-reinforced CrMnFeNiCu-, CrMnFeNiAg-, or CrMnFeNiCuAg-based high-entropy alloy formed of an in-situ composite material.

[0003] High-entropy alloys may be alloys that reduce the overall level of free energy, since increases in the configuration entropy due to mixtures of various elements are greater than decreases in free energy through the formation of intermetallic compounds, and may refer to alloys in which a metallic compound or an amorphous alloy, among multi-alloying elements, is not formed, but in which a solid solution having various alloying elements mixed therein is preferentially formed.

[0004] In a published article, entitled: "Microstructural development in equiatomic multicomponent alloys" by B. Cantor, et al., appearing in *Materials Science & Engineering A*, Vols. 375-377 (2004) pp. 213-218, the disclosed high-entropy alloy is an alloy attracting interest since the alloy, Fe₂₀Cr₂₀Mn₂₀Ni₂₀Co₂₀, manufactured in expectation of formation of an amorphous alloy or a complex intermetallic compound exhibits a crystalline face-centered cubic (FCC) solid solution, contrary to expectations. By comparison with conventional alloys in which other alloying elements are added to primary alloying elements of 60 to 90 at. %, the high-entropy alloy has a specific property that even when alloying elements having a four or five or more element system are mixed at a similar ratio, a single phase is formed, and this is found in alloys having a higher level of configuration entropy due to mixing.

[0005] The high-entropy alloy is an alloying system containing four or more types of metallic elements of 5 to 35 at. %, all of the added alloying elements acting as primary elements, and a high level of mixing entropy may be caused by similar atomic fractions within the alloy. Thus, a solid solution having a stable, simple structure may be formed at high temperatures, in lieu of an intermetallic compound or an intermediate compound.

[0006] US 2013/0108502 A1 discloses a high-entropy alloy that may achieve high levels of hardness and modulus of elasticity and that may consist of a single-phase solid solution having a FCC and/or body-centered cubic (BCC)

structure as an alloying system that contains five or more metallic elements as multiple metallic elements including respective elements of ± 15 at. % or less, such as V, Nb, Ta, Mo, and Ti, and that has all of the added elements acting as primary elements. However, patent document 1, as described above, includes various types of relatively expensive, heavy alloying elements added, and has difficulties in the manufacturing process due to the difference in melting points among the added alloying elements.

[0007] Meanwhile, US 2009/0074604 A1 pertains to a high-entropy alloy that may achieve a high level of hardness and that may be manufactured by a powder metallurgy process using a ceramic phase (typically, tungsten carbide) and a multiple element high-entropy alloy powder, and to a technique for achieving excellent mechanical properties by forming the high-entropy alloy as a single-phase solid solution having a FCC and/or BCC structure reinforced with strong ceramic phase. However, when the alloy is manufactured using a ceramic-based material as in US 2009/0074604 A1, it may be difficult to manufacture the alloy because of the requirement for a high-temperature process.

[0008] In recent years, apart from the manufacturing of a high-entropy alloy using a single-phase solid solution, interest in a high-entropy alloy having a single phase matrix reinforced with a second phase is increasing, and research taking advantage of the various strengthening mechanisms, such as solid solution strengthening, precipitation hardening, and composite strengthening, has been extensively conducted.

SUMMARY

[0009] An aspect of the present disclosure may provide a high-entropy alloy in which a single-phase solid solution matrix and a Cr-rich phase, containing Cr as a main element, may be separately formed in an alloy comprising main elements, such as Cr, Mn, Fe, Ni, and Cu and/or Ag and which may have excellent levels of strength and ductility by distributing the Cr-rich phase within the matrix through solidification and thermo-mechanical processes and developing a filamentary structure through thermos-mechanical and deformation processes, and a method for manufacturing the high-entropy alloy with second phase reinforcement.

[0010] According to an aspect of the present disclosure, a high-entropy alloy includes: by at. %, Cr in an amount greater than 5% and less than 42%, Mn in an amount greater than 5% and less than 35%, Fe in an amount greater than 5% and less than 35%, Ni in an amount greater than 5% and less than 35%, and at least one of Cu in an amount greater than 3% and less than 35%, and Ag in an amount greater than 3% and less than 35%; and residual inevitable impurities, in which the high-entropy alloy has a dual phase in which a Cr or a Cr-rich phase is distributed within a matrix of the high-entropy alloy in filament or ribbon form.

[0011] The high-entropy alloy may further include at least one of, by at. %, Ti in an amount of 0.02 to 5%, Zr in an amount of 0.02 to 5%, Hf in an amount of 0.02 to 5%, Mo in an amount of 0.02 to 5%, W in an amount of 0.02 to 5%, Si in an amount of 0.02 to 5%, Al in an amount of 0.02 to 5%, V in an amount of 0.02 to 5%, and Ta in an amount of 0.02 to 5%, and precipitates may be formed in the matrix.

[0012] The high-entropy alloy having the dual phase may be a plate, rod, or wire product.

[0013] According to an aspect of the present disclosure, a method for manufacturing a high-entropy alloy includes:

preparing a metallic material, the metallic material including, by at. %, Cr in an amount greater than 5% and less than 42%, Mn in an amount greater than 5% and less than 35%, Fe in an amount greater than 5% and less than 35%, Ni in an amount greater than 5% and less than 35%, and at least one of Cu in an amount greater than 3% and less than 35%, and Ag in an amount greater than 3% and less than 35%, and residual inevitable impurities; manufacturing an alloy with the prepared metallic material by melting (casting) or powder metallurgy; carrying out a homogenization heat treatment for the manufactured alloy; primarily processing the homogenization heat treated alloy and then cooling it thus obtained; carrying out an intermediate heat treatment for the cooled alloy at a temperature of 350 to 600° C.; and secondarily processing the intermediate heat treated alloy so as to form a composite structure in which a Cr or a Cr-rich phase is distributed within a matrix of the alloy in filament or ribbon form.

[0014] The metallic material may further include at least one of, by at. %, Ti in an amount of 0.02 to 5%, Zr in an amount of 0.02 to 5%, Hf in an amount of 0.02 to 5%, Mo in an amount of 0.02 to 5%, W in an amount of 0.02 to 5%, Si in an amount of 0.02 to 5%, Al in an amount of 0.02 to 5%, V in an amount of 0.02 to 5%, and Ta in an amount of 0.02 to 5%, and precipitates may be formed in the Cr filament-reinforced matrix through the intermediate heat treatment.

[0015] The method may further include, prior to the homogenization heat treatment of the melted (cast) alloy, rapidly solidifying (quenching) the melted (cast) alloy.

[0016] The homogenization heat treatment may be performed at a temperature within a range of 600 to 1,200° C. for 1 to 48 hours.

[0017] The primary and secondary processing may be at least one of hot working, rolling, extruding, and room-temperature working.

[0018] At least one of the primary and secondary processing may be processing the alloy into one of a plate, a rod, and a wire.

BRIEF DESCRIPTION OF DRAWINGS

[0019] 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:

[0020] FIG. 1A is schematic views illustrating microstructures of a high-entropy alloy before thermo-mechanical processing, and FIG. 1B is schematic views illustrating microstructures of a high-entropy alloy with Cr-rich filaments or second phase after thermo-mechanical processing, according to an exemplary embodiment;

[0021] FIG. 2 is an image obtained by observing microstructures of Inventive Example 1;

[0022] FIGS. 3A and 3B are images obtained by observing microstructures of Inventive Example 8;

[0023] FIG. 4 is a process flowchart illustrating an example of a method for manufacturing a high-entropy alloy, according to an exemplary embodiment; and

[0024] FIG. 5 is an X-ray diffraction (XRD) analysis graph of Inventive Example 1.

DETAILED DESCRIPTION

[0025] Hereinafter, embodiments of the present disclosure will be described with reference to the attached drawings.

[0026] The present disclosure may, however, be exemplified in many different forms and should not be construed as being limited to the specific embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the disclosure to those skilled in the art.

[0027] The terminology used herein describes particular embodiments only, and the present disclosure is not limited thereby. As used herein, the singular forms “a,” “an,” and “the” are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms “comprises,” and/or “comprising” when used in this specification, specify the presence of stated features, integers, steps, operations, members, elements, and/or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps, operations, members, elements, and/or groups thereof.

[0028] Hereinafter, embodiments of the present disclosure will be described with reference to schematic views illustrating embodiments of the present disclosure. In the drawings, for example, due to manufacturing techniques and/or tolerances, modifications of the shape shown may be estimated. Thus, embodiments of the present disclosure should not be construed as being limited to the particular shapes of regions shown herein, for example, to include a change in shape resulting from manufacturing. The following embodiments may also be constituted alone or as a combination of several or all thereof.

[0029] The contents of the present disclosure described below may have a variety of configurations, and only a required configuration is proposed herein, but the present disclosure is not limited thereto. Unless otherwise indicated, elemental contents and ranges thereof are expressed by atomic percentage (“at. %”).

[0030] Hereinafter, exemplary embodiments in the present disclosure will be described.

[0031] The inventors of the present disclosure conducted various research on a method for increasing mechanical or physical properties, such as strength and ductility, of a high-entropy alloy. As a result, when a composition of a portion of various alloying elements is separated or forms other ductile phases, or when segregation or phase separation occurs, instead of various alloying elements forming a solid solution with a single-phase face-centered cubic (FCC) or body-centered cubic (BCC) structure, the inventors have found that both the strength and toughness were increased after the thermo-mechanical processing. Further, the inventors have confirmed that when a second phase (a Cr-rich phase) present in the matrix is refined through powder metallurgy or rapid solidification (quenching) in manufacturing the alloy, and furthermore when a fine filament structure is distributed through processing, a high-entropy alloy, having excellent levels of strength and ductility, may be formed, and have proposed the present disclosure.

[0032] The high-entropy alloy having the composite structure, according to an exemplary embodiment, may include, by at. %, Cr in an amount greater than 5% and less than 42%, Mn in an amount greater than 5% and less than 35%, Fe in an amount greater than 5% and less than 35%, Ni in an amount greater than 5% and less than 35%, and at least one of Cu in an amount greater than 3% and less than 35%, and

Ag in an amount greater than 3% and less than 35%, and residual inevitable impurities. A Cr or a Cr-rich phase may be distributed as filament or ribbon form in a matrix of the high-entropy alloy

[0033] A composition of the high-entropy alloy, according to an exemplary embodiment, will hereinafter be described in detail.

[0034] In an exemplary embodiment, Cr, Mn, Fe, Ni, and at least one of Cu and Ag may be basic elements constituting the high-entropy alloy, may be the transition metal group in period 4, and elements suitable to form a solid solution or the like because of the small difference in atomic radius, or the like.

[0035] Mn and Ni may be elements promoting a solid solution having a FCC structure, Cr may have a BCC structure, when Cu or Ag is added, the Cr-rich phase may be separated, and since the Cr-rich phase is changed into the form of a filament during thermo-mechanical processing, mechanical properties may be increased.

[0036] In an exemplary embodiment, limiting the contents of Cr, Mn, Fe, Ni elements to, by at. %, greater than 5%, and 35% or less, respectively, is to induce changes in partial entropy in equivalent composition that may significantly increase entropy as far as possible, but to prevent the contents from being beyond an entropy range for forming the solid solution.

[0037] In addition, Cu may be an element inducing separation of the Cr-rich phase in the matrix, which may increase ductility, and subsequent to thermo-mechanical processing, the Cr-rich phase may be elongated so as to form a filament, thus increasing strength. For example, the separated Fe—Mn—Ni—Cu (Ag) phase may have a FCC structure, the separated Cr-rich phase may have a BCC structure, and different slip systems of the two phases may cause the Cr-rich phase to be extremely twisted during thermo-mechanical processing, so as to form a filament having a ribbon shape, thus reinforcing the matrix.

[0038] In an exemplary embodiment, the reason for limiting the content of Cu to greater than 3%, and 35% or less, is to induce changes in strength and ductility according to fractions of the separated phase, thus leading to increases in ductility and strength due to the effect of adding an alloying element.

[0039] In addition, the reason for limiting the content of Ag to greater than 3%, and less than 35%, is to reinforcing the matrix without forming a complete solid solution with Fe, Mn, and Ni. This may increase ductility, may allow an Ag-rich phase to be elongated after thermo-mechanical processing, so as to form a filament, thus increasing strength.

[0040] The high-entropy alloy, according to an exemplary embodiment, may further include at least one of Ti in an amount of 0.02 to 5%, Zr in an amount of 0.02 to 5%, Hf in an amount of 0.02 to 5%, Mo in an amount of 0.02 to 5%, W in an amount of 0.02 to 5%, Si in an amount of 0.02 to 5%, Al in an amount of 0.02 to 5%, V in an amount of 0.02 to 5%, and Ta in an amount of 0.02 to 5%. With the addition of these constituent elements, precipitates may be formed in the matrix. The precipitates formed in such a manner may be uniformly distributed within the matrix to reinforce the matrix and hinder dislocation movement, thus increasing mechanical properties of the high-entropy alloy. The added alloying elements may form fine precipitates in the matrix of

the filament-reinforced high-entropy alloy, and may further reinforce the high-entropy alloy, in addition to the increase in strength by the filament.

[0041] The reason for limiting the contents of Ti, Zr, Hf, Mo, W, Si, Al, V, and Ta to 0.02 to 5%, respectively, is that when the contents are less than 0.02%, a precipitation hardening effect may be extremely less, whereas when the contents exceed 5%, the ratio of precipitates may be extremely high to degrade workability, causing brittleness.

[0042] FIGS. 1A and 1B are schematic views illustrating microstructures of the high-entropy alloy, according to an exemplary embodiment, and the exemplary embodiment will be described in detail, with reference to FIGS. 1A and 1B.

[0043] It is desirable that before thermo-mechanical processing, the microstructures of the high-entropy alloy, according to an exemplary embodiment, may have, for example, a second phase distributed within a matrix, which is a single-phase solid solution, as illustrated in FIG. 1A. In the high-entropy alloy, according to an exemplary embodiment, for example, a filament structure formed by elongation of the second phase having ductility, as illustrated in FIG. 1B, may be distributed within the matrix after thermo-mechanical processing.

[0044] In an exemplary embodiment, the matrix may mean a solid solution formed of elements such as Fe, Mn, Ni, and Cu.

[0045] The second phase may refer to all various forms or structures, such as a solid solution (a second solid solution) of a phase having other elements, single-phase dendrites, segregation, a phase separation region, and crystal grains. For example, the second phase may mean a structure different from the matrix. The high-entropy alloy, having the second phase distributed therein, may ensure excellent ductility.

[0046] The second phase may be a Cr-rich phase not fully dissolved in the solid solution of the high-entropy alloy, and may have a higher level of ductility than the matrix, thus increasing ductility of the high-entropy alloy.

[0047] When the high-entropy alloy is processed by rolling, extruding, or the like, cooled, subjected to an intermediate heat treatment, and formed into a plate, a rod, or a wire, a Cr or a Cr-rich phase may be developed in filament or ribbon form to reinforce the matrix of the high-entropy alloy. For example, the high-entropy alloy may be a plate, rod, or wire product.

[0048] The second phase, as illustrated in FIGS. 2, 3A, and 3B, may be elongated after being processed to be present as a Cr-rich filament elongated with a thickness of 0.05 to 2 μm and a length of 10 to 1,000 μm , thus reinforcing the matrix. When present with a thickness of 0.05 to 2 μm and a length of 10 to 1,000 μm , the Cr-rich filament may not be damaged by deformation and may have optimized resistance to deformation to increase strength. The elongated composite phase may be present in the matrix of the high-entropy alloy in Cr-rich filament or ribbon form to provide an interface present as an obstacle to deformation of the high-entropy alloy, thus increasing strength of the high-entropy alloy.

[0049] As a result, strength and ductility of the high-entropy alloy, having a Cr-rich filament- or ribbon-shaped structure containing a precipitation phase in the matrix by the processing, may be simultaneously increased.

[0050] A method for manufacturing a high-entropy alloy, according to an exemplary embodiment, will be described in detail.

[0051] The method for manufacturing a high-entropy alloy may include: preparing a metallic material containing, by at. %, Cr in an amount greater than 5% and less than 42%, Mn in an amount greater than 5% and less than 35%, Fe in an amount greater than 5% and less than 35%, Ni in an amount greater than 5% and less than 35%, and at least one of Cu in an amount greater than 3% and less than 35%, and Ag in an amount greater than 3% and less than 35%, and residual inevitable impurities; manufacturing an alloy with the prepared metallic material by melting (casting) or powder metallurgy; carrying out a homogenization heat treatment for the manufactured alloy; primarily processing the homogenization heat treated alloy and then cooling it thus obtained; carrying out an intermediate heat treatment for the cooled alloy at a temperature of 350 to 600° C.; and secondarily processing the intermediate heat treated alloy so as to form a composite structure in which a Cr or a Cr-rich phase is distributed within a matrix of the alloy in filament or ribbon form.

[0052] FIG. 4 is a process flowchart illustrating a schematic sequence of manufacturing processes, according to an exemplary embodiment.

[0053] As illustrated in FIG. 4, a metallic material may be prepared containing, by at. %, Cr in an amount greater than 5% and less than 42%, Mn in an amount greater than 5% and less than 35%, Fe in an amount greater than 5% and less than 35%, Ni in an amount greater than 5% and less than 35%, and at least one of Cu in an amount greater than 3% and less than 35%, and Ag in an amount greater than 3% and less than 35%, and residual inevitable impurities.

[0054] The metallic material may further include, for example, at least one of, by at. %, Ti in an amount of 0.02 to 5%, Zr in an amount of 0.02 to 5%, Hf in an amount of 0.02 to 5%, Mo in an amount of 0.02 to 5%, W in an amount of 0.02 to 5%, Si in an amount of 0.02 to 5%, Al in an amount of 0.02 to 5%, V in an amount of 0.02 to 5%, and Ta in an amount of 0.02 to 5%.

[0055] Subsequently, an alloy may be manufactured with the prepared metallic material, using melting (casting) or powder metallurgy.

[0056] The melting (casting) or the like may be performed to alloy the prepared metallic material, an alloying method for the same is not limited thereto, and the metallic material may be alloyed by a known method. For example, the alloy may be manufactured by casting, arc melting, or powder metallurgy. The manufactured alloy may subsequently be cooled, but a detailed cooling method for the same is not limited, and slow cooling, and air cooling, or rapid solidification (quenching) may be used.

[0057] For example, a rapid solidification (quenching) method may be used to cool the melted (cast) alloy. This is because the second phase (the Cr-rich phase) present within the matrix may be refined by the quenching, and hence mechanical properties may be increased.

[0058] Subsequently, the manufactured alloy may be subjected to a homogenization heat treatment. The homogenization heat treatment may be performed to induce diffusion, for example, at a temperature within a range of 600 to 1,200° C. for 1 to 48 hours.

[0059] Subsequent to the homogenization heat treatment, the alloy may be cooled. The cooling method is not particularly limited, and an air cooling or furnace cooling method may be used.

[0060] The alloy subjected to the homogenization heat treatment may be primarily processed and then cooled at room temperature. The primary processing method is not particularly limited, and any known processing method may also be applied. The primary processing method may be at least one of hot working, rolling, extruding, and room-temperature working. By the first processing method, as illustrated in FIG. 1B, the second phase within the high-entropy alloy may be changed into the filament structure.

[0061] The cooled alloy may be subjected to an intermediate heat treatment at a temperature of 350 to 600° C. In such an intermediate heat treatment, a precipitation phase, including at least one of Ti, Zr, Hf, Mo, W, V, Ta, Si, and Al, may be formed within the matrix of the alloy. Further, a portion of Cr-rich filament phases formed by the above-mentioned primary processing method may be rendered spherical by recovery, and the Cr-rich filament phases rendered spherical may be elongated by a subsequent secondary method.

[0062] Thus, precipitates formed within the matrix may be uniformly distributed within the matrix to reinforce the matrix, and may simultaneously increase strength and ductility of the high-entropy alloy, together with the second phase (the Cr-rich phase) formed to have the filament or ribbon shape.

[0063] Ultimately, a composite structure, having a Cr or a Cr-rich phase distributed within the matrix in fine filament or ribbon form, may be formed by secondarily processing the alloy subjected to the intermediate heat treatment.

[0064] The secondary processing method is not particularly limited, and any known processing method may also be applied. For example, the secondary processing method may be at least one of hot working, rolling, extruding, and room-temperature working. By the secondary processing method, as illustrated in FIG. 1B, the second phase within the high-entropy alloy may be elongated into the filament structure.

[0065] At least one of the primary and secondary processing may be forming the alloy into one of a plate, a rod, and a wire.

[0066] The primary and secondary processing and the intermediate heat treatment, as described above, may allow the high-entropy alloy according to an exemplary embodiment to be simultaneously increased in strength and ductility.

[0067] Hereinafter, exemplary embodiments in the present disclosure will be described in more detail through examples.

Example 1

[0068] Metallic materials, having compositions (at. %) as shown in Table 1 below, were prepared, and were arc melted in a vacuum atmosphere and then air cooled to manufacture high-entropy alloys according to Comparative Examples 1 to 3 and Inventive Examples 1 to 9. Subsequently, the manufactured high-entropy alloys were subjected to a homogenization heat treatment.

[0069] The high-entropy alloys manufactured in such a manner were cooled, and then the high-entropy alloys according to Inventive Examples 1 to 7 were subjected to

primary hot rolling at a total reduction ratio of 75%, to an intermediate heat treatment at 450° C. for 2 hours, and to secondary cold rolling at a total reduction ratio of 95% to manufacture plates having a thickness of 1 mm. The high-entropy alloys according to Inventive Examples 8 and 9 were subjected to primary hot rolling at a total reduction ratio of 75%, to an intermediate heat treatment at 450° C. for 2 hours, and to drawing at a total drawing ratio of 99% to manufacture wires having a diameter of 1 mm.

[0070] The high-entropy alloys according to Inventive Examples 10 and 11 had increased formability by refining

second phases (Cr-rich phases) present within matrixes by arc melting and then rapid solidification (quenching), and were subjected to primary hot rolling at a throughput of 75%, to an intermediate heat treatment at 450° C. for 2 hours, and to secondary cold rolling at a total reduction ratio of 95% to manufacture plates having a thickness of 1 mm.

[0071] Tensile tests were performed on the plates and wires of the high-entropy alloys manufactured as described above, and mechanical properties thereof were estimated. The results of estimation are shown in Table 1.

TABLE 1

Classification	Alloy composition	Form	Microstructures	Cooling type after casting	Tensile strength (MPa)	Yield strength (MPa)	Elongation percentage (%)
Comparative Example 1	Co ₂₀ Cr ₂₀ Fe ₂₀ Mn ₂₂ Ni ₁₈	Plate	Single phase	Air cooling	620	480	40
Comparative Example 2	Fe ₂₅ Ni ₂₅ Co ₂₅ Cr ₂₅	Plate	Single phase	Air cooling	1000	870	35
Comparative Example 3	Fe ₂₀ Mn ₂₀ Ni ₂₀ Co ₂₀ Cr ₂₀	Plate	Single phase	Air cooling	760	640	17
Inventive Example 1	Fe ₂₀ Ni ₂₀ Cr ₂₀ Mn ₂₀ Cu ₂₀	Plate	Matrix + Cr-rich filament	Air cooling	1560	1420	30
Inventive Example 2	Fe ₂₀ Ni ₂₀ Cr ₂₀ Mn ₂₀ Ag ₂₀	Plate	Matrix + Cr-rich filament	Air cooling	1620	1550	27
Inventive Example 3	Fe ₂₀ Cr ₂₀ Ni ₂₀ Mn _{19.65} Cu ₂₀ Ag _{0.35}	Plate	Matrix + Precipitation phase + Cr-rich filament	Air cooling	1920	1780	28
Inventive Example 4	Fe ₂₀ Cr ₂₀ Ni ₂₀ Mn _{19.65} Cu ₂₀ Ti _{0.35}	Plate	Matrix + Precipitation phase + Cr-rich filament	Air cooling	1850	1630	31
Inventive Example 5	Fe ₂₀ Cr ₂₀ Ni ₂₀ Mn _{19.65} Cu ₂₀ Mo _{0.35}	Plate	Matrix + Precipitation phase + Cr-rich filament	Air cooling	1910	1820	24
Inventive Example 6	Fe ₂₀ Cr ₂₀ Ni ₂₀ Mn _{19.65} Cu ₂₀ Al _{0.35}	Plate	Matrix + Precipitation phase + Cr-rich filament	Air cooling	1740	1560	29
Inventive Example 7	Fe ₂₀ Cr ₂₀ Ni ₂₀ Mn _{19.65} Cu ₂₀ Ta _{0.35}	Plate	Matrix + Precipitation phase + Cr-rich filament	Air cooling	1820	1590	25
Inventive Example 8	Fe ₂₀ Ni ₂₀ Cr ₂₀ Mn ₂₀ Cu ₂₀	Wire	Matrix + Cr-rich filament	Air cooling	2350	2100	25
Inventive Example 9	Fe ₂₀ Cr ₂₀ Ni ₂₀ Mn _{19.65} Cu ₂₀ Ag _{0.35}	Wire	Matrix + Precipitation phase + Cr-rich filament	Air cooling	2470	2180	23
Inventive Example 10	Fe ₂₀ Ni ₂₀ Cr ₂₀ Mn ₂₀ Cu ₂₀	Plate	Matrix + Cr-rich filament	Rapid cooling	1610	1540	32
Inventive Example 11	Fe ₂₀ Ni ₂₀ Cr ₂₀ Mn ₂₀ Ag ₂₀	Plate	Matrix + Cr-rich filament	Rapid cooling	1720	1630	29

[0072] As shown in Table 1 above, the high-entropy alloys, according to Inventive Examples 1 to 7, satisfying the composition according to an exemplary embodiment and including the matrixes containing precipitates and Cr-rich filaments may have excellent strength, as compared to those according to Comparative Examples 1 to 3, and in particular, when formed into wires, the high-entropy alloys, according to Inventive Examples 1 to 7, may exhibit outstanding mechanical properties. The high-entropy alloys, according to Inventive Examples 10 and 11, having increased formability by refining the second phases (the Cr-rich phases) present within the matrixes by arc melting and then rapid solidification (quenching), may exhibit excellent mechanical properties, as compared to those, according to Inventive Examples 1 and 2, manufactured by arc melting and then air cooling.

[0073] FIG. 2 is an image obtained by observing microstructures of Inventive Example 1, and after the thermo-mechanical processing, the Cr-rich phase was changed to a filament structure.

[0074] FIGS. 3A and 3B are images obtained by observing microstructures of Inventive Example 8. In detail, FIG. 3A is the image illustrating the longitudinal microstructures, and depicts a ribbon-shaped structure. FIG. 3B is the image illustrating the microstructures in a forming direction (for example, a transverse direction), and after the thermo-mechanical processing, the Cr-rich phase was changed to an elongated filament structure.

TABLE 2

	Cr (at. %)	Mn (at. %)	Fe (at. %)	Ni (at. %)	Cu (at. %)
Matrix	9.52	17.75	13.07	15.47	44.20
Dendrite arm	54.17	10.17	28.25	5.53	1.87

[0075] Table 2 shows a summary of EDS analysis values measured from the dendrite arms and the matrix of Inventive Example 1. As shown in Table 2, a large amount of Cr may be distributed within the dendrite arms, and the Cu alloying element may be dominantly distributed within the matrix between the dendrite arms.

[0076] Further, the Ni and Mn alloying elements may be distributed even in the dendrite arms, but may be dominantly distributed within the matrix. In the matrix between the dendrite arms, Cu may be dominantly distributed, but high contents of other alloying elements, such as Fe, Mn, and Ni, may be distributed.

[0077] Thus, a main alloying element of the dendrite arms may be Cr, and may include a significant amount of the Mn and Fe alloying elements.

[0078] Since melting temperatures of Cu and Mn are lower than those of Fe and Cr, Cu and Mn may tend to be separated while being solidified at early stage to be grown as Cu—Mn dendrites. A melting temperature of the Ni alloying element may be higher than that of the Cu and Mn alloying element, but may have a high degree of solid solubility of Cu unlike other alloying elements. Thus, the Ni alloying element may be distributed within the matrix in an amount similar to that of a Cu phase.

[0079] Cu and Mn may form a solid solution at a high temperature higher than 900° C., and when the content of Mn exceeds 20%, Cu and Mn may be separated into two phases below 700° C. Since Cr has a higher melting tem-

perature than other alloying elements, Cr may be first solidified during solidification process, and may be separated into two phases.

[0080] FIG. 5 is a graph illustrating an X-ray diffraction (XRD) analysis results of Inventive Example 1.

[0081] As illustrated in FIG. 5, the diffraction peaks may be indicated as FCC (111), FCC (200), and FCC (220), and the peaks of BCC (111) and BCC (200) may indicate the presence of the Cr-rich phase. Further, it can be seen that a separated phase of the FCC phase may be present in view of partial separation of the diffraction peak of (220) displayed on the XRD data.

[0082] 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 disclosure, as defined by the appended claims.

What is claimed is:

1. A high-entropy alloy comprising:

by at. %, Cr in an amount greater than 5% and less than 42%, Mn in an amount greater than 5% and less than 35%, Fe in an amount greater than 5% and less than 35%, Ni in an amount greater than 5% and less than 35%, and at least one of Cu in an amount greater than 3% and less than 35%, and Ag in an amount greater than 3% and less than 35%; and residual inevitable impurities, wherein the high-entropy alloy has a dual phase in which a Cr or a Cr-rich phase is distributed within a matrix of the high-entropy alloy in filament or ribbon form.

2. The high-entropy alloy of claim 1, wherein the high-entropy alloy further includes, by at. %, at least one of Ti in an amount of 0.02 to 5%, Zr in an amount of 0.02 to 5%, Hf in an amount of 0.02 to 5%, Mo in an amount of 0.02 to 5%, W in an amount of 0.02 to 5%, Si in an amount of 0.02 to 5%, Al in an amount of 0.02 to 5%, V in an amount of 0.02 to 5%, and Ta in an amount of 0.02 to 5%, and precipitates are formed in the matrix.

3. The high-entropy alloy of claim 1, wherein the high-entropy alloy, having the dual phase, is a plate, rod, or wire product.

4. A method for manufacturing a high-entropy alloy comprising:

preparing a metallic material, the metallic material comprising, by at. %, Cr in an amount greater than 5% and less than 42%, Mn in an amount greater than 5% and less than 35%, Fe in an amount greater than 5% and less than 35%, Ni in an amount greater than 5% and less than 35%, and at least one of Cu in an amount greater than 3% and less than 35%, and Ag in an amount greater than 3% and less than 35%, and residual inevitable impurities;

manufacturing an alloy with the prepared metallic material by melting (casting) or powder metallurgy; carrying out a homogenization heat treatment for the manufactured alloy;

primarily processing the homogenization heat treated alloy and then cooling it thus obtained;

carrying out an intermediate heat treatment for the cooled alloy at a temperature of 350 to 600° C.; and

secondarily processing the intermediate heat treated alloy so as to form a composite structure in which a Cr or a Cr-rich phase is distributed within a matrix of the alloy in filament or ribbon form.

5. The method of claim 4, wherein the metallic material further includes, by at. %, at least one of Ti in an amount of 0.02 to 5%, Zr in an amount of 0.02 to 5%, Hf in an amount of 0.02 to 5%, Mo in an amount of 0.02 to 5%, W in an amount of 0.02 to 5%, Si in an amount of 0.02 to 5%, Al in an amount of 0.02 to 5%, V in an amount of 0.02 to 5%, and Ta in an amount of 0.02 to 5%, and precipitates are formed in the Cr filament-reinforced matrix through the intermediate heat treatment.

6. The method of claim 4, further comprising, prior to the homogenization heat treatment of the melted (cast) alloy, rapidly solidifying (quenching) the melted (cast) alloy.

7. The method of claim 4, wherein the homogenization heat treatment is performed at a temperature within a range of 600 to 1,200° C. for 1 to 48 hours.

8. The method of claim 4, wherein the primary and secondary processing is at least one of hot working, rolling, extruding, and room-temperature working.

9. The method of claim 4, wherein at least one of the primary and secondary processing is to form the alloy into one of a plate, a rod, and a wire.

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