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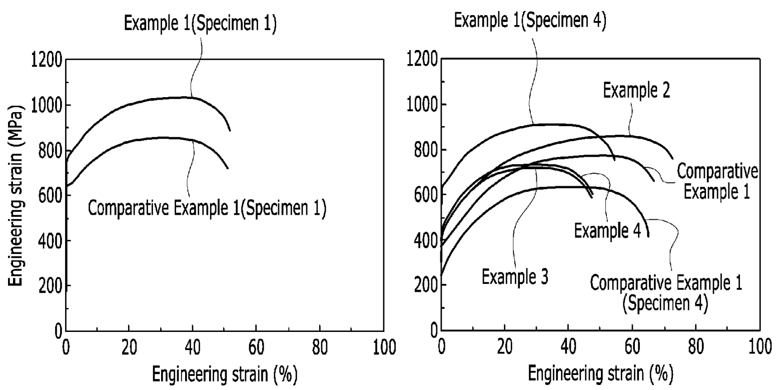
(54) BORON-DOPED HIGH-ENTROPY ALLOY AND MANUFACTURING METHOD THEREFOR

(57) The present invention introduces a high entropy alloy doped with boron, comprising four or more metals selected from iron (Fe), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), molybdenum (Mo), aluminum (Al) and copper (Cu), and boron (B) which has single phase FCC structure.

【Fig. 3】



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Description

[TECHNICAL FIELD]

[0001] The present invention relates to a method for improving the mechanical properties at room temperature of a high entropy alloy through boron doping, and a high entropy alloy doped with boron with improved mechanical properties at room temperature while maintaining intrinsic properties of the entropy alloy by adding boron which improves the cohesive strength of grain boundary.

[BACKGRAOUND]

[0002] The traditional alloy design, which has been ongoing for a long time, is designed to a direction to improve the physical properties of materials by adding a small amount of heteroatoms based on one or two main metal elements. Commercial alloys such as steel, nickel alloys, titanium alloys and aluminum alloys are representative examples.

[0003] However, the newly developed high-entropy alloy (HEA), in contrast to the existing alloy design, is an alloy consisting of multi-component main elements that alloy five or more constituent elements at the composition of atoms having the same or similar ratio but without a main element. This is a metal material that forms a single phase structure such as face-centered cubic (FCC) or body-centered cubic (BCC) without forming an intermetallic compound or an intermediate phase, by increasing the mixed entropy in the alloy through the substitutional type properties of the multiatom.

[0004] These entropy alloys should constitute of a mixture of at least five elements, and each alloy constituent element should contain a composition ratio of 5 to 35 at%. If an alloy element other than the main element is added, the addition amount should be 5 at% or less.

[0005] Among the high entropy alloys designed through the above definition, the FCC-based high entropy alloy exhibits excellent mechanical properties, and the Fe-Mn-Cr-Co-Ni-based high entropy alloy, which has attracted attention as a material appliable as a structure material in an extreme environment by having excellent cryogenic properties which have not be seen in conventional structure materials due to the expression of mechanical twinned crystal between cryogenic deformations, high fracture toughness and corrosion resistance.

[0006] However, at room temperature, unlike cryogenic temperatures, the formation of mechanical twinned crystal is not active so that it exhibits very low mechanical properties compared to commercial structure materials. In addition, considering the yield strength, which is one of important factors in the application of structure materials, the high entropy alloy also exhibits the low yield strength which is the limit of FCC-based metals, so that limiting the application range as structure materials and having a limitation in replacing conventional commercial materials.

[0007] There have been many studies to solve this problem, and among them, there is a method of improving the mechanical properties by adding a trace amount of a heteroatom other than the main element to the high entropy alloy to form a precipitate in the material.

[0008] As the content of boron in the Cu-Co-Ni-Cr-$Al_{0.5}$-Fe based high entropy alloy was varied from 3.5 to 15.4 at%, the amount of boride precipitation was increased to improve the hardness and compressive yield strength but it showed a limitation with low ductility and toughness due to formation of boride.

[0009] Therefore, it is essential to increase the yield strength and simultaneously to secure excellent mechanical properties at room temperature while maintaining the properties to be shown by existing high entropy alloys for application as structure materials in various fields of high entropy alloys.

[CONTENTS OF THE INVENTION]

[PROBLEM TO SOLVE]

[0010] An object of the present invention to provide a high entropy alloy which realizes a high yield strength and excellent mechanical properties at room temperature while maintaining the properties exhibited by the high entropy alloy by adding a trace amount of boron, which is an interstitial element, to the conventional FCC-based high entropy alloy.

[SUMMARY OF THE INVENTION]

[0011] A high entropy alloy doped with boron according to the present invention, comprises four or more metals selected from iron (Fe), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), molybdenum (Mo), aluminum (Al) and copper (Cu), and boron (B) and has single phase FCC structure.

[0012] The content of the four or more metals may be 5 to 35 at% respectively, and the content of boron (B) may be 3 at% or less (0 is not included).

[0013] The alloy may comprise 18 to 42 % of iron (Fe), 18 to 42 % of manganese (Mn), 9 to 22 % of chromium (Cr), 9 to 22 % of cobalt (Co), 9 to 22 % of nickel (Ni) and 0.001 to 0.01 % of boron (B) on the basis of weight%.

[0014] The alloy may comprise 18 to 42 % of iron (Fe), 18 to 42 % of manganese (Mn), 9 to 22 % of chromium (Cr), 9 to 22 % of cobalt (Co) and 0.001 to 0.01 % of boron (B) on the basis of weight%.

[0015] The alloy may comprise 0.004 to 0.005 % of boron (B).

[0016] The alloy may comprise boron (B) segregated in grain boundary.

[0017] The maximum concentration of the boron (B) segregated in the grain boundary may be 0.20 at%

[0018] The boron (B) segregated in the grain boundary may be 95 % or more of the total boron (B).

[0019] The average grain size of the alloy may be 60 μm or less.

[0020] The yield strength of the alloy may be 450 MPa or more.

[0021] A method for manufacturing a high entropy alloy doped with boron according to the present invention, comprises preparing a raw material of four or more metals selected from iron (Fe), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), molybdenum (Mo), aluminum (Al) and copper (Cu), and a raw material of boron (B); dissolving the raw materials to cast an ingot; cold-rolling the ingot to produce an alloy material; and annealing the alloy material; wherein the alloy material has a single phase FCC structure.

[0022] The steps of homogenization heat treating the ingot; and removing oxides generated on the surface of the ingot; after the step of casting the ingot may be further comprised.

[0023] In the step of annealing the alloy material, the annealing temperature may be 650 to 1100 °C.

[0024] The step of forming mechanical twinned crystal by deformation of the alloy material; after the step of annealing the alloy material may be further comprised.

[EFFECTS OF THE INVENTION]

[0025] The high entropy alloy doped with boron according to the present invention suppresses growth of grain boundary and improves cohesive strength by adding a trace amount of boron which is an interstitial element to segregates into a grain boundary.

[0026] In addition, it does not affect the formation of mechanical twinned crystal, which is the main strengthening mechanism of FCC-based high entropy alloys, and thus has excellent properties of high elongation while obtaining high yield strength and tensile strength.

[DESCRIPTION OF THE DRAWINGS]

[0027]

Fig. 1 is a graph showing changes in average grain size when annealing is performed for specimens 1 to 7 of Example 1 and Specimens 1 to 7 of Comparative Example 1 at different temperature conditions.

Fig. 2 shows boron segregated in grain boundary by atomic probe spectroscopy analysis according to Example 2.

Fig. 3 is a graph showing tensile properties at room temperature in Examples and Comparative Examples.

Fig. 4 shows ESBD analysis results on whether mechanical twinned crystal is formed after tensile deformation of Example 2 and Comparative Example 2.

[DETAILED DESCRIPTION OF THE INVENTION]

[0028] Hereinafter, some embodiments of the present invention will be described in detail with reference to the accompanying drawings so that those people who are having ordinary knowledge will easily carry out. The present invention may be implemented in several different forms and is not limited to the embodiments described herein.

[0029] In order to clearly illustrate the present invention, parts that are not related to the description are omitted, and the same or similar components are denoted by the same reference numerals throughout the description.

[0030] In addition, the size and thickness of each component shown in the drawings are arbitrarily shown for convenience of explanation, and thus the present invention is not necessarily limited to those shown in the drawings. In the drawings, the thicknesses are enlarged to clearly indicate layers and regions. In the drawings, for the convenience of explanation, the thicknesses of some layers and regions are exaggerated.

[0031] Also, when a portion of a layer, film, region, plate, etc. is referred to as being "on" or "above" another portion, it includes not only the case where it is "directly on" another part but also the case where there is another part in the middle. Conversely, when a part is "directly on" another part, it means that there is no other part in the middle. In addition, to be "on" or "above" the reference portion is located above or below the reference portion and does not necessarily mean "on" or "above" toward the opposite direction of gravity.

[0032] Also, throughout the specification, when referring that a certain part "comprises" a certain component, it means that it may comprise other components as well, rather than excluding other components, unless specifically stated otherwise.

A HIGH ENTROPY ALLOY DOPED WITH BORON

[0033] A high entropy alloy doped with boron according to the present invention comprises four or more metals selected from iron (Fe), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), molybdenum (Mo), aluminum (Al) and copper (Cu), and boron (B) and has single phase FCC structure.

[0034] The content of the four or more metals may be 5 to 35 at% respectively, and the content of boron (B) may be 3 at% or less (0 is not included),

[0035] The high entropy alloy has excellent mechanical properties in a cryogenic environment. On the other hand, it was studied to improve low yield strength and mechanical properties at room temperature which are pointed out as limit of high entropy alloy.

[0036] As a result, it was found that when boron which is an interstitial element is added in a trace amount, not only the grain boundary cohesion stress is improved but also the grain growth resistance is improved, so that a high yield strength and excellent mechanical properties at room temperature can be obtained due to grain refining effect.

[0037] In particular, when boron was added, it was found and reached the present invention that the mechanical properties at room temperature could be further improved due to effect of the segregation of boron into grain boundary while maintaining the characteristics of the FCC-based high entropy alloy having the expression of mechanical twinned crystal as the main enhancement mechanism.

[0038] There is no particular limitation on the composition of high entropy alloy doped with boron according to the present invention.

[0039] However, since the FCC single phase is realized, and the cryogenic mechanical properties are excellent so that it is high possibility of application to cryogenic structure materials.

[0040] But it has low yield strength and mechanical properties at room temperature, so it is sufficient that the high entropy alloy is required improvement.

[0041] For example, it comprises four or more metals selected from iron (Fe), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), molybdenum (Mo), aluminum (Al) and copper (Cu), wherein content of metal is from 5 to 35 at% respectively, so it may be the composition of atoms having the same or similar ratio.

[0042] Accordingly, this may be a alloy forming FCC structure without forming an intermetallic compound or an intermediate phase, by increasing the mixed entropy in the alloy through the substitutional type properties of the metal elements.

[0043] Boron is added to alloys and it serves to improve grain boundary cohesion stress and grain growth resistance. Boron may be added at 3 at% or less. Accordingly, the grains become refiner and the low yield strength and insufficient mechanical properties at room temperature of the conventional high entropy alloy may be improved.

[0044] However, if the amount of boron to be added is excessive, a boron compound having a weak brittleness is formed in the alloy, which may cause a serious effect on the mechanical properties.

[0045] Specifically, the high entropy alloy doped with boron according to the present invention may comprises 18 to 42 % of iron (Fe), 18 to 42 % of manganese (Mn), 9 to 22 % of chromium (Cr), 9 to 22 % of cobalt (Co), 9 to 22 % of nickel (Ni) and 0.001 to 0.01 % of boron (B) on the basis of wt% and it may be expressed as the following composition formula 1.

[Composition Formula 1] $Fe_{18\text{-}42}Mn_{18\text{-}42}Cr_{9\text{-}22}Co_{9\text{-}22}Ni_{9\text{-}22}B_{0.001\text{-}0.01}$ (wt%)

[0046] In addition, specifically, the high entropy alloy doped with boron according to the present invention may comprises 18 to 42 % of iron (Fe), 18 to 42 % of manganese (Mn), 9 to 22 % of chromium (Cr), 9 to 22 % of cobalt (Co), and 0.001 to 0.01 % of boron (B) on the basis of wt% and it may be expressed as the following composition formula 2.

[Composition Formula 2] $Fe_{18\text{-}42}Mn_{18\text{-}42}Cr_{9\text{-}22}Co_{9\text{-}22}B_{0.001\text{-}0.01}$ (wt%)

[0047] As in the composition formula 1 and the composition formula 2, 0.001 to 0.01% of boron may be added.

[0048] When boron is added in an amount less than 0.001%, the grain refining effect is not large, and when it is added in excess of 0.01%, boron compounds having weak brittleness can be formed in the alloy.

[0049] More specifically, 0.004 to 0.005% of boron may be added in order to prevent the formation of the boron compound as much as possible and to maximize the grain refining effect.

[0050] The high entropy alloy doped with boron according to the present invention may comprise boron segregated in grain boundary.

[0051] Boron is segregated into grain boundary by the addition of boron, which is an interstitial element, to suppress growth of grain boundary and improve cohesion strength.

[0052] Specifically, as can be seen in FIG. 2, the concentration of boron in the grain boundary between the FCC grains and the FCC grains may be 0.20 at% maximum. In addition, boron (B) segregated in the grain boundary may be 95 % or more of the total boron.

[0053] On the other hand, the boron concentration of FCC grains may be confirmed to be 0.075 at% maximum. More than 95% of the boron added is concentrated in the grain boundary to suppress the growth of the grains.

[0054] In addition, it does not affect the formation of mechanical twinned crystal, which is the main enhancement mechanism of FCC-based high entropy alloys, and thus has excellent properties of high elongation while obtaining high yield strength and tensile strength.

[0055] The average grain size of the high entropy alloy doped with boron according to the present invention by addition of boron may be 60 μm or less. Specifically, it may be 8 μm or less, and more specifically may be 4 μm or less. As mentioned above, excellent yield strength and mechanical properties at room temperature may be expected as the grain becomes refiner.

[0056] The yield strength of the high entropy alloy doped with boron according to the present invention may be 440 MPa or more. Specifically, it may be 650 MPa or more.

METHOD FOR MANUFACTURING HIGH ENTROPY ALLOY DOPED WITH BORON

[0057] A method for manufacturing a high entropy alloy doped with boron according to the present invention, comprises preparing a raw material of four or more metals selected from iron (Fe), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), molybdenum (Mo), aluminum (Al) and copper (Cu), and a raw material of boron (B), dissolving the raw materials to cast an ingot, cold-rolling the ingot to produce an alloy material, and annealing the alloy material.

[0058] First, in the step of preparing a raw material of four or more metals selected from, iron (Fe), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), molybdenum (Mo), Aluminum (Al) and copper (Cu) having a purity of 99.9% or more are prepared, and then boron (B) raw materials are prepared, and then it may be weighed so as to have a mixing ratio single phase FCC structure.

[0059] Next, in the step of casting the ingot, the raw materials prepared are charged into the crucible, and then melted by heating at 1400 to 1800 °C, and then the ingot may cast using the mold.

[0060] Thereafter, the ingot is cold-rolled so as to have a reduction ratio of 50 to 80% to produce an alloy material, and the alloy material produced through cold rolling be annealed.

[0061] During the annealing treatment, boron is preferentially segregated in grain boundary having high energy, so that the yield strength and the room temperature mechanical properties may be improved.

[0062] The annealing temperature may be a temperature of 650 to 1100 °C. Specifically, it may be a temperature of 700 to 800 °C. The annealing time may be 10 to 100 minutes.

[0063] Generally, as the temperature during the annealing process increases, the grain size grows, but boron is segregated into grain boundary due to the addition of boron, thereby suppressing the growth of grains. As a result, excellent yield strength and mechanical properties at room temperature may be exhibited due to grain refining.

[0064] It may include a step of homogenizing heat treating the ingot and a step of removing oxides generated on the surface of the ingot after the step of casting the ingot.

[0065] In a step of homogenizing heat treating, the ingot from which the oxide has been removed may be subjected to homogenizing heat treating at a temperature of 1000 to 1200 °C for 4 to 8 hours to homogenize the structure.

[0066] In the step of removing the oxide, the oxide formed on the surface of the ingot may be removed by grinding the surface of the cast ingot.

[0067] On the other hand, step of forming mechanical twinned crystal by deformation of the alloy material after the step of annealing the alloy material may be further comprised.

[0068] The alloy material may be intentionally deformed or may be deformed naturally in the environment of use after application to the product. It does not depend on the method of transformation.
Despite the addition of boron, it is possible to maintain the characteristics of the FCC-based high entropy alloy having the expression of mechanical twinned crystal as the main enhancement mechanism.

[0069] Hereinafter, specific examples of the present invention will be described. However, the following examples are only specific examples of the present invention, and the present invention is not limited to the following examples.

Producing high entropy alloys according to Examples and Comparative Examples

[Example 1]

[0070] Raw material of iron (Fe), manganese (Mn), chromium (Cr), cobalt (Co), nickel (Ni) and boron (B) having a purity of 99.9% or more was prepared so as to have the mixing ratio shown in Table 1 below.

[0071] The metal prepared as above was charged into a crucible and then melted by heating at 1550 °C, a plurality of ingots which are rectangular parallelepiped shapes having a thickness of 7.8 mm, 150 g, a width of 33 mm, and a length of 80 mm, were cast using a mold.

[0072] The surface of the cast ingot was subjected to surface grinding to remove the oxide generated on the surface, and the thickness of the ground ingot became 7 mm.

[0073] The ingot which had been subjected to surface grinding and has a thickness of 7 mm was subjected to homogenizing heat treatment at a temperature of 1100 °C for 6 hours, followed by cold rolling from a thickness of 7 mm to 1.5 mm to prepare a plurality of alloy plates (specimens 1 to 7 of Example 1).

[0074] Next, each alloy sheet was subjected to annealing under the conditions shown in Table 2 below.

[Example 2]

[0075] Raw material of iron (Fe), manganese (Mn), chromium (Cr), cobalt (Co), and boron (B) having a purity of 99.9% or more was prepared so as to have the mixing ratio shown in Table 1 below.

[0076] The metal prepared as above was charged into a crucible and then melted by heating at 1550 °C, a ingot which is a rectangular parallelepiped shape having a thickness of 7.8 mm, 150 g, a width of 33 mm, and a length of 80 mm, was cast using a mold.

[0077] The surface of the cast ingot was subjected to surface grinding to remove the oxide generated on the surface, and the thickness of the ground ingot became 7 mm.

[0078] The ingot which had been subjected to surface grinding and has a thickness of 7 mm was subjected to homogenizing heat treatment at a temperature of 1100 °C for 6 hours, followed by cold rolling from a thickness of 7 mm to 1.5 mm to prepare an alloy plate. Next, the alloy sheet material was subjected to annealing at 800 °C for 60 minutes.

[Example 3]

[0079] Raw material of iron (Fe), manganese (Mn), chromium (Cr), cobalt (Co), nickel (Ni), and boron (B) having a purity of 99.9% or more was prepared so as to have the mixing ratio shown in Table 1 below.

[0080] Thereafter, the alloy plate was prepared in the same manner as in Example 2.

[Example 4]

[0081] Raw material of iron (Fe), manganese (Mn), chromium (Cr), cobalt (Co), nickel (Ni), and boron (B) having a purity of 99.9% or more was prepared so as to have the mixing ratio shown in Table 1 below.

[0082] Thereafter, the alloy plate was prepared in the same manner as in Example 2.

[Comparative Example 1]

[0083] Raw material of iron (Fe), manganese (Mn), chromium (Cr), cobalt (Co), and nickel (Ni) having a purity of 99.9% or more was prepared so as to have the mixing ratio shown in Table 1 below.

[0084] Thereafter, a plurality of alloy plates (specimens 1 to 7 of Comparative Example 1) was prepared in the same manner as in Example 1.

[0085] Next, each alloy sheet was subjected to annealing under the conditions shown in Table 2 below.

[Comparative Example 2]

[0086] Raw material of iron (Fe), manganese (Mn), chromium (Cr), and cobalt (Co) having a purity of 99.9% or more was prepared so as to have the mixing ratio shown in Table 1 below.

[0087] Thereafter, the alloy plate was prepared in the same manner as in Example 2.

[Table 1]

	Mixing Ratio of the Raw Material (wt%)					
	Fe	Mn	Cr	Co	Ni	B
Example 1	19.915	19.591	18.542	21.016	20.931	0.005
Example 2	40.318	39.663	9.381	10.633	-	0.004
Example 3	19.914	19.59	18.541	21.015	20.93	0.02
Example 4	19.91	19.586	18.537	21.011	20.926	0.03

(continued)

	Mixing Ratio of the Raw Material (wt%)					
	Fe	Mn	Cr	Co	Ni	B
Comparative Example 1	19.916	19.592	18.543	21.017	20.932	-
Comparative Example 2	40.317	39.662	9.385	10.637	-	-

[Table 2]

Classification		Annealing conditions	
Species	Specimen No.	Annealing Temperature (°C)	Annealing Time (min)
Example 1/Comparative Example 1	Specimen 1	650	60
	Specimen 2	700	60
	Specimen 3	750	60
	Specimen 4	800	60
	Specimen 5	900	60
	Specimen 6	1000	60
	Specimen 7	1100	60

1. Results of grain boundary size analysis

[0088] FIG. 1 shows grain size changes with annealing temperature through electron backscatter diffraction (EBSD) analysis of alloys of specimens 1 to 7 of Example 1 and specimens 1 to 7 of Comparative Example 1 which are subjected to annealing.

[0089] As can be seen from FIG. 1, in both of Example 1 and Comparative Example 1, the grain size grows as the annealing temperature increases, in the case of Example 1, however, since boron is further added, the grain size is relatively small as compared with Comparative Example 1. In addition, it can be seen that the difference in grain size between Example 1 and Comparative Example 1 is gradually increased as annealing temperature is increased.

[0090] That is, in the Fe-Mn-Cr-Co-Ni alloy system, by keeping the composition of the other elements constant while adding 0.005 wt% of boron to suppress grain growth during the annealing, it can be seen that it finally has relatively fine grains as compared with Comparative Example 1.

2. Results of atomic probe spectroscopy analysis

[0091] FIG. 2 shows the result of the atomic probe spectroscopy analysis of the annealed Example 2. Atomic probe spectroscopy analysis is a method to identify atomic images by element, which is a method to analyze atomic distribution through ionization of material and detection using electric field by applying electrical pulses to atomic probe samples (~ 50 nm) manufactured in conical shape.

[0092] As can be seen from FIG. 2, iron (Fe), manganese (Mn), chromium (Cr), cobalt (Co), and nickel (Ni) are randomly distributed uniformly over the whole area, while it can be seen that the boron added of 0.004 wt% is segregated in a specific region, and this region corresponds to grain boundary.

[0093] That is, boron is preferentially segregated in the grain boundary having a relatively higher energy than the matrix in the annealing.

3. Tensile test results

[0094] Fig. 3 and Table 3 show the results of the room temperature tensile test of the specimens 1 and 4 of Example 1, Example 2, the specimens 1 and 4 of Comparative Example 1, and Comparative Example 2, respectively.

[Table 3]

Specimen	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation (%)
Specimen 1 of Example 1	800	1035	51
Specimen 1 of Comparative Example 1	652	854	50
Specimen 4 of Example 1	650	910	55
Specimen 4 of Comparative Example 1	275	635	65
Example 2	441	858	73
Comparative Example 2	380	773	67
Example 3	451	734	47
Example 4	476	716	48

[0095] As can be seen from FIG. 3 and Table 3, the specimen 4 of Example 1, Example 2, Example 3, Example 4, the specimen 4 of Comparative Example 1 and Comparative Example 2 of the high entropy alloy doped with boron according to the present invention are which are all subjected to annealing at 800 °C and the specimen 4 of Comparative Example 1 In Example 2, the annealing was carried out at 800 °C so when comparing the physical properties, the tensile strength of the examples were improved compared to the specimens 1 and 4 of Comparative Example 1 and Comparative Example 2 in which boron was not added, showing excellent mechanical properties.

[0096] Comparing the specimen 1 of Example 1 with the specimen 1 of Comparative Example 1, it can be seen that the tensile strength is greatly improved due to the influence of boron.

[0097] Particularly, comparing the specimen 4 of Example 1 with the specimen 4 of Comparative Example 1, it has been confirmed that the yield strength and the tensile strength are improved remarkably by adding boron (yield strength: 275 MPa → 650 MPa, tensile strength: 635 MPa → 910 MPa), while the elongation shows similar results to the case where boron was not added.

[0098] In addition, in the alloy of Example 2, the result has been confirmed that the yield strength and tensile strength were improved and at the same time, the elongation was also slightly increased by the effect of adding boron compared to the alloy of Comparative Example 2.

[0099] Comparing the specimen 4 of Example 1 and Example 2 in which boron is added to 0.01 % or less with Example 3 and Example 4 in which boron is added in excess of 0.01%, it has been confirmed that in Example 3 and Example 4, the boron is added in excess to lower all of the yield strength, the tensile strength and the elongation, thereby deteriorating the mechanical properties.

[0100] Therefore, it has been confirmed that the method of adding boron, which is an interstitial element, to the optimum range as a means for solving the low yield strength of the FCC-based high entropy alloy is more effective as an improving method for mechanical properties than other means.

4. The expression of the mechanical twinned crystal

[0101] FIG. 4 shows the transmission-electron backscatter diffraction (t-EBSD) analysis results of the expression of mechanical twinned crystal during tensile deformation of the high entropy alloys according to Example 2 and Comparative Example 2.

[0102] As shown in Fig. 4, it has been confirmed that the mechanical twinned crystal between deformations was also expressed at the same level as in Comparative Example 2 in which boron was not added even in the Example 2 alloy in which boron was added.

[0103] Therefore, it can be seen that the mechanical properties at room temperature is further improved due to boron segregated in grain boundary while retaining the properties of FCC-based high entropy alloys having the expression of mechanical twinned crystal as the main enhancement mechanism.

[0104] The present invention is not limited to the above-mentioned embodiments and/or examples and may be manufactured in various forms, those who have ordinary knowledge of the technical field to which the present invention belongs may understand that it may be carried out in different and concrete forms without changing the technical idea or fundamental feature of the present invention. Therefore, the aforementioned embodiments and/or examples are exemplary in all the ways but not limited thereto.

Claims

1. A high entropy alloy doped with boron, comprising:

    four or more metals selected from iron (Fe), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), molybdenum (Mo), aluminum (Al) and copper (Cu), and boron (B) and
    having single phase FCC structure.

2. The high entropy alloy doped with boron of claim 1, wherein
the content of the four or more metals is 5 to 35 at% respectively, and
the content of boron (B) is 3 at% or less (0 is not included).

3. The high entropy alloy doped with boron of claim 1, wherein
the alloy comprises 18 to 42 % of iron (Fe), 18 to 42 % of manganese (Mn), 9 to 22 % of chromium (Cr), 9 to 22 % of cobalt (Co), 9 to 22 % of nickel (Ni) and 0.001 to 0.01 % of boron (B) on the basis of weight%.

4. The high entropy alloy doped with boron of claim 1, wherein
the alloy comprises 18 to 42 % of iron (Fe), 18 to 42 % of manganese (Mn), 9 to 22 % of chromium (Cr), 9 to 22 % of cobalt (Co) and 0.001 to 0.01 % of boron (B) on the basis of weight%.

5. The high entropy alloy doped with boron of claim 3 or 4, wherein
the alloy comprises 0.004 to 0.005 % of boron (B).

6. The high entropy alloy doped with boron of claim 1, wherein
the alloy comprises boron (B) segregated in grain boundary.

7. The high entropy alloy doped with boron of claim 6, wherein
the maximum concentration of the boron (B) segregated in the grain boundary is 0.20 at%.

8. The high entropy alloy doped with boron of claim 6, wherein
the boron (B) segregated in the grain boundary is 95 % or more of the total boron (B).

9. The high entropy alloy doped with boron of claim 1, wherein
the average grain size of the alloy is 60 μm or less.

10. The high entropy alloy doped with boron of claim 1, wherein
the yield strength of the alloy is 450 MPa or more.

11. A method for manufacturing a high entropy alloy doped with boron, comprising:

    preparing a raw material of four or more metals selected from iron (Fe), chromium (Cr), nickel (Ni), cobalt (Co), manganese (Mn), molybdenum (Mo), aluminum (Al) and copper (Cu), and a raw material of boron (B);
    dissolving the raw materials to cast an ingot;
    cold-rolling the ingot to produce an alloy material; and
    annealing the alloy material;
    wherein the alloy material has a single phase FCC structure.

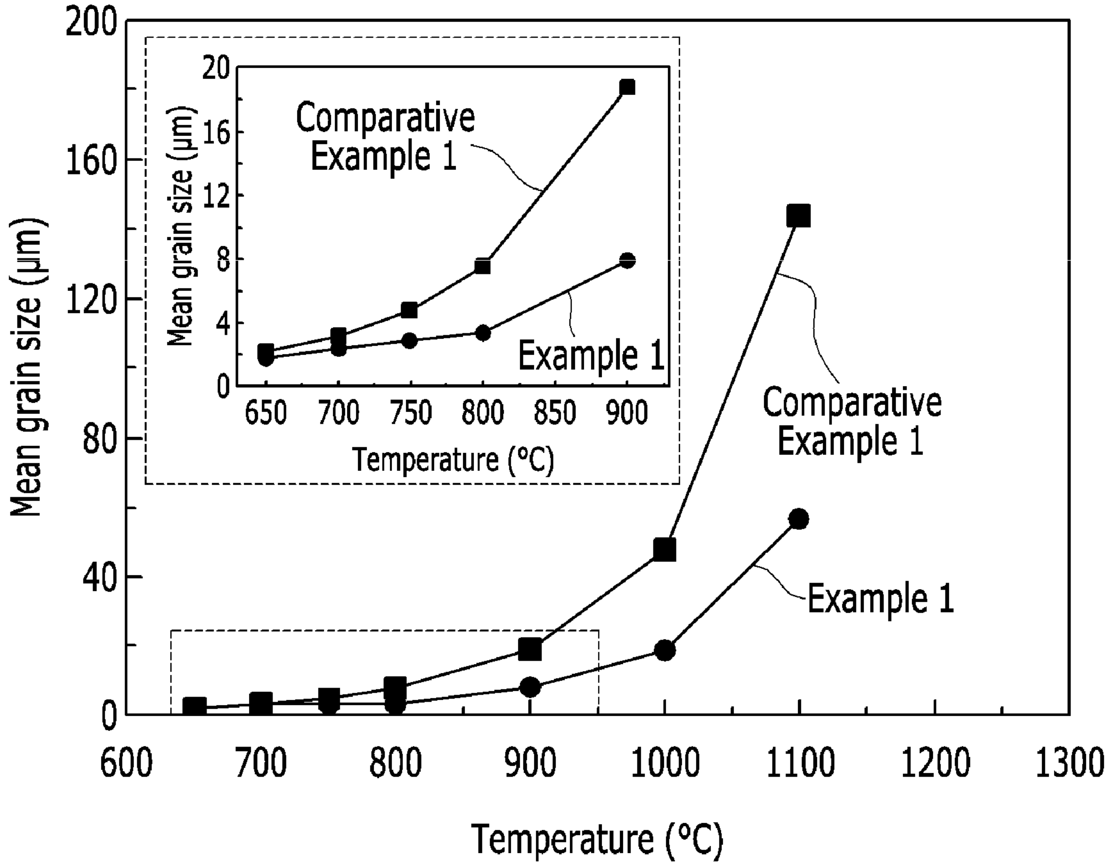
12. The method of claim 11, further comprising:

    homogenizing heat treating the ingot; and
    removing oxides generated on the surface of the ingot; after the step of casting the ingot.

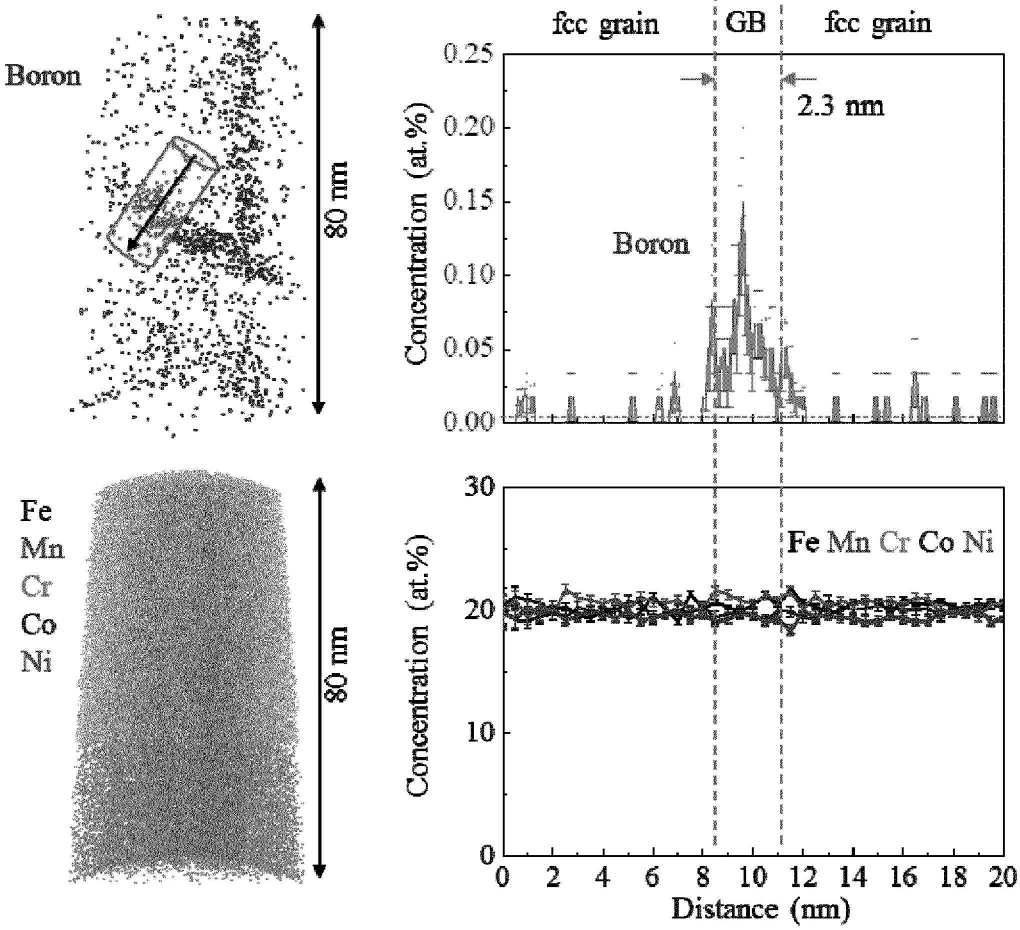
13. The method of claim 11, wherein
in the step of annealing the alloy material,
the annealing temperature is 650 to 1100 °C.

14. The method of claim 11, further comprising:
forming mechanical twinned crystal by deformation of the alloy material; after the step of annealing the alloy material.

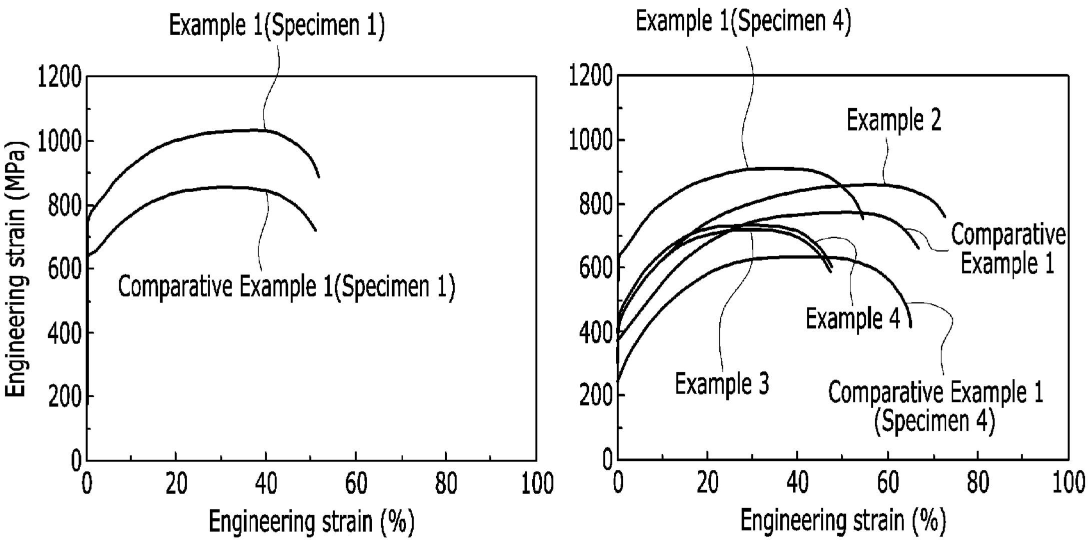
【Fig. 1】


Mean grain size (μm)
Temperature (°C)
0
40
80
120
160
200
600
700
800
900
1000
1100
1200
1300
Comparative Example 1
Example 1
0
4
8
12
16
20
650
700
750
800
850
900
Comparative Example 1
Example 1
Mean grain size (μm)
Temperature (°C)

【Fig. 2】

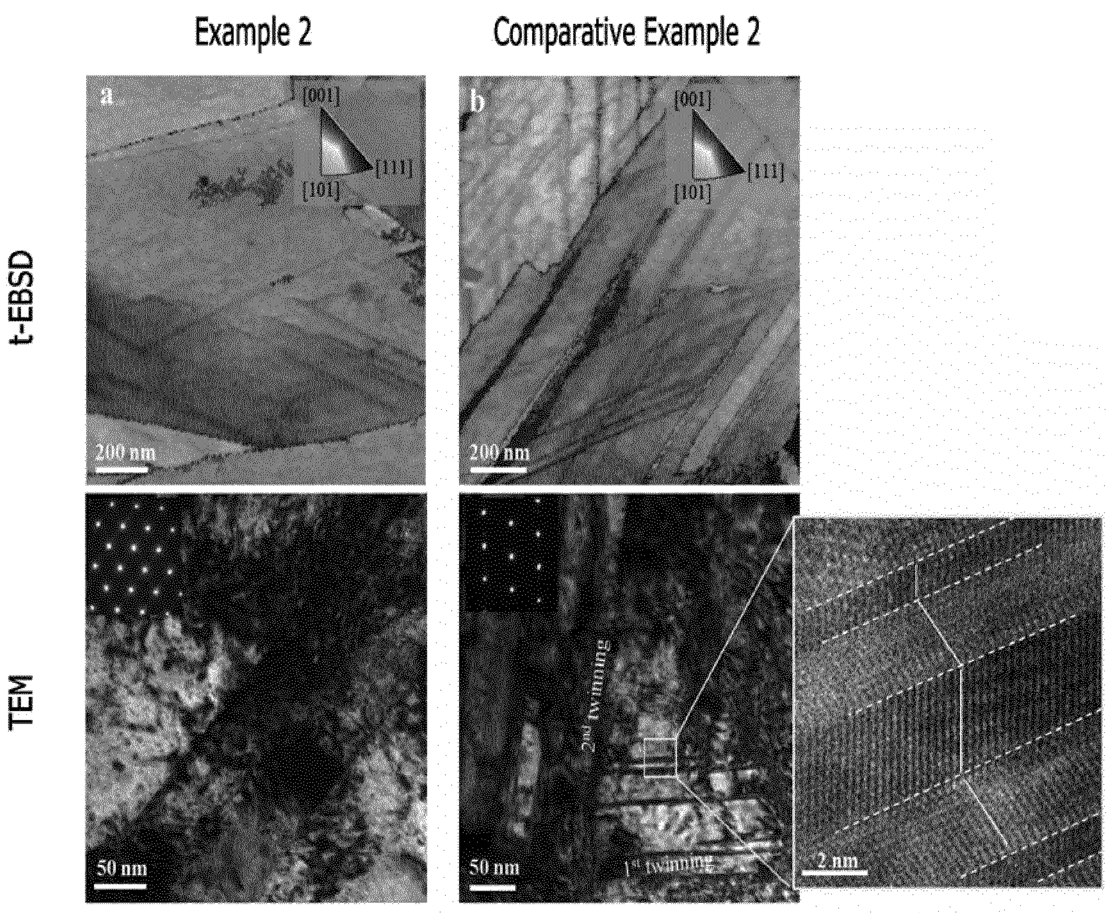

Boron
80 nm
Fe
Mn
Cr
Co
Ni
80 nm
fcc grain
GB
fcc grain
2.3 nm
Boron
Concentration (at.%)
0.25
0.20
0.15
0.10
0.05
0.00
Fe Mn Cr Co Ni
Concentration (at.%)
30
20
10
0
0 2 4 6 8 10 12 14 16 18 20
Distance (nm)

【Fig. 3】



Example 1(Specimen 1)
Comparative Example 1(Specimen 1)
Engineering strain (MPa)
Engineering strain (%)
1200
1000
800
600
400
200
0
0
20
40
60
80
100
Example 1(Specimen 4)
Example 2
Comparative Example 1
Example 4
Example 3
Comparative Example 1 (Specimen 4)
Engineering strain (%)

【Fig. 4】


Example 2
Comparative Example 2
t-EBSD
TEM
a
b
[001]
[111]
[101]
200 nm
50 nm
2nd twinning
1st twinning
2 nm

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2017/012543

A. CLASSIFICATION OF SUBJECT MATTER

C22C 30/00(2006.01)i, C22C 30/02(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C 30/00; C22C 38/06; C23C 24/10; B22F 1/00; C23C 24/08; C22C 30/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models: IPC as above
Japanese Utility models and applications for Utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS (KIPO internal) & Keywords: single phase FCC, boron doping, high entropy, multiple component, yield strength, annealing

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 103290404 A (ZHEJIANG UNIVERSITY OF TECHNOLOGY et al.) 11 September 2013 See paragraphs [0009], [0020]-[0022], [0059] and claim 1.	1-3,5
Y		6-14
A		4
Y	US 2017-0167003 A1 (THE TRUSTEES OF DARTMOUTH COLLEGE) 15 June 2017 See paragraphs [0040], [0064], [0074].	6-14
A	CN 104561990 A (SHENYANG UNIVERSITY OF TECHNOLOGY) 29 April 2015 See paragraphs [0069]-[0070] and claim 1.	1-14
A	CN 105950947 A (ZHEJIANG ASIA GENERAL SOLDERING & BRAZING MATERIAL CO., LTD.) 21 September 2016 See paragraphs [0028]-[0029] and claim 1.	1-14
A	HSU, Chin-You et al., Wear Resistance and High-temperature Compression Strength of Fcc CuCoNiCrAl0.5Fe Alloy with Boron Addition, Metallurgical and Materials Transactions A, Volume 35A, May 2004, pages 1465-1469. See pages 1465-1469.	1-14

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 JUNE 2018 (05.06.2018)	**05 JUNE 2018 (05.06.2018)**

Name and mailing address of the ISA/KR	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2017/012543

Patent document cited in search report	Publication date	Patent family member	Publication date
CN 103290404 A	11/09/2013	CN 103290404 B	18/11/2015
US 2017-0167003 A1	15/06/2017	NONE	
CN 104561990 A	29/04/2015	CN 104561990 B	30/06/2017
CN 105950947 A	21/09/2016	NONE	

Form PCT/ISA/210 (patent family annex) (January 2015)