

SPECIFICATION

TITLE OF THE INVENTION

**HIGH ENTROPY ALLOY ARTICLE, METHOD FOR MANUFACTURING SAME,
AND PRODUCT USING SAME**

5

TECHNICAL FIELD OF THE INVENTION

[0001]

The present invention relates to technology of high
entropy alloys and particularly to high entropy alloy
10 articles manufactured by a powder-based additive
manufacturing method, the method for manufacturing the
alloy articles, and products using the alloy articles.

DESCRIPTION OF BACKGROUND ART

15 [0002]

A high entropy alloy (HEA) has recently been developed
as an alloy based on a new technological concept which is
completely different from the concept of conventional
alloys (e.g., an alloy in which a tiny amount of multiple
20 kinds of subcomponent elements is added to one to three
kinds of main component elements). The HEA is defined as an
alloy configuring more than five kinds of main metallic
elements, each having a content of 5 to 35 atomic percent,
and it is known that the HEA expresses characteristics as
25 described below.

[0003]

(a) Stabilization of the mixed state resulting from the negatively-increasing mixing entropy term in the formula of Gibbs free energy; (b) diffusion delay due to complicated
5 microstructure; (c) high degree of hardness resulting from high lattice strain due to different sizes of constituent atoms, and decrease in temperature dependency of mechanical characteristics; and (d) improved corrosion resistance as the result of combined effects of coexistence of multiple
10 elements (also referred to as a "cocktail effect").

[0004]

For example, patent literature 1 (JP 2002-173732 A) discloses a high entropy multicomponent alloy produced by casting or synthesizing multiple kinds of metallic elements,
15 wherein the alloy contains five to eleven kinds of main metallic elements and the molar number of each kind of main metallic element is 5% to 30% of the total molar number of the alloy. Furthermore, the main metallic elements are selected from a metallic element group containing aluminum,
20 titanium, vanadium, chromium, iron, cobalt, nickel, copper, zirconium, molybdenum, palladium, and silver.

[0005]

According to the patent literature 1, it seems to be possible to provide a high entropy multicomponent alloy
25 that is significantly harder, more heat resistant and more

corrosion resistant than conventional carbon steel and alloy carbon steel, in the casting state.

CITATION LIST

5 PATENT LITERATURE

[0006]

Patent literature 1: JP 2002-173732 A.

SUMMARY OF THE INVENTION

10 PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

However, the inventors of the present invention studied the high entropy alloys (HEAs) in various ways and found out that the segregation of elements and unevenness of the microstructure were prone to occur during the casting process because of the complicated alloy composition, and that it was difficult to obtain a uniform HEA ingot. The segregation of elements and unevenness of the microstructure of the alloy article would result in inconsistent characteristics depending on the regions and are therefore regarded as problems to be solved.

[0008]

Furthermore, the HEAs are difficult to process because of its significant hardness and resistance to become soft by tempering. Accordingly, it is difficult to form an

article into a desired shape by means of mechanical processing and/or plastic deformation processing. This is a major problem to be solved before putting the HEA articles into practical and commercial use.

5 [0009]

On the other hand, as stated above, the HEAs have attractive characteristics that cannot be obtained from conventional alloys. Therefore, development of HEA articles that have excellent homogeneity in the alloy composition and microstructure as well as significant shape controllability and a method for manufacturing the HEA articles has been strongly required.

[0010]

Thus, to satisfy the above requirements, it is an objective of the present invention to provide an HEA article that has excellent homogeneity in the alloy composition and microstructure as well as significant shape controllability, using an HEA with significant mechanical strength and high corrosion resistance, and a method for manufacturing the HEA article. Also, another objective of the invention is to provide a product using the HEA article.

SOLUTION TO PROBLEMS

[0011]

25 (I) According to one aspect of the present invention,

there is provided a high entropy alloy article comprising:
Co (cobalt), Cr (chromium), Fe (iron), Ni (nickel), and Ti
(titanium) elements, each element in content of 5 atomic
percent to 35 atomic percent; more than 0 atomic percent to
5 8 atomic percent of Mo (molybdenum); and remainder
substances of unavoidable impurities. And, acicular
crystals of an intermetallic compound phase are dispersedly
precipitated in the matrix phase crystals of the high
entropy alloy article.

10 [0012]

In the above high entropy alloy article (I) of the
invention, the following modifications and changes can be
made.

(i) The acicular crystals may be dispersedly
15 precipitated in a three-dimensional grid-like pattern.

(ii) Chemical composition of the high entropy alloy may
include 20 atomic percent to 35 atomic percent of Co, 10
atomic percent to 25 atomic percent of Cr, 10 atomic
percent to 25 atomic percent of Fe, 15 atomic percent to 30
20 atomic percent of Ni, and 5 atomic percent to 15 atomic
percent of Ti.

(iii) Chemical composition of the high entropy alloy
may include 25 atomic percent to 33 atomic percent of Co,
15 atomic percent to 23 atomic percent of Cr, 15 atomic
25 percent to 23 atomic percent of Fe, 17 atomic percent to 28

atomic percent of Ni, 5 atomic percent to 10 atomic percent of Ti, and 1 atomic percent to 7 atomic percent of Mo.

(iv) Chemical composition of said high entropy alloy may include 27 atomic percent to 33 atomic percent of Co, 5 18 atomic percent to 23 atomic percent of Cr, 18 atomic percent to 23 atomic percent of Fe, 17 atomic percent to 24 atomic percent of Ni, 5 atomic percent to 8 atomic percent of Ti, and 1 atomic percent to 3 atomic percent of Mo.

(v) The intermetallic compound phase may contain an 10 Ni_3Ti phase.

(vi) Tensile strength thereof may be 1000 MPa or more and breaking elongation thereof may be 3% or more.

(vii) The matrix phase crystal may be a columnar crystal and its crystal structure may contain a simple 15 cubic crystal. Herein, "Its crystal structure contains a simple cubic crystal" means "the main crystal structure is the simple cubic crystal."

[0013]

(II) According to another aspect of the invention, 20 there is provided a method for manufacturing the above high entropy alloy article, comprising the steps of:

mixing and melting raw materials for the high entropy alloy to form molten metal;

atomizing to form a high entropy alloy powder from the 25 molten metal; and

additive manufacturing to form an additive manufactured article with a desired shape by means of a metal powder-based additive manufacturing method using the high entropy alloy powder.

5 [0014]

In the above method for manufacturing the above high entropy alloy article (II) of the invention, the following modifications and changes can be made.

(viii) The additive manufacturing step may comprise: a
10 powder bed forming substep to form a powder bed of the high entropy alloy powder; a powder bed calcination substep to form a calcined object of the powder bed by heating the entire powder bed; and a local melting and solidified layer forming substep. In the local melting and solidified layer
15 forming substep, the calcined object is locally heated to form a minute molten pool of the high entropy alloy, and the minute alloy molten pools are moved and sequentially solidified by means of scanning of the local heating on the plane of the calcined object, thereby forming a solidified
20 layer of the high entropy alloy.

[0015]

(III) According to still another aspect of the invention, there is provided a product using the above high entropy alloy article. The product is an impeller of a
25 fluid machine.

[0016]

In the above product using the high entropy alloy article (III) of the invention, the following modifications and changes can be made.

- 5 (ix) The product using the high entropy alloy article may be a centrifugal compressor incorporating the impeller.

ADVANTAGES OF THE INVENTION

[0017]

- 10 According to the present invention, it is possible to provide a high entropy alloy (HEA) article that has excellent homogeneity in the alloy composition and microstructure as well as significant shape controllability, using an HEA with significant mechanical strength and high
- 15 corrosion resistance, and a method for manufacturing the HEA article. Furthermore, it is possible to provide a product using the HEA article.

BRIEF DESCRIPTION OF THE DRAWINGS

- 20 [0018]

[FIG. 1] FIG. 1 is an exemplary process chart showing a method for manufacturing a high entropy alloy article according to the present invention;

- [FIG. 2] FIG. 2 is an exemplary schematic illustration
- 25 showing cross-sectional view of a configuration of an EBM

powder-based additive manufacturing apparatus and an additive manufacturing method;

[FIG. 3A] FIG. 3A is an exemplary electron microscopy image showing a microstructure of a cross sectional view of the additive manufactured article made of the HEA according to the invention;

[FIG. 3B] FIG. 3B is an exemplary electron microscopy image showing a microstructure of a longitudinal sectional view of the additive manufactured article made of the HEA according to the invention;

[FIG. 4] FIG. 4 is a photograph of an impeller of a fluid machine showing an example of a product using the HEA article according to the invention;

[FIG. 5] FIG. 5 is a schematic illustration showing a cross-sectional view of a centrifugal compressor into which the impeller according to the invention is incorporated; and

[FIG. 6] FIG. 6 is an exemplary electron microscopy image showing a microstructure of the HEA article 1c.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019]

(Basic concept of the present invention)

As stated before, although the HEA has attractive characteristics (e.g., significant hardness and resistance

to become soft by tempering) that cannot be obtained from conventional alloys, it is difficult to process the HEA and form an HEA article into a desired shape. As the result of various studies conducted by the inventors, it is revealed
5 that the HEA ingot having a general cast microstructure is significantly resistant to deformation and poor in ductility.

[0020]

Accordingly, the inventors intensively carried out
10 studies of alloy composition and shape control methods to develop HEA articles excellent in shape controllability and ductility without having to sacrifice the attractive characteristics of the HEA. As a result, the inventors found it possible to obtain an HEA article that can solve
15 the problem by forming an additive manufactured article by means of an additive manufacturing method using the Co-Cr-Fe-Ni-Ti-Mo alloy powder. The present invention is based on that concept.

[0021]

20 Hereinafter, preferred embodiments of the invention will be described with reference to the drawings according to the HEA article production procedures. However, the invention is not limited to specific embodiments described below, and various combinations and modifications are
25 possible without departing from a technical concept of the

invention.

[0022]

[Method for Manufacturing HEA Article]

FIG. 1 is an exemplary process chart showing a method
5 for manufacturing a high entropy alloy article according to
the invention. As shown in FIG. 1, the manufacturing method
of the invention includes a raw material mixing and melting
step, an atomizing step, an additive manufacturing step,
and a removal step. Hereinafter, each step of the
10 manufacturing method will be described more specifically.

[0023]

(Raw Material Mixing and Melting Step)

As shown in FIG. 1, firstly the raw material mixing and
melting step is performed in which molten metal 10 is
15 formed by mixing and melting raw materials having desired
HEA composition (Co-Cr-Fe-Ni-Ti-Mo). A raw material mixing
method and a melting method are not particularly limited,
and any conventional method for manufacturing high
mechanical strength and high corrosion-resistant alloys can
20 be utilized. For example, vacuum melting is preferable as a
melting method. It is also preferable to refine molten
metal 10 by simultaneously utilizing a vacuum carbon
deoxidizing technique or the like.

[0024]

25 As main components, the HEA composition of the

invention contains five elements, Co, Cr, Fe, Ni and Ti;
content of each element is between 5 atomic percent and 35
atomic percent. As a subcomponent, it contains more than 0
atomic percent to 8 atomic percent of Mo. Remainder
5 substances are unavoidable impurities.

[0025]

More specifically, content of the component Co is
preferably between 20 atomic percent and 35 atomic percent;
more preferably between 25 atomic percent and 33 atomic
10 percent; and further preferably between 27 atomic percent
and 33 atomic percent.

[0026]

Content of the component Cr is preferably between 10
atomic percent and 25 atomic percent; more preferably
15 between 15 atomic percent and 23 atomic percent; and
further preferably between 18 atomic percent and 23 atomic
percent.

[0027]

Content of the component Fe is preferably between 10
20 atomic percent and 25 atomic percent; more preferably
between 15 atomic percent and 23 atomic percent; and
further preferably between 18 atomic percent and 23 atomic
percent.

[0028]

25 Content of the component Ni is preferably between 15

atomic percent and 30 atomic percent; more preferably between 17 atomic percent and 28 atomic percent; and further preferably between 17 atomic percent and 24 atomic percent.

5 [0029]

Content of the component Ti is preferably between 5 atomic percent and 15 atomic percent; more preferably between 5 atomic percent and 10 atomic percent; and further preferably between 5 atomic percent and 8 atomic percent.

10 [0030]

Content of the component Mo is preferably more than 0 atomic percent to 8 atomic percent; more preferably between 1 atomic percent and 7 atomic percent; and further preferably between 1 atomic percent and 3 atomic percent.

15 [0031]

If the content of each component is out of the preferable composition range, it is difficult to attain desired characteristics.

[0032]

20 (Atomizing Step)

Next, the atomizing step to form a high entropy alloy powder 20 from the molten metal 10 is performed. An atomizing method is not particularly limited, and any conventional method can be utilized. For example, a gas
25 atomizing technique or a centrifugal atomizing technique

that enables high purity, uniform composition, and formation of spherical particles can be preferably used.

[0033]

For handling and filling characteristics, the average
5 particle diameter of the alloy powder 20 is preferably
between 10 μm and 1 mm, and the more preferable diameter is
between 20 μm and 500 μm . If the average particle diameter
is less than 10 μm , the alloy powder 20 is prone to fly up
easily in the subsequent additive manufacturing step, which
10 could result in decreasing the accuracy of the shape of an
additive manufactured article. On the other hand, if the
average particle diameter exceeds 1 mm, surface roughness
of the resultant additive manufactured article could
increase in the subsequent additive manufacturing process
15 or the alloy powder 20 could melt insufficiently.

[0034]

(Additive Manufacturing Step)

Next, the additive manufacturing step is performed to
shape an additive manufactured article 230 with a desired
20 shape by a metal powder-based additive manufacturing method
using the alloy powder 20 prepared as mentioned above. By
applying a metal powder-based additive manufacturing method
by which near-net-shape metal articles are formed by
melting and solidification instead of sintering, it is
25 possible to form a three-dimensional metal article having a

complicated shape as hard as or harder than a metal cast article. An additive manufacturing method is not particularly limited, and any conventional method is usable. For example, an electron beam melting (EBM) technique and a
5 selective laser melting (SLM) technique can be preferably utilized for the metal powder-based additive manufacturing method.

[0035]

The additive manufacturing step will be described using
10 the EBM technique as an example. FIG. 2 is an exemplary schematic illustration showing cross-sectional view of a configuration of an EBM powder-based additive manufacturing apparatus and an additive manufacturing method. As shown in the drawing, the EBM powder-based additive manufacturing
15 apparatus 100 configures a vacuum chamber having an electron beam control part 110 and a powder control part 120.

[0036]

An exemplary procedure of the EBM powder-based additive
20 manufacturing method is as follows. 1) A stage 121 is descended by the thickness of one layer (e.g., approximately 30 to 800 μm) of the additive manufactured article 230 to be shaped. The alloy powder 20 is supplied from a powder hopper 123 on a base plate 122 located on the
25 upper surface of the stage 121, the alloy powder 20 is then

planarized by a rake arm 124 to form a powder bed 210
(layered powder) (powder bed forming substep).

[0037]

2) Thermal electrons are radiated from a tungsten
5 filament 111 heated (e.g., to 2500°C or higher) and
accelerated by an anode 112 (e.g., to nearly half the speed
of light) to form an electron beam 113. The accelerated
electron beam 113 is shaped into an exact circle by an
astigmatic correction apparatus 114 and converges on the
10 powder bed 210 by a focus coil 115.

[0038]

3) The powder bed 210 overall is preliminary heated by
scanning relatively weak (blunt) focused beam using a
deflection coil 116 to form a calcined object of the powder
15 bed. In the EBM technique, it is preferable that the
substep (powder bed calcination substep) to form a calcined
object of the powder bed be performed before the powder bed
is locally melted and solidified. This is conducted to
prevent the powder bed from flying up due to the
20 electrification of the alloy powder resulting from the
radiation of a focused electron beam that is intended to
locally melt the powder bed. Also, heating in this substep
is additionally effective because subsequent deformation of
the additive manufactured article 230 can be suppressed.

25 [0039]

The calcination temperature for calcining the powder bed 210 is preferably between 900°C and 1000°C. When the calcination temperature drops below 900°C, sintering of the alloy powder does not progress much, making it difficult to form a calcined object. On the other hand, when the calcination temperature rises above 1000°C, sintering of the alloy powder progresses too quickly, making it difficult to remove the additive manufactured article 230 (i.e. difficult separation of the additive manufactured article 230 from the calcined object).

[0040]

4) Next, a local melting and solidified layer forming substep is performed. That is, a minute alloy molten pool is first formed by radiating a strong focused electron beam for the local melting onto the calcined object of the powder bed, based on 2D (two-dimensional) slice data converted from 3D CAD (three-dimensional computer-aided design) data of the additive manufactured article 230 to be shaped. The minute alloy molten pool is then moved and sequentially solidified by means of scanning of the focused electron beam. Thus, 2D slice solidified layer 220 is formed.

[0041]

5) The above procedure from 1) to 4) is repeated to form an additive manufactured article 230 having a desired

shape.

[0042]

(Removal Step)

The additive manufactured article 230 formed through
5 the above steps is buried in the calcined object. Therefore,
a step to get out the additive manufactured article 230
from the calcined object is then performed. A method to get
out the additive manufactured article 230 (i.e., a method
of separating the additive manufactured article 230 from
10 the calcined object, and a method of separating the
additive manufactured article 230 from the base plate 122)
is not particularly limited, and any conventional method
can be utilized. For example, a sandblasting technique
using the alloy powder 20 is preferable. The sandblasting
15 technique using the alloy powder 20 enables the removed
calcined object to be ground together with the blasted
alloy powder 20, and the obtained alloy powder can be
reused as an alloy powder 20.

[0043]

20 [HEA Article]

After the removal step, a specimen was sampled from the
additive manufactured article 230 and a microstructure of
the specimen was observed by means of an optical microscope
and an electron microscope. As a result, it is revealed
25 that a matrix phase of the additive manufactured article

230 has a structure (so-called, quench-solidified structure) in that minute columnar crystals (average particle diameter of 100 μm or less) stand together in large numbers along the lamination direction of the additive manufactured article 230. In addition, further observation has revealed that acicular crystals of an intermetallic compound phase are dispersedly precipitated in a grid-like pattern in the matrix phase crystals of the additive manufactured article 230.

10 [0044]

FIG. 3A is an exemplary electron microscopy image showing a microstructure of a cross sectional view (i.e., a plane perpendicular to the lamination direction, a plane whose normal line is along the lamination direction) of the additive manufactured article made of the HEA according to the invention. FIG. 3B is an exemplary electron microscopy image showing a microstructure of a longitudinal sectional view (i.e., a plane along the lamination direction, a plane whose normal line is perpendicular to the lamination direction) of the additive manufactured article made of the HEA according to the invention.

20 [0045]

As shown in FIGs. 3A and 3B, the acicular crystals are dispersedly precipitated in a grid-like pattern in both the cross sectional view and the longitudinal sectional view of

the additive manufactured article 230. It is therefore deemed that the acicular crystals are dispersedly precipitated in a three-dimensional grid-like pattern.

[0046]

5 [Products Using HEA Article]

FIG. 4 is a photograph of an impeller of a fluid machine showing an example of a product using the HEA article according to the invention. Since an HEA product according to the invention is manufactured by a metal
10 powder-based additive manufacturing method, it is possible to easily form an object that has a complicated shape as shown in FIG. 4. Furthermore, the impeller using the HEA article according to the invention has both excellent mechanical characteristics and high corrosion resistance;
15 therefore, it is significantly durable even in environments exposed to severe stress and corrosion.

[0047]

FIG. 5 is a schematic illustration showing a cross-sectional view of a centrifugal compressor into which the
20 impeller according to the invention is incorporated. This is another example of a product made of an HEA article according to the invention. The use of the impeller, which is significantly durable even in environments exposed to severe stress and corrosion, will contribute to the
25 improved long-term reliability of the centrifugal

compressor.

EXAMPLES

[0048]

5 Hereinafter, the present invention will be described more specifically by showing examples and comparative examples. However, the invention is not limited to those examples.

[0049]

10 [Experimental 1]

(Preparation of HEA Powders 1 to 6)

First, the raw material mixing and melting step was conducted, in which raw materials were mixed so as to have nominal composition shown in Table 1 and melted by the vacuum melting technique to form a molten metal. Then, the atomizing step was conducted using the gas atomizing technique to form an alloy powder from the molten metal. Subsequently, the obtained alloy powder was sieved into a particle diameter range from 45 μm to 105 μm . Thus, HEA powders 1 to 6 were prepared. Then, the particle size distributions of the HEA powders 1 to 6 were measured by means of a laser diffraction particle size distribution measuring apparatus. The result indicates that the average particle diameter of each powder was approximately 70 μm .

25 [0050]

Table 1 Nominal composition of HEA powders 1 to 6 (unit: atomic %).

	Co	Cr	Fe	Ni	Ti	Mo
HEA powder 1	26.8	17.9	17.9	26.8	8.9	1.8
HEA powder 2	26.3	17.5	17.5	26.3	8.8	3.5
HEA powder 3	25.4	17.0	17.0	25.4	8.5	6.8
HEA powder 4	25.0	16.7	16.7	25.0	8.3	8.3
HEA powder 5	28.9	19.2	19.2	23.1	7.7	1.9
HEA powder 6	31.3	20.8	20.8	18.8	6.3	2.1

[0051]

[Experimental 2]

5 (Production of HEA articles 1e to 6e of additive
manufactured article)

Using the HEA powder 1 prepared in experimental 1, an
additive manufactured article was formed by the EBM
technique according to the additive manufacturing processes
10 with the powder-based additive manufacturing apparatus
(made by Arcam AB, model: A2X) as shown in FIG. 2. The
additive manufactured article is a columnar object with a
diameter of 14 mm and a height of 85 mm, and the height
direction is the lamination direction. The calcination
15 temperature for the powder bed was set to 950°C.

[0052]

After the additive manufacturing step, the removal step
was conducted in which the calcined object around the
additive manufactured article was removed by the
20 sandblasting technique using the HEA powder 1. Thus, the

HEA article 1e of the additive manufactured article was obtained.

[0053]

In the same manner as the above, the additive
5 manufacturing step and the removal step were performed for
the HEA powders 2 to 6. Thus, HEA articles 2e to 6e of the
additive manufactured article were fabricated.

[0054]

[Experimental 3]

10 (Production of HEA articles 1c to 4c of general cast
article)

By means of an arc melting technique using a water-
cooling copper mold, the HEA powder 1 prepared in
experimental 1 was cast into a general cast article which
15 is a prismatic object with a width of 14 mm, a length of 80
mm and a height of 15 mm. Thus, an HEA article 1c of
general cast article was formed. Herein, in order to
suppress the segregation of constituent elements and
unevenness of the microstructure as much as possible during
20 the casting process, melting was repeatedly conducted more
than five times.

[0055]

The same procedures to form the HEA article 1c were
performed for the HEA powders 2 to 4. Thus, HEA articles 2c
25 to 4c of general cast article were fabricated.

[0056]

[Experimental 4]

(Observation of microstructure of HEA articles)

A test specimen for the observation of microstructure
5 was sampled from each HEA article and the microstructure of
the specimen was observed using an optical microscope, a
scanning electron microscope (SEM) and an X-ray diffraction
(XRD) apparatus. Table 2 shows the production
specifications of each HEA article and the microstructure
10 observation results.

[0057]

Table 2 Production specifications of each HEA article and microstructure observation results.

HEA article	HEA powder	Production method	Matrix phase structure		Intermetallic compound	
			Crystal shape	Crystal structure	Main precipitation phase	Precipitation morphology
1e	1	Additive manufacturing	Columnar crystal	SC	Ni ₃ Ti	Three-dimensional grid-like pattern
1c		General casting	Equiaxed crystal	FCC		Random aggregation
2e	2	Additive manufacturing	Columnar crystal	SC (FCC)		Three-dimensional grid-like pattern
2c		General casting	Equiaxed crystal	SC + FCC		Random aggregation
3e	3	Additive manufacturing	Columnar crystal	SC (FCC)		Three-dimensional grid-like pattern
3c		General casting	Equiaxed crystal	SC + FCC		Random aggregation
4e	4	Additive manufacturing	Columnar crystal	SC (FCC)		Three-dimensional grid-like pattern
4c		General casting	Equiaxed crystal	SC + FCC		Random aggregation
5e	5	Additive manufacturing	Columnar crystal	SC	Ni ₃ Ti	Three-dimensional grid-like pattern
6e	6					

5 [0058]

As shown in Table 2, the matrix phase of the HEA articles 1e to 6e produced by the additive manufacturing method has a structure (so-called, quench-solidified structure) in that minute columnar crystals (average particle diameter of 100 μm or less) stand together in large numbers along the lamination direction of the

10

additive manufactured article. The structure of the columnar crystals has a simple cubic crystal structure (SC). However, based on the XRD measurement results, when it is difficult to identify whether the structure has a simple
5 cubic crystal structure (SC) or a face-centered cubic crystal structure (FCC), being difficult to conclude it to be FCC, "SC (FCC)" is indicated.

[0059]

In contrast, the matrix phase of the HEA articles 1c to
10 4c formed by the general casting technique has a structure consisting of equiaxed crystals whose average particle diameter is more than 100 μm . The structure of the equiaxed crystals apparently contained FCC.

[0060]

15 Based on the observation results of the matrix phase structure, it is deemed that "whether the matrix phase structure configures columnar crystals or equiaxed crystals" and "whether the matrix phase crystal structure apparently contains face-centered cubic crystals or not"
20 strongly depend on a rate of solidification of the HEA. In other words, they strongly depend on the duration of existence in the temperature range in which atoms of the HEA can be rearranged.

[0061]

25 Furthermore, with regard to the precipitation of the

intermetallic compound, the XRD measurement results verify that the main precipitation phase of all HEA articles is the Ni_3Ti phase. However, the XRD measurement results do not deny the precipitation of an NiTi phase or an NiTi_2 phase. In other words, there is a possibility that slight precipitation may be occurring as the NiTi phase and the NiTi_2 phase.

[0062]

Concerning the precipitation morphology of the intermetallic compound, there is a large difference depending on HEA article manufacturing methods. FIGs. 3A and 3B shown before are images observed by an electron microscope showing examples of a microstructure of the HEA article 1e. FIG. 6 is an electron microscopy image showing an example of a microstructure of the HEA article 1c.

[0063]

As stated above, in the HEA articles 1e to 6e produced by the additive manufacturing method, the main precipitation phase of the acicular crystal is dispersedly precipitated in a three-dimensional grid-like pattern. In comparison, as shown in FIG. 6, it is observed that acicular crystals randomly aggregate in the HEA articles 1c to 4c made by the general casting technique.

[0064]

[Experimental 5]

(Measurement of mechanical properties and corrosion resistance of HEA articles)

A test specimen (diameter of the parallel portion: 4 mm, length of the parallel portion: 20 mm) was sampled from each HEA article for tensile test. The test specimens of the HEA articles 1e to 6e made by the additive manufacturing method were taken so that the longitudinal direction of the test specimen matches the additive manufacturing direction (lamination direction).

[0065]

Using a material universal testing machine, the room-temperature tensile test was conducted for each test specimen in accordance with JIS Z 2241 at a rate of strain of $5 \times 10^{-5} \text{ s}^{-1}$, and the tensile strength and the breaking elongation were measured. From 10 measurements of the tensile test, the maximum value and the minimum value were excluded, and the average value of the remaining 8 measurements was obtained. To evaluate the tensile strength, the value of 1000 MPa or more is judged to be "Passed" and the value of less than 1000 MPa is judged to be "Failed". To evaluate the breaking elongation, the value of 3% or more is judged to be "Passed" and the value of less than 3% is judged to be "Failed". The results are shown in Table 3.

[0066]

Furthermore, from each HEA article made above, a

polarization test specimen (length of 15 mm, width of 15 mm, and thickness of 2 mm) was sampled for the pitting corrosion test. The pitting corrosion test was conducted for each polarization test specimen in accordance with JIS
5 G 0577. Specifically, under the conditions of "Test area: 1 cm², clearance corrosion prevention electrodes attached to the polarization test specimen, reference electrode: saturated silver/silver chloride electrode, test solution: 3.5% sodium chloride solution deaerated by argon gas, test
10 temperature: 30°C, potential sweep rate: 20 mV/min," the anode polarization curve of the polarization test specimen was measured and the pitting potential corresponding to the current density of 100 $\mu\text{A}/\text{cm}^2$ was obtained. To evaluate the pitting potential, the value of 1.0 V or more is judged to
15 be "Passed" and the value less than 1.0 V is judged to be "Failed". Results of the pitting corrosion test are also shown in Table 3.

[0067]

Table 3 Measurement results of mechanical properties and corrosion resistance of each HEA article.

HEA article	Mechanical properties		Corrosion resistance
	Tensile strength (MPa)	Breaking elongation (%)	Pitting potential (V vs. Ag/AgCl)
1e	1065 / Passed	5.3 / Passed	1.066 / Passed
1c	780 / Failed	3.3 / Passed	1.091 / Passed
2e	1080 / Passed	4.1 / Passed	1.101 / Passed
2c	813 / Failed	2.1 / Failed	1.098 / Passed
3e	1052 / Passed	3.2 / Passed	1.082 / Passed
3c	795 / Failed	1.7 / Failed	1.069 / Passed
4e	780 / Failed	1.1 / Failed	1.065 / Passed
4c	623 / Failed	0.5 / Failed	1.110 / Passed
5e	1215 / Passed	30 / Passed	1.120 / Passed
6e	1010 / Passed	45 / Passed	1.162 / Passed

5 [0068]

As shown in Table 3, it is verified that the HEA articles 1e to 3e, 5e, and 6e produced by the additive manufacturing method, which are the examples of the invention, have excellent mechanical properties; tensile strength of 1000 MPa or more and breaking elongation of 3% or more. Furthermore, it is also verified that the HEA articles 5e and 6e which contain a relatively small amount of Ni component and Ti component have an excellent breaking elongation property.

15 [0069]

On the other hand, the HEA articles 1c to 4c of general

cast article and the HEA article 4e whose alloy composition is out of specifications of the invention are the comparative examples. In those comparative examples, the tensile strength is less than 1000 MPa and/or breaking
5 elongation is less than 3%, and then the mechanical properties are failed as a whole. As to the HEA article 4e, the mechanical properties are failed although it was made by the additive manufacturing method. This verifies that addition of more than 8 atomic percent of Mo is not
10 preferable.

[0070]

Regarding the corrosion resistance, all of the HEA articles show pitting potential of 1.0 V vs. Ag/AgCl or more, which verifies that all of the HEA articles have
15 excellent corrosion resistance independent of manufacturing methods or microstructure. In other words, the HEA articles according to the invention are deemed to have excellent corrosion resistance because of the combination of the elements (Co-Cr-Fe-Ni-Ti-Mo).

20 [0071]

[Experimental 6]

(Production and inspection of product using HEA article)

By means of the manufacturing method used to produce
25 the HEA article 1e (i.e., the additive manufacturing method

using the HEA powder 1), an impeller shown in FIG. 4 was
fabricated. For the obtained impeller, an internal defect
inspection by X-ray CT scan was conducted and the size was
measured. As a result, no particular internal defect was
5 found and deformation out of the design dimension was not
detected either. This experiment verifies the effectiveness
of the invention.

[0072]

The above-described embodiments and Examples have been
10 specifically given in order to help with understanding on
the present invention, but the invention is not limited to
the configuration equipped with all the components
described above. For example, some of the configurations of
a certain embodiment may be replaced with the
15 configurations of the other embodiments, and the
configurations of the other embodiments may be added to the
configurations of the subject embodiment. Furthermore, some
of the configurations of each embodiment and example may be
omitted, replaced with other configurations, and added to
20 other configurations.

LEGEND

[0073]

10 ... molten metal;
25 20 ... alloy powder;

100 ... EBM powder-based additive manufacturing
apparatus;
110 ... electron beam control part;
120 ... powder control part;
5 111 ... tungsten filament;
112 ... anode;
113 ... electron beam;
114 ... astigmatic correction apparatus;
115 ... focus coil;
10 116 ... deflection coil;
121 ... stage;
122 ... base plate;
123 ... powder hopper;
124 ... rake arm;
15 210 ... powder bed;
220 ... solidified layer; and
230 ... additive manufactured article.

CLAIMS

[Claim 1]

A high entropy alloy article comprising
Co, Cr, Fe, Ni, and Ti elements, each element in
5 content of 5 atomic percent to 35 atomic percent,
more than 0 atomic percent to 8 atomic percent of Mo,
and
remainder substances of unavoidable impurities, wherein
an intermetallic compound phase of acicular crystals is
10 dispersedly precipitated in the matrix phase crystals of
the high entropy alloy article.

[Claim 2]

The high entropy alloy article according to claim 1,
15 wherein
the acicular crystals are dispersedly precipitated in a
three-dimensional grid-like pattern.

[Claim 3]

20 The high entropy alloy article according to claim 1 or
2, wherein
chemical composition of the high entropy alloy
comprises
20 atomic percent to 35 atomic percent of Co,
25 10 atomic percent to 25 atomic percent of Cr,

10 atomic percent to 25 atomic percent of Fe,
15 atomic percent to 30 atomic percent of Ni, and
5 atomic percent to 15 atomic percent of Ti.

5 [Claim 4]

The high entropy alloy article according to claim 1 or
2, wherein

chemical composition of the high entropy alloy
comprises

10 25 atomic percent to 33 atomic percent of Co,
15 atomic percent to 23 atomic percent of Cr,
15 atomic percent to 23 atomic percent of Fe,
17 atomic percent to 28 atomic percent of Ni,
5 atomic percent to 10 atomic percent of Ti, and
15 1 atomic percent to 7 atomic percent of Mo.

[Claim 5]

The high entropy alloy article according to claim 1 or
2, wherein

20 chemical composition of said high entropy alloy
comprises

27 atomic percent to 33 atomic percent of Co,
18 atomic percent to 23 atomic percent of Cr,
18 atomic percent to 23 atomic percent of Fe,
25 17 atomic percent to 24 atomic percent of Ni,

5 atomic percent to 8 atomic percent of Ti, and
1 atomic percent to 3 atomic percent of Mo.

[Claim 6]

5 The high entropy alloy article according to any one of
claims 1 to 5, wherein
the intermetallic compound phase contains an Ni₃Ti phase.

[Claim 7]

10 The high entropy alloy article according to any one of
claims 1 to 6, wherein
tensile strength thereof is 1000 MPa or more and
breaking elongation thereof is 3% or more.

15 [Claim 8]

The high entropy alloy article according to any one of
claims 1 to 7, wherein
the matrix phase crystal is a columnar crystal, and the
crystal structure thereof contains a simple cubic crystal.

20

[Claim 9]

A method for manufacturing the high entropy alloy
article according to any one of claims 1 to 7, comprising
the steps of:

25 mixing and melting raw materials for the high entropy

alloy to form molten metal;

atomizing to form a high entropy alloy powder from the molten metal; and

additive manufacturing to form an additive manufactured
5 article with a desired shape by means of a metal powder-
based additive manufacturing method using the high entropy
alloy powder.

[Claim 10]

10 The method for manufacturing the high entropy alloy
article according to claim 9, wherein

the additive manufacturing step comprises:

a powder bed forming substep to form a powder bed of
the high entropy alloy powder;

15 a powder bed calcination substep to form a calcined
object of the powder bed by heating the entire powder bed;
and

a local melting and solidified layer forming substep
wherein

20 the calcined object is locally heated to form a minute
molten pool of the high entropy alloy, and the minute alloy
molten pools are moved and sequentially solidified by means
of scanning of the local heating on the plane of the
calcined object, thereby forming a solidified layer of the
25 high entropy alloy.

[Claim 11]

A product using a high entropy alloy article,
said high entropy alloy article being the high entropy
5 alloy article according to any one of claims 1 to 8, and
the product being an impeller of a fluid machine.

[Claim 12]

A centrifugal compressor incorporating the impeller
10 according to claim 11.