

SPECIFICATION

TITLE OF THE INVENTION

COBALT BASED ALLOY PRODUCT

5 TECHNICAL FIELD OF THE INVENTION

[0001]

The present invention relates to cobalt based alloy materials having excellent mechanical properties and, in particular, to a cobalt based alloy product applied with an additive manufacturing method.

DESCRIPTION OF BACKGROUND ART

[0002]

Cobalt (Co) based alloy materials, along with nickel (Ni) based alloy ones, are representative heat resistant alloy materials. Also referred to as superalloys, they are widely used for high temperature members (components used under high temperature environment, e.g. gas turbine members, steam turbine members, etc.). Although Co based alloy materials are higher in material costs than Ni based alloy ones, they have been used for applications such as turbine stator blades and combustor members because of their excellence in corrosion resistance and abrasion resistance, and their ease of solid solution strengthening.

25 [0003]

In Ni based alloy materials, various improvements that have been made so far in composition and manufacturing processes of heat resistant alloy materials have led to the development of strengthening through γ' phase (e.g. $\text{Ni}_3(\text{Al},$
5 $\text{Ti})$ phase) precipitation, which has now become mainstream. On the other hand, in Co based alloy materials, an intermetallic compound phase that contributes to improving mechanical properties, like the γ' phase in Ni based alloy ones, hardly precipitates, which has prompted research on
10 carbide phase precipitation strengthening.

[0004]

For example, Patent Literature 1 (JP Shou 61 (1986)-
243143 A) discloses a Co based superplastic alloy made up
of a Co based alloy matrix having a crystal grain size of
15 equal to or less than 10 μm and carbide grains in a granular form or a particulate form having a grain size of 0.5 to 10 μm precipitated in the matrix. The Co based alloy includes 0.15 to 1 wt. % of C, 15 to 40 wt. % of Cr, 3 to 15 wt. % of W or Mo, 1 wt. % or less of B, 0 to 20 wt. % of
20 Ni, 0 to 1.0 wt. % of Nb, 0 to 1.0 wt. % of Zr, 0 to 1.0 wt. % of Ta, 0 to 3 wt. % of Ti, 0 to 3 wt. % of Al, and the balance of Co.

[0005]

Meanwhile, in recent years, three dimensional shaping
25 technology (the so-called 3D printing) such as additive

manufacturing or AM has received much attention as a technique for manufacturing finished products with a complicated shape by near net shaping. To apply the three dimensional shaping technology to heat resistant alloy components, vigorous research and development activities are currently being carried out.

CITATION LIST

PATENT LITERATURE

10 [0006]

Patent Literature 1: JP Shou 61 (1986)-243143 A, and

Patent Literature 2: JP 2019-049022 A.

SUMMARY OF THE INVENTION

15 PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

Since the 3D printing is capable of directly forming even components of complicated shape, manufacturing of turbine high temperature components by the 3D printing is very attractive in terms of reduction of manufacturing work time and improvement of manufacturing yield (i.e. reduction of manufacturing cost).

[0008]

On the other hand, manufacturing the Co based alloy materials does not require precipitation of an

intermetallic compound phase such as the γ' phase as in Ni based alloy materials, so Co based alloy materials do not contain plenty of Al or Ti, which is easily oxidized. This means melting and forging processes in the air atmosphere are available for their manufacturing. Therefore, such Co based alloy materials are considered to be advantageous in manufacturing of alloy powder for AM and manufacturing of AM articles. Also, the Co based alloy materials have advantages with corrosion resistance and abrasion resistance comparable to or superior to those of Ni based alloy materials.

[0009]

However, conventional Co based alloy materials have disadvantages of mechanical properties inferior to those of γ' phase precipitation-strengthened Ni based alloy materials. In other words, if a Co based alloy material could achieve mechanical properties comparable to or superior to those of γ' phase precipitation-strengthened Ni based alloy materials, AM articles of the Co based alloy material would become attractive materials suitable for high temperature components.

[0010]

The present invention was made in view of the foregoing and has an objective to provide a Co based alloy product having mechanical properties comparable to or superior to

those of precipitation strengthened Ni based alloy materials.

SOLUTION TO PROBLEMS

5 [0011]

(I) According to one aspect of the present invention, there is provided a product formed of a cobalt based alloy material. The cobalt based alloy product has a chemical composition including: 0.08 to 0.25 mass % of carbon (C);
10 more than 0.04 mass % and 0.2 mass % or less of nitrogen (N), the total amount of the C and the N being more than 0.12 mass % and 0.28 mass % or less; 0.1 mass % or less of boron (B); 10 to 30 mass % of chromium (Cr); 5 mass % or less of iron (Fe) and 30 mass % or less of nickel (Ni), the
15 total amount of the Fe and the Ni being 30 mass % or less; tungsten (W) and/or molybdenum (Mo), the total amount of the W and the Mo being 5 to 12 mass %; 0.5 mass % or less of silicon (Si); 0.5 mass % or less of manganese (Mn); 0.5 to 2 mass % of an M component being a transition metal
20 other than W and Mo and having an atomic radius of more than 130 pm; and the balance being cobalt (Co) and impurities. The impurities include 0.5 mass % or less of aluminum (Al), and 0.04 mass % or less of oxygen (O). The product is a polycrystalline body of matrix phase crystal
25 grains. Particles of MC type carbide phase, M(C,N) type

carbonitride phase and/or MN type nitride phase including the M component are precipitated at an average interparticle distance of 0.13 to 2 μm .

Meanwhile, in the above-described MC, M(C,N) and MN
5 types, "M" means a transition metal, "C" means carbon and "N" means nitrogen.

[0012]

(II) According to another aspect of the invention, there is provided a cobalt based alloy product. The cobalt
10 based alloy product has a chemical composition including: 0.08 to 0.25 mass % of C; more than 0.04 mass % and 0.2 mass % or less of N, the total amount of the C and the N being more than 0.12 mass % and 0.28 mass % or less; 0.1 mass % or less of B; 10 to 30 mass % of Cr; 5 mass % or
15 less of Fe and 30 mass % or less of Ni, the total amount of the Fe and the Ni being 30 mass % or less; W and/or Mo, the total amount of the W and the Mo being 5 to 12 mass %; 0.5 mass % or less of Si; 0.5 mass % or less of Mn; 0.5 to 2 mass % of an M component being a transition metal other
20 than W and Mo and having an atomic radius of more than 130 pm; and the balance being Co and impurities. The impurities include 0.5 mass % or less of Al, and 0.04 mass % or less of O. The product is a polycrystalline body of matrix phase crystal grains. In the matrix phase crystal grains,
25 segregation cells with an average size of 0.13 to 2 μm are

formed, in that the M component is segregated in boundary regions of the segregation cells.

[0013]

In the above Co based alloy products (I) and (II) of
5 the invention, the following changes and modifications can be made.

(i) On the boundary regions of the segregation cells, particles of MC type carbide phase, M(C,N) type carbonitride phase and/or MN type nitride phase including
10 the M component of the chemical composition may be precipitated.

(ii) The M component of the chemical composition may be at least one of titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb) and tantalum (Ta).

15 (iii) In the case that the chemical composition includes the Ti as the M component, content of the Ti may be 0.01 to 1 mass %; in the case that the chemical composition includes the Zr as the M component, content of the Zr may be 0.05 to 1.5 mass %; in the case that the
20 chemical composition includes the Hf as the M component, content of the Hf may be 0.01 to 0.5 mass %, in the case that the chemical composition includes the V as the M component, content of the V may be 0.01 to 0.5 mass %; in the case that the chemical composition includes the Nb as
25 the M component, content of the Nb may be 0.02 to 1 mass %;

and in the case that the chemical composition includes the Ta as the M component, content of the Ta may be 0.05 to 1.5 mass %.

(iv) The Zr may be an essential component as the M
5 component of the chemical composition.

(v) The M component of the chemical composition may be three or more of titanium, zirconium, hafnium, vanadium, niobium and tantalum.

(vi) The product may exhibit a creep rupture time of
10 1,000 hours or more and a steady state creep rate in the secondary creep of $6 \times 10^{-3} \text{ h}^{-1}$ or less by a creep test under conditions of a temperature of 900°C and a stress of 98 MPa.

(vii) The product may be a high temperature member.

(viii) The high temperature member may be a turbine
15 stator blade, a turbine rotor blade, a turbine combustor nozzle, or a heat exchanger.

ADVANTAGES OF THE INVENTION

[0014]

20 According to the present invention, there can be provided a Co based alloy product having mechanical properties comparable to or superior to those of precipitation strengthened Ni based alloy materials.

25 BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

FIG. 1 is a flow diagram showing an exemplary process of a method for manufacturing a Co based alloy product according to an embodiment of the present invention;

5 FIG. 2 is a scanning electron microscopy (SEM) image showing an exemplary microstructure of a Co based alloy additively manufactured article obtained by a selective laser melting step;

FIG. 3 is an SEM image showing an exemplary
10 microstructure of a Co based alloy product obtained by a second heat treatment step;

FIG. 4 is a schematic illustration of a perspective view showing a turbine stator blade which is a Co based alloy product as a high temperature member according to an
15 embodiment of the invention;

FIG. 5 is a schematic illustration of a cross-sectional view showing a gas turbine equipped with a Co based alloy product according to an embodiment of the invention; and

FIG. 6 is a schematic illustration of a perspective
20 view showing a heat exchanger which is another Co based alloy product as a high temperature member according to an embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

25 [0016]

[Basic Concept of the Present Invention]

As mentioned before, various research and development activities have been carried out on strengthening of Co based alloy materials by means of precipitation of a
5 carbide phase of a transition metal. Examples of the carbide phase that can be precipitated include MC type, M_2C type, M_3C type, M_6C type, M_7C type, and $M_{23}C_6$ type carbide phases. Meanwhile, in the types of carbide phases "M" means a transition metal and "C" means carbon, as described
10 before.

[0017]

In the conventional Co based alloy materials, particles of the carbide phases often precipitate along final solidification portions (e.g. dendrite boundaries, crystal
15 grain boundaries, etc. of the matrix phase) at the casting stages of the Co based alloys. In a general cast material of a Co based alloy, for example, the average spacing between dendrite boundaries and the average crystal grain size are on the order of 10^1 to 10^2 μm , and therefore the
20 average spacing between carbide phase particles is also on the order of 10^1 to 10^2 μm . Furthermore, even with the relatively fast solidification rate of laser welding, for example, the average spacing between carbide phase particles at the solidified portions is around 5 μm .

25 [0018]

Precipitation strengthening in alloys is generally known to be inversely proportional to the average spacing between precipitates, and it is considered that precipitation strengthening is effective only when the
5 average spacing between precipitates is around 2 μm or less. However, with the above-mentioned conventional technology, the average spacing between precipitates has not reached this level in a Co based alloy material, and sufficient precipitation strengthening effect has not been achieved.
10 In other words, with the conventional technology, it has been difficult to finely and dispersedly precipitate carbide phase particles that might contribute to strengthening alloys. This would be the main factor behind the fact that Co based alloy materials have been said to
15 have mechanical properties inferior to those of precipitation-strengthened Ni based alloy materials.

[0019]

The present inventors thought that if they were able to dispersedly precipitate carbide phase particles
20 contributing to precipitation strengthening in the matrix phase crystal grains, they would be able to dramatically improve mechanical properties of Co based alloy materials.

[0020]

In the initial stages of the research, the inventors
25 had considered that it would be effective to generate a

carbide phase of a metal element that is highly solid soluble and hardly segregate in the Co based alloy matrix phase, so that the carbide phase was easy to precipitate dispersedly in the matrix phase crystal grains. However, 5 precipitation of the Cr carbide phase (in this case, Cr_{23}C_6 phase) was not so effective to strengthen the Co based alloy material. Then, as an idea of reversal, the inventors considered to intentionally form carbides of metal elements having tendency to segregate at the solidification stages 10 of the Co based alloys. The inventors focused on the atomic radii of metal elements constituting the Co based alloys.

[0021]

For example, the Co based alloy disclosed in Patent Literature 1 includes, as a metal element, Co (atomic 15 radius: 125 pm), Cr (atomic radius: 128 pm), Ni (atomic radius: 124 pm), W (atomic radius: 139 pm), Mo (atomic radius: 139 pm), Nb (atomic radius: 146 pm), Zr (atomic radius: 160 pm), Ta (atomic radius: 146 pm), Ti (atomic radius: 147 pm), and Al (atomic radius: 143 pm). In the Co 20 based alloy of Patent Literature 1, since more than 70% by mass is made from Co, Cr and Ni, the atomic radius of most constituent atoms of the alloy is 130 pm or less. In other words, it was considered that each of W, Mo, Nb, Zr, Ta, Ti and Al having the atomic radius of more than 130 pm might 25 be easy to segregate at the solidification stage of the Co

based alloy. And then, the inventors carried out the research on a method for dispersedly precipitating the carbide phases of these transition metals except Al in the matrix phase crystal grains.

5 [0022]

As a result, the inventors found that segregation cells with a small size were formed, in which specific components (components forming carbide phases contributing to alloy strengthening) were segregated, in the matrix phase crystal grains of a Co based alloy additively manufactured article by means of optimizing the alloy composition and controlling the amount of heat input for local melting and rapid solidification in an additive manufacturing method (in particular, selective laser melting), as described in Patent Literature 2 (JP 2019-049022 A). Also, they found that particles of precipitation reinforcing carbide phase were dispersedly precipitated at portions assumed to be the triple points/quadruple points of the boundary regions among the segregation cells. And then, it was confirmed that such Co based alloy material had the mechanical properties comparable to or superior to those of precipitation strengthened Ni based alloy materials.

20 [0023]

The inventors continued to study the optimizations of the alloy composition and the manufacturing method.

Consequently, it has been revealed that the mechanical properties of Co based alloy material are further improved in the alloy composition with high nitrogen content which was considered undesirable at the time of study of Patent Literature 2. The present invention has been made based on these findings.

[0024]

Preferred embodiments of the invention will be hereinafter described along a manufacturing procedure with reference to the accompanying drawings.

[0025]

[Method for Manufacturing Co Based Alloy Product]

FIG. 1 is a flow diagram showing an exemplary process of a method for manufacturing a Co based alloy product according to an embodiment of the invention. As shown in FIG. 1, the method for manufacturing a Co based alloy product roughly includes: an alloy powder preparation step S1 of preparing a Co based alloy powder; a selective laser melting step S2 of forming the prepared Co based alloy powder into an AM article with a desired shape; a first heat treatment step S3 of subjecting the formed AM article to a first heat treatment; and a second heat treatment step S4 of subjecting the first heat treated AM article to a second heat treatment.

[0026]

Although the manufacturing procedure shown in FIG. 1 is roughly similar to that of Patent Literature 2, there is a difference between Patent Literature 2 and the invention in controlling the amount (existence ratio) of nitrogen atoms
5 in the atmosphere during the alloy powder preparation step S1 in order to control the nitrogen content in Co based alloy. Furthermore, a Co based alloy product of the invention may be an article that is applied a corrosion resistant coating layer formation step and/or a surface
10 finishing step, not shown in FIG. 1, to the article obtained by the second heat treatment step S4.

[0027]

Each step will be hereinafter described in more detail.

[0028]

15 (Alloy Powder Preparation Step)

In the step S1, a Co based alloy powder having a predetermined chemical composition is prepared. The chemical composition preferably includes: 0.08 to 0.25 mass % of C; more than 0.04 mass % and 0.2 mass % or less
20 of N, the total amount of the C and the N being more than 0.12 mass % and 0.28 mass % or less; 0.1 mass % or less of B; 10 to 30 mass % of Cr; 5 mass % or less of Fe and 30 mass % or less of Ni, the total amount of the Fe and the Ni being 30 mass % or less; W and/or Mo, the total amount of
25 the W and the Mo being 5 to 12 mass %; 0.5 mass % or less

of Si; 0.5 mass % or less of Mn; 0.5 to 2 mass % of an M component being a transition metal other than W and Mo and having an atomic radius of more than 130 pm; and the balance being Co and impurities. As impurities, 0.5 mass %
5 or less of Al and 0.04 mass % or less of O may be included.

[0029]

C: 0.08 to 0.25 mass %

The C component is an important component that constitutes an MC type carbide phase (carbide phase of Ti,
10 Zr, Hf, V, Nb and/or Ta) and/or an M(C,N) type carbonitride phase (carbonitride phase of Ti, Zr, V, Nb and/or Ta) to serve as a precipitation strengthening phase. The content of the C component is preferably 0.08 to 0.25 mass %, more preferably 0.1 to 0.2 mass %, and even more preferably 0.12
15 to 0.18 mass %. When the C content is less than 0.08 mass %, the amount of precipitation of the precipitation strengthening phase (MC type carbide phase and/or M(C,N) type carbonitride phase) is insufficient, resulting in an insufficient effect of improving the mechanical properties.
20 By contrast, when the C content is over 0.25 mass %, carbide phases other than the MC type carbide phase precipitate excessively, and/or the alloy material becomes excessively hard, which leads to deteriorated toughness.

[0030]

25 N: more than 0.04 mass % and 0.2 mass % or less

The N component is an important component that constitutes the M(C,N) type carbonitride phase and/or an MN type nitride phase (nitride phase of Ti, Zr, V, Nb and/or Ta). The content of the N component is preferably more than
5 0.04 mass % and 0.2 mass % or less, more preferably 0.06 to 0.19 mass %, and even more preferably 0.13 to 0.18 mass %. When the N content is 0.04 mass % or less, while the advantageous effects of precipitation of the M(C,N) type carbonitride phase and/or the MN type nitride phase are
10 insufficient, there is no particular problem (only becoming the same as Patent Literature 2). In contrast, when the N content is over 0.2 mass %, the mechanical properties of the final product would deteriorate.

[0031]

15 Mechanism of improving the mechanical properties of Co based alloy materials at a higher N content than before has not been clarified at the present. However, by coexisting the C and N components in pointful amounts, it would be possible that the MC type carbide phase, the M(C,N) type
20 carbonitride phase and/or the MN type nitride phase are formed well-balanced and stably, and contribute to dispersed precipitation. The total amount of the C and the N is preferably more than 0.12 mass % and 0.28 mass % or less, more preferably 0.16 to 0.25 mass %.

25 [0032]

B: 0.1 mass % or less

The B component contributes to improving bondability between crystal grain boundaries (so-called grain boundary strengthening). Although the B is not an essential

5 component, when it is contained in the alloy, the content of the B component is preferably 0.1 mass % or less and more preferably 0.005 to 0.05 mass %. When the B component is over 0.1 mass%, cracking (e.g. solidification cracking) is prone to occur during formation of the AM article.

10 [0033]

Cr: 10 to 30 mass %

The Cr component contributes to improving corrosion resistance and oxidation resistance. The content of the Cr component is preferably 10 to 30 mass % and more preferably

15 15 to 27 mass %. In the case where a corrosion resistant coating layer is provided on the outermost surface of the Co based alloy product, the content of the Cr component is even more preferably 10 to 18 mass %. When the Cr content is less than 10 mass %, advantageous effects such as

20 improvements of the corrosion resistance and the oxidation resistance are insufficient. When the Cr content is over 30 mass %, the brittle σ phase and/or the excessive amount of Cr carbide phase are generated, resulting in deteriorated mechanical properties (i.e. toughness, ductility, strength,

25 etc.). Meanwhile, in the invention Cr carbide phase

generation itself in the article is not denied.

[0034]

Ni: 30 mass % or less

Being similar to Co component in properties but less
5 expensive than Co, the Ni component may be used to replace
part of the Co component. Although the Ni is not an
essential component, when it is contained in the alloy, the
content of the Ni component is preferably 30 mass % or less,
more preferably 20 mass % or less, and even more preferably
10 5 to 15 mass %. When the Ni content is over 30 mass %, the
abrasion resistance and the local stress resistance, which
are characteristics of Co based alloys, deteriorate. This
is attributable to the difference in stacking fault energy
between Co and Ni.

15 [0035]

Fe: 5 mass % or less

Being much less expensive than Ni and similar to Ni
component in properties, the Fe component may be used to
replace part of the Ni component. The total content of the
20 Fe and Ni is preferably 30 mass % or less, more preferably
20 mass % or less, and even more preferably 5 to 15 mass %.
Although the Fe is not an essential component, when it is
contained in the alloy, the content of the Fe component is
preferably 5 mass % or less and more preferably 3 mass % or
25 less in the range less than the Ni content. When the Fe

content is over 5 mass %, the corrosion resistance and mechanical properties deteriorate.

[0036]

W and/or Mo: 5 to 12 mass % in total

5 The W component and the Mo component contribute to solution-strengthening the matrix. The total content of the W component and/or the Mo component (at least one of W and Mo components) is preferably 5 to 12 mass % and more preferably 7 to 10 mass %. When the total content of the W
10 component and the Mo component is less than 5 mass %, the solution strengthening of the matrix is insufficient. In contrast, when the total content of the W component and the Mo component is over 12 mass %, the brittle σ phase tends to be generated easily, resulting in deteriorated
15 mechanical properties (i.e. toughness, ductility, etc.).

[0037]

Re: 2 mass % or less

 The Re component contributes to solution-strengthening the matrix and improving corrosion resistance. Although the
20 Re is not an essential component, when it is contained in the alloy to replace part of the W component or the Mo component, the content of the Re component is preferably 2 mass % or less and more preferably 0.5 to 1.5 mass %. When the Re content is over 2 mass %, the advantageous effects
25 of the Re component become saturated, and the material

costs become too high.

[0038]

M component of transition metal other than W and Mo and
with atomic radius of more than 130 pm: 0.5 to 2 mass % in
5 total

As an M component being a transition metal other than W
and Mo, having an atomic radius of more than 130 pm, and
being capable to forming an MC type carbide phase of a
simple cubic crystal system, there can be listed Ti, Zr, Hf,
10 V, Nb and Ta components. These MC type carbide phases could
become a precipitation strengthening (reinforcing) phase
for the product of the invention. In addition, there can be
listed Ti, Zr, V, Nb and Ta components as a component being
capable to forming an MN type nitride phase. These MN type
15 nitride phases could also become the precipitation
strengthening phase. Moreover, the Ti, Zr, V, Nb and Ta
components could form an M(C,N) type carbonitride phase of
the precipitation strengthening phase.

[0039]

20 In other words, it is preferable that at least one of
the Ti, Zr, Hf, V, Nb and Ta components is included. The
total content of the Ti, Zr, Hf, V, Nb and Ta components is
preferably 0.5 to 2 mass % and more preferably 0.5 to 1.8
mass %. When the total content is less than 0.5 mass %, the
25 amount of precipitation of the precipitation strengthening

phases such as the MC type carbide phase, the M(C,N) type carbonitride phase and/or the MN type nitride phase is insufficient, and, as a result, the effect of improving the mechanical properties is insufficient. In contrast, when
5 the total content is over 2 mass %, the mechanical properties deteriorate due to coarsening of the particles of the precipitation strengthening phase, accelerated generation of a brittle phase (e.g. σ phase), generation of particles of an oxide phase that does not contribute to
10 precipitation strengthening, etc.

[0040]

Furthermore, in the viewpoints of dispersed precipitation of particles of the precipitation strengthening phase (suppression of coarsening of the
15 precipitation strengthening phase particles), it is more preferable that three or more of the Ti, Zr, Hf, V, Nb and Ta elements are contained in the alloy, and even more preferably four or more.

[0041]

20 More specifically, when the Ti component is included the Ti content is preferably 0.01 to 1 mass % and more preferably 0.05 to 0.8 mass %.

[0042]

When the Zr component is included, the Zr content is
25 preferably 0.05 to 1.5 mass % and more preferably 0.1 to

1.2 mass %. From the viewpoint of the mechanical strength, it is preferable that the Zr component is included. In contrast, from the viewpoint of the toughness, it is preferable that the Zr component is not included.

5 [0043]

When the Hf component is included, the Hf content is preferably 0.01 to 0.5 mass % and more preferably 0.02 to 0.1 mass %.

[0044]

10 When the V component is included, the V content is preferably 0.01 to 0.5 mass % and more preferably 0.02 to 0.1 mass %.

[0045]

When the Nb component is included, the Nb content is
15 preferably 0.02 to 1 mass % and more preferably 0.05 to 0.8 mass %.

[0046]

When the Ta component is included, the Ta content is preferably 0.05 to 1.5 mass % and more preferably 0.1 to
20 1.2 mass %.

[0047]

Si: 0.5 mass % or less

The Si component serves as a deoxidant agent and contributes to improving the mechanical properties.

25 Although the Si is not an essential component, when it is

contained in the alloy, the content of the Si component is preferably 0.5 mass % or less and more preferably 0.01 to 0.3 mass %. When the Si content is over 0.5 mass %, coarse grains of an oxide (e.g. SiO_2) are generated, which causes
5 deterioration of the mechanical properties.

[0048]

Mn: 0.5 mass % or less

The Mn component serves as a deoxidant agent and a desulfurizing agent and contributes to improving the
10 mechanical properties and the corrosion resistance. The Mn is not included in the above-described M component since the Mn has the atomic radius of 127 pm. Although the Mn is not an essential component, when it is contained in the alloy, the content of the Mn component is preferably 0.5
15 mass % or less and more preferably 0.01 to 0.3 mass %. When the Mn content is over 0.5 mass %, coarse grains of a sulfide (e.g. MnS) are generated, which causes deterioration of the mechanical properties and the corrosion resistance.

20 [0049]

Balance: Co component and Impurities

The Co component is one of the key components of the alloy and its content is the largest of all the components. As mentioned above, Co based alloy materials have the
25 advantages of having corrosion resistance and abrasion

resistance comparable to or superior to those of Ni based alloy materials.

[0050]

The Al component is one of the impurities of the alloy
5 and is not to be intentionally included in the alloy.

However, an Al content of 0.5 mass % or less is acceptable as it does not have any serious negative influence on the mechanical properties of the Co based alloy product. When the Al content is over 0.5 mass %, coarse grains of an
10 oxide or nitride (e.g. Al_2O_3 or AlN) are generated, which causes deterioration of the mechanical properties.

[0051]

The O component is also one of the impurities of the alloy and is not to be intentionally included in the alloy.
15 However, an O content of 0.04 mass % or less is acceptable as it does not have any serious negative influence on the mechanical properties of the Co based alloy product. When the O content is over 0.04 mass %, coarse grains of each oxide (e.g. Ti oxide, Zr oxide, Al oxide, Fe oxide, Si
20 oxide, etc.) are generated, which causes deterioration of the mechanical properties.

[0052]

The alloy powder preparation step S1 is a step of preparing a Co based alloy powder having a predetermined
25 chemical composition, in particular the predetermined

nitrogen content. There is no particular limitation on the method and techniques for preparing the Co based alloy powder, and any conventional method and technique may be used. For example, a master ingot manufacturing substep S1a
5 of manufacturing a master ingot by mixing, melting and casting the raw materials such that the ingot has a desired chemical composition and an atomization substep S1b of forming the alloy powder from the master ingot may be performed.

10 [0053]

It is preferable that controlling the nitrogen content is conducted in the atomization substep S1b. As an atomization method, any conventional method and technique may be used except for controlling the nitrogen content in
15 the Co based alloy. For example, gas atomizing or centrifugal force atomizing with controlling the amount of nitrogen (nitrogen partial pressure) in the atomization atmosphere may be preferably used.

[0054]

20 Furthermore, after the atomization substep S1b, a nitriding heat treatment substep S1c may be performed in which the alloy powder is subjected to a nitriding heat treatment (e.g., a heat treatment at 300°C or higher and 520°C or lower in an ammonia gas atmosphere) as needed. As
25 the ammonia gas atmosphere, a mixed gas of ammonia (NH₃) gas

and N₂ gas or a mixed gas of NH₃ gas and hydrogen (H₂) gas can be preferably used.

[0055]

For ease of handling and ease of filling the alloy
5 powder bed in the following selective laser melting step S2,
the particle size of the alloy powder is preferably 5 to
100 μm, more preferably 10 to 70 μm, and even more
preferably 10 to 50 μm. When the particle size of the alloy
powder is less than 5 μm, fluidity of the alloy powder
10 decreases in the following step S2 (i.e. formability of the
alloy powder bed decreases), which causes deterioration of
shape accuracy of the AM article. In contrast, when the
particle size of the alloy powder is over 100 μm,
controlling the local melting and rapid solidification of
15 the alloy powder bed in the following step S2 becomes
difficult, which leads to insufficient melting of the alloy
powder and increased surface roughness of the AM article.

[0056]

In view of the above, an alloy powder classification
20 substep S1d is preferably performed so as to regulate the
alloy powder particle size to 5 to 100 μm. In the invention,
when the particle size distribution of the obtained alloy
powder is observed to fall within the desired range, it is
assumed that the substep S1d has been performed. The alloy
25 powder manufactured by the alloy powder preparation step S1

is one of a Co based alloy material according to the invention.

[0057]

(Selective Laser Melting Step)

5 The selective laser melting step S2 is a step of forming an AM article with a desired shape by selective laser melting (SLM) using the prepared Co based alloy. Specifically, this step comprises alternate repetition of an alloy powder bed preparation substep S2a and a laser
10 melting solidification substep S2b. In the step S2a, the Co based alloy powder is laid such that it forms an alloy powder bed having a predetermined thickness, and in the step S2b, a predetermined region of the alloy powder bed is irradiated with a laser beam to locally melt and rapidly
15 solidify the Co based alloy powder in the region.

[0058]

 In this step S2, in order to obtain a finished Co based alloy product having a desired microstructure (a microstructure in which particles of the precipitation
20 strengthening phases such as the MC type carbide phase, the M(C,N) type carbonitride phase and/or the MN type nitride phase are dispersedly precipitated in the matrix phase crystal grains), the microstructure of the AM article, which is a precursor of the finished product, is controlled
25 by controlling the local melting and the rapid

solidification of the alloy powder bed.

[0059]

More specifically, the thickness of the alloy powder bed h (unit: μm), the output power of the laser beam P (unit: W), and the scanning speed of the laser beam S (unit: mm/s) are preferably controlled to satisfy the following formulas: " $15 < h < 150$ " and " $67 \times (P/S) - 3.5 < h < 2222 \times (P/S) + 13$ ". When these formulas are not satisfied, an AM article having a desired microstructure cannot be obtained.

[0060]

While the output power P and the scanning speed S of the laser beam basically depend on configurations of the laser apparatus, they may be determined so as to satisfy the following formulas: " $10 \leq P \leq 1000$ " and " $10 \leq S \leq 7000$ ".

[0061]

FIG. 2 is a scanning electron microscopy (SEM) image showing an exemplary microstructure of the Co based alloy AM article obtained by the SLM step S2. As shown in FIG. 2, the Co based alloy AM article obtained by the SLM step S2 have a unique microstructure.

[0062]

The AM article is a polycrystalline body of matrix phase crystal grains. In the matrix phase crystal grains of the polycrystalline body, segregation cells with an average

size of 0.13 to 2 μm are formed. In the viewpoint of the mechanical strength, segregation cells with an average size of 0.15 to 1.5 μm are more preferable. It may be recognized that particles of the precipitation strengthening phases
5 are precipitated on a part of boundary regions of the segregation cells. In addition, from various experiments by the inventors, it can be recognized that the matrix phase crystal grains with an average size of 5 to 150 μm are preferable.

10 [0063]

In the present invention, the size of segregation cells is basically defined as the average of the long diameter and the short diameter. However, when an aspect ratio of the longer diameter and the short diameter is three or more,
15 twice the short diameter may be adopted as the size of segregation cell. Furthermore, in the invention the average spacing of the particles of the precipitation strengthening phases is defined as being represented by the size of the segregation cell because the particles are precipitated on
20 the boundary region of the segregation cell.

[0064]

A more detailed microstructure observation by scanning transmission electron microscopy-energy dispersive X-ray spectrometry (STEM-EDX) has revealed that the components
25 constituting the precipitation strengthening phases (Ti, Zr,

Hf, V, Nb, Ta, C and N) segregate in the boundary regions between the neighboring segregation cells (i.e. in outer peripheral regions of micro-cells, similar to cell walls). It has also been observed that particles precipitating on
5 the boundary regions among these segregation cells are particles of the precipitation strengthening phases.

[0065]

Meanwhile, the segregation of the M components constituting the precipitation strengthening phases and the
10 precipitation of particles of the precipitation strengthening phases can be observed also on the grain boundaries of the matrix phase crystal grains. The AM article manufactured by the selective laser melting step S2 is one aspect of a Co based alloy product according to the
15 invention.

[0066]

(First Heat Treatment Step)

The first heat treatment step S3 is a step subjecting the formed Co based alloy AM article to a first heat
20 treatment. The first heat treatment is preferably performed at temperatures ranging from 1,100°C to 1,200°C. Holding duration of the heat treatment may be appropriately set in a range of 0.5 hour or more and 10 hours or less in consideration of the heat capacity and the temperature of
25 the AM article to be heat treated. There is no particular

limitation on a cooling method after the first heat treatment, and water cooling, oil cooling, air cooling, or furnace cooling may be adopted.

[0067]

5 By the first heat treatment, it has been found that the components segregated in the boundary regions of the segregation cells begin to diffuse, combine and form the precipitation strengthening phases on/along the boundary regions, and as a result, the segregation cells almost
10 disappear (more precisely, cell walls of the segregation cells become difficult to be observed by the microstructure observation). The aggregation points starting to form the precipitation strengthening phases are considered to be on former boundaries of the segregation cell (on regions
15 assumed of the cell walls existed former), which causes the fine dispersion of the precipitation strengthening phases throughout the matrix phase crystal grains (within each crystal grain and on the crystal grain boundaries).

In addition, during the first heat treatment the matrix
20 phase crystal grains of the AM article recrystallize, thereby capable of relaxing the residual internal strain in the AM article that has possibly generated by a rapid cooling solidification in the SLM step S2. Consequently, undesirable deformations can be prevented in the latter
25 steps of the manufacturing method and during use of the

final alloy product.

[0068]

(Second Heat Treatment Step)

The second heat treatment step S4 is a step subjecting
5 the Co based alloy AM article heat-treated by the step S3
to a second heat treatment. The second heat treatment is
preferably performed at temperatures ranging from 750°C to
1,000°C. Holding duration of the heat treatment may be
appropriately set in a range of 0.5 hour or more and 20
10 hours or less in consideration of the heat capacity and the
temperature of the AM article to be heat treated. There is
no particular limitation on a cooling method after the
second heat treatment, and water cooling, oil cooling, air
cooling, or furnace cooling may be adopted.

15 [0069]

FIG. 3 is an SEM image showing an exemplary
microstructure of a Co based alloy product obtained by the
second heat treatment step S4. As shown in FIG. 3, by the
second heat treatment, it is possible to obtain a
20 microstructure in which the particles of the precipitation
strengthening phases are finely and dispersedly
precipitated within the matrix phase crystal grains while
suppressing the coarsening of the matrix phase crystal
grains. In other words, the Co based alloy product obtained
25 through the second heat treatment step S4 shows a

microstructure having the matrix phase crystal grains with an average size of 5 to 150 μm and the particles of the precipitation strengthening phases finely and dispersedly precipitated in each matrix phase crystal grain at an average interparticle distance of 0.13 to 2 μm . Meanwhile, the particles of the precipitation strengthening phases are dispersedly precipitated also on the grain boundaries of the matrix phase crystal grains in the Co based alloy product, as mentioned before.

10 [0070]

As a result of STEM-EDX analysis, it has been confirmed that the precipitation strengthening phases are regarded as the MC type carbide phase, the M(C,N) type carbonitride phase and/or the MN type nitride phase based on the Ti, Zr, Hf, V, Nb and/or Ta.

[0071]

(Co Based Alloy Product)

FIG. 4 is a schematic illustration of a perspective view showing a turbine stator blade which is a Co based alloy product as a high temperature member according to an embodiment of the invention. As shown in FIG. 4, the turbine stator blade 100 includes an inner ring side end wall 101, a blade part 102, and an outer ring side end wall 103. Inside the blade part 102 is often formed a cooling structure.

[0072]

Meanwhile, a Co based alloy product of the invention can be used as a turbine rotor blade.

[0073]

5 FIG. 5 is a schematic illustration of a cross-sectional view showing a gas turbine equipped with a Co based alloy product according to an embodiment of the invention. As shown in FIG. 5, the gas turbine 200 roughly includes a compression part 210 for compressing intake air and a
10 turbine part 220 for blowing combustion gas of a fuel on turbine blades to obtain rotation power. The high temperature member according to the embodiment of the invention can be preferably used as a turbine nozzle 221 or the turbine stator blade 100 inside the turbine part 220.
15 The high temperature member according to the embodiment of the invention is not limited to gas turbine applications but may be used for other turbine applications (e.g. steam turbines) and component used under high temperature environment in other machines/apparatuses.

20 [0074]

FIG. 6 is a schematic illustration of a perspective view showing a heat exchanger which is another Co based alloy product as a high temperature member according to an embodiment of the invention. A heat exchanger 300 shown in
25 FIG. 6 is an example of a plate-fin type heat exchanger,

and has a basic structure in which a separation layer 301 and a fin layer 302 are alternatively stacked each other. Both ends in the width direction of flow channels in the fin layer 302 are sealed by a side bar portion 303. Heat
5 exchanging between high temperature fluid and low temperature fluid can be done by flowing the high temperature fluid and the low temperature fluid alternately into adjacent fin layers 302 via the separation layer 301.

[0075]

10 A heat exchanger 300 according to an embodiment of the invention is formed integrally without soldering joining or welding joining the conventional parts constituting a heat exchanger such as separation plates, corrugated fins and side bars. Consequently, the heat exchanger 300 has
15 advantages improving heat resistance and weight reduction than the conventional heat exchangers. In addition, the heat transfer efficiency can be higher by forming an appropriate concavo-convex pattern on the surfaces of the flow channels and making the fluid into turbulence.
20 Improving the heat transfer efficiency leads to downsizing of the heat exchanger.

EXAMPLES

[0076]

25 The present invention will be hereinafter described in

more detail with experimental examples. It should be noted that the invention is not limited to these examples.

[0077]

(Preparation of Co Based Alloy Powders IA-1, IA-2 and
5 RA-1)

Co based alloy powders having the chemical compositions shown in Table 1 were prepared (alloy powder preparation step S1). Specifically, first, the master ingot manufacturing substep S1a was performed, in which the raw
10 materials were mixed and subjected to melting and casting by a vacuum high frequency induction melting method so as to form a master ingot (weight: approximately 2 kg) for each powder. Next, the atomization substep S1b was performed to form each alloy powder. In the substep S1b,
15 each master ingot was remelted and subjected to gas atomizing in a N₂ gas atmosphere. The alloy powder IA-2 was further performed to the nitriding heat treatment substep S1c in which a heat treatment at 500°C in a mixed atmosphere of NH₃ gas and N₂ gas was conducted, after the
20 atomization substep S1b. In addition, as a reference sample, a reference alloy powder RA-1 was prepared separately by performing the atomization substep S1b with the gas atomizing method in an argon gas atmosphere.

[0078]

25 Then, each alloy powder thus obtained was subjected to

the alloy powder classification substep S1c to control the particle size of alloy powder. Each alloy powder was classified into an alloy powder with a particle size of 5 to 25 μm .

[0079]

TABLE 1 Chemical Compositions of Co Based Alloy Powders IA-1, IA-2 and RA-1.

Alloy Powder	Chemical Composition (mass %)																		
	C	N	B	Cr	Ni	Fe	W	Ti	Zr	Hf	V	Nb	Ta	Si	Mn	Co	Al	O	Ti+Zr+Hf+ V+Nb+Ta
IA-1	0.12	0.067	0.009	24.7	10.4	0.01	7.5	0.22	0.45	-	-	0.11	0.30	0.01	0.01	Bal.	0.01	0.005	1.08
IA-2	0.09	0.17	0.011	25.5	10.3	0.90	7.4	0.20	0.60	0.02	0.05	0.15	0.40	0.30	0.20	Bal.	0.06	0.020	1.42
RA-1	0.16	0.005	0.01	25.0	10.0	0.01	7.5	0.21	0.50	-	-	0.10	0.28	0.01	0.01	Bal.	0.01	0.005	1.09

“-” indicates that the element was not intentionally included.

“Bal.” indicates inclusion of impurities other than Al and O.

[0080]

As shown in Table 1, the inventive alloy powders IA-1 and IA-2 have chemical compositions that satisfy the specifications of the invention. In contrast, the reference
5 alloy powder RA-1 is an alloy powder corresponding to Patent Literature 2, and only the N content is out of the specifications of the invention.

[0081]

[Experiment 2]

10 (Examination of SLM Conditions in Selective Laser Melting Step)

AM articles (8 mm in diameter × 10 mm in length) were formed of the alloy powder IA-1 prepared in Experiment 1 by the SLM process (selective laser melting step S2). The
15 output power of the laser beam P was set at 85 W, and the local heat input P/S (unit: W × s/mm = J/mm) was controlled by varying the thickness of the alloy powder bed h and the scanning speed (mm/s) of the laser beam S. Controlling the local heat input corresponds to controlling the cooling
20 rate.

[0082]

The AM articles formed above were each subjected to microstructure observation to measure the average segregation cell size. The microstructure observation was
25 performed by SEM. Also, the obtained SEM images were

subjected to image analysis using an image processing program (ImageJ, a public domain program developed at the National Institutes of Health in U.S.A., NIH) to measure the average size of segregation cells.

5 [0083]

The AM articles having an average segregation cell size within a range of 0.13 to 2 μm were judged as "Passed", and the other AM articles were judged as "Failed". Based on the results of the measurement, it has been confirmed that in
10 the selective laser melting step S2, the SLM process is preferably performed while controlling the thickness of the alloy powder bed h (unit: μm), the output power of the laser beam P (unit: W), and the scanning speed of the laser beam S (unit: mm/s) such that they satisfy the following
15 formulas: " $15 < h < 150$ " and " $67 \times (P/S) - 3.5 < h < 2222 \times (P/S) + 13$ ".

[0084]

[Experiment 3]

(Manufacturing of Co Based Alloy Products IAP-1, IAP-2
20 and RAP-1)

An AM article (10 mm in diameter $\times$ 50 mm in length) was formed of each of the inventive alloy powders IA-1 and IA-2 and the reference alloy powder RA-1 prepared in Experiment 1 by the SLM process (selective laser melting step S2). The
25 thickness of each alloy powder bed h and the output power

of the laser beam P were set at 100 μm and 100 W,
respectively. The local heat input P/S (unit: $\text{W} \times \text{s}/\text{mm} =$
J/mm) was controlled by varying the scanning speed (mm/s)
of the laser beam S so as to satisfy the passing conditions
5 examined in Experiment 2.

[0085]

Each AM article formed above was subjected to a heat
treatment at 1,150°C with a holding duration of 4 hours
(first heat treatment step S3). Next, each AM article
10 first-heat-treated above was subjected to another heat
treatment at 900°C with a holding duration of 4 hours
(second heat treatment step S4) to manufacture Co based
alloy products IAP-1 and IAP-2 formed of the alloy powders
IA-1 and IA-2 and Co based alloy product RAP-1 formed of
15 the alloy powder RA-1.

[0086]

(Microstructure Observation and Mechanical Properties
Testing)

Test pieces for microstructure observation and
20 mechanical properties testing were taken from the Co based
alloy products IAP-1, IAP-2 and RAP-1 and subjected to
microstructure observation and mechanical properties
testing.

[0087]

25 The microstructure observation was performed by SEM and

through image analysis of SEM images thereof in a similar manner to Experiment 2 to measure the average interparticle distance of the precipitation strengthening phase particles in the matrix phase crystal grains. As the results , it has
5 been confirmed that the average interparticle distance of the precipitation strengthening phase particles is within a range from 0.13 to 2 μm in all of the Co based alloy products IAP-1, IAP-2 and RAP-1.

[0088]

10 As to the mechanical properties testing, the Co based alloy product IAP-1 and RAP-1 were subjected to a creep test at 850°C under a stress of 157 MPa to measure the steady state creep rate in the secondary creep region (steady state creep region) and the creep rupture time.
15 Similarly, the Co based alloy product IAP-2 and RAP-1 were subjected to a creep test at 900°C under a stress of 98 MPa to measure the steady state creep rate and the creep rupture time.

[0089]

20 From the description of Patent Literature 2, it can be considered that the reference alloy product RAP-1 has mechanical properties equal to or higher than those of a precipitation strengthened Ni based alloy material. Then, in this experiment, the creep property of a steady state
25 creep rate lower than and a creep rupture time longer than

the reference alloy product RAP-1 was judged as "Passed". Furthermore, the creep property of a steady state creep rate of $6 \times 10^{-3} \text{ h}^{-1}$ or less and a creep rupture time of 1,000 hours or more by the creep test at 900°C under a stress of 98 MPa was judged as "Excellent". The results of the mechanical properties testing are shown in Table 2.

[0090]

Table 2 Creep Testing Results of Co Based Alloy Products IAP-1, IAP-2 and RAP-1.

Alloy Product No.	Alloy Powder No.	Creep Testing Conditions		Steady State Creep Rate (h^{-1})	Creep Rupture Time (h)	Evaluation
		Temperature ($^{\circ}\text{C}$)	Stress (MPa)			
IAP-1	IA-1	850	157	1.62×10^{-2}	362	Passed
IAP-2	IA-2	900	98	4.53×10^{-3}	1105	Excellent
RAP-1	RA-1	850	157	3.25×10^{-2}	267	
		900	98	7.03×10^{-3}	897	

[0091]

As shown in Table 2, the inventive alloy products IAP-1 and IAP-2 exhibit a steady creep rate lower than and a creep rupture time longer than those of the reference alloy product RAP-1, and are evaluated as "Passed". Moreover, the inventive alloy product IAP-2 exhibit a steady creep rate of $6 \times 10^{-3} \text{ h}^{-1}$ or less and a creep rupture time of 1,000 hours or more, and is evaluated as "Excellent".

[0092]

The above-described embodiments and experimental

examples have been specifically given in order to help with understanding on the present invention, but the invention is not limited to the described embodiments and experimental examples. For example, a part of an embodiment
5 may be replaced by known art, or added with known art. That is, a part of an embodiment of the invention may be combined with known art and modified based on known art, as far as no departing from a technical concept of the invention.

10

LEGEND

[0093]

100 ... turbine stator blade;

101 ... inner ring side end wall;

15 102 ... blade part;

103 ... outer ring side end wall;

200 ... gas turbine;

210 ... compression part;

220 ... turbine part;

20 221 ... turbine nozzle;

300 ... heat exchanger;

301 ... separation layer;

302 ... fin layer; and

303 ... side bar portion.

25

CLAIMS

[Claim 1]

A product formed of a cobalt based alloy material,
having a chemical composition comprising:

5 0.08 to 0.25 mass % of carbon;

more than 0.04 mass % and 0.2 mass % or less of
nitrogen, the total amount of the carbon and the nitrogen
being more than 0.12 mass % and 0.28 mass % or less;

0.1 mass % or less of boron;

10 10 to 30 mass % of chromium;

5 mass % or less of iron, 30 mass % or less of nickel,
the total amount of the iron and the nickel being 30 mass %
or less;

tungsten and/or molybdenum, the total amount of the
15 tungsten and the molybdenum being 5 to 12 mass %;

0.5 mass % or less of silicon;

0.5 mass % or less of manganese;

0.5 to 2 mass % of an M component being a transition
metal other than tungsten and molybdenum and having an
20 atomic radius of more than 130 pm; and

the balance being cobalt and impurities, the impurities
including 0.5 mass % or less of aluminum, and 0.04 mass %
or less of oxygen,

wherein the product is a polycrystalline body of matrix
25 phase crystal grains, and

wherein particles of MC type carbide phase, M(C,N) type carbonitride phase and/or MN type nitride phase including the M component are precipitated at an average interparticle distance of 0.13 to 2 μm .

5

[Claim 2]

The product according to claim 1, wherein

the M component of the chemical composition is at least one of titanium, zirconium, hafnium, vanadium, niobium and
10 tantalum.

[Claim 3]

The product according to claim 2, wherein:

in the case that the chemical composition includes the
15 titanium as the M component, content of the titanium is
0.01 to 1 mass %;

in the case that the chemical composition includes the
zirconium as the M component, content of the zirconium is
0.05 to 1.5 mass %;

20 in the case that the chemical composition includes the
hafnium as the M component, content of the hafnium is 0.01
to 0.5 mass %;

in the case that the chemical composition includes the
vanadium as the M component, content of the vanadium is
25 0.01 to 0.5 mass %;

in the case that the chemical composition includes the niobium as the M component, content of the niobium is 0.02 to 1 mass %; and

in the case that the chemical composition includes the tantalum as the M component, content of the tantalum is 0.05 to 1.5 mass %.

[Claim 4]

The product according to claim 2 or 3, wherein the zirconium is an essential component as the M component of the chemical composition.

[Claim 5]

The product according to claim 2 or 3, wherein the M component of the chemical composition is three or more of titanium, zirconium, hafnium, vanadium, niobium and tantalum.

[Claim 6]

The product according to any one of claims 1 to 5, wherein

the product exhibits a creep rupture time of 1,000 hours or more and a steady state creep rate in the secondary creep of $6 \times 10^{-3} \text{ h}^{-1}$ or less by a creep test under conditions of a temperature of 900°C and a stress of 98 MPa.

[Claim 7]

The product according to any one of claims 1 to 6,
wherein

5 the product is a high temperature member.

[Claim 8]

The product according to claim 7, wherein
the high temperature member is a turbine stator blade,
10 a turbine rotor blade, a turbine combustor nozzle, or a
heat exchanger.

[Claim 9]

A product made of a cobalt based alloy material, having
15 a chemical composition comprising:

0.08 to 0.25 mass % of carbon;

more than 0.04 mass % and 0.2 mass % or less of
nitrogen, the total amount of the carbon and the nitrogen
being more than 0.12 mass % and 0.28 mass % or less;

20 0.1 mass % or less of boron;

10 to 30 mass % of chromium;

5 mass % or less of iron, 30 mass % or less of nickel,
the total amount of the iron and the nickel being 30 mass %
or less;

25 tungsten and/or molybdenum, the total amount of the

tungsten and the molybdenum being 5 to 12 mass %;

0.5 mass % or less of silicon;

0.5 mass % or less of manganese;

0.5 to 2 mass % of an M component being a transition
5 metal other than tungsten and molybdenum and having an
atomic radius of more than 130 pm; and

the balance being cobalt and impurities, the impurities
including 0.5 mass % or less of aluminum, and 0.04 mass %
or less of oxygen,

10 wherein the product is a polycrystalline body of matrix
phase crystal grains, and

wherein in the matrix phase crystal grains, segregation
cells with an average size of 0.13 to 2 μm are formed, in
that the M component is segregated in boundary regions of
15 the segregation cells.

[Claim 10]

The product according to claim 9, wherein

on the boundary regions of the segregation cells,
20 particles of MC type carbide phase, M(C,N) type
carbonitride phase and/or MN type nitride phase including
the M component of the chemical composition are
precipitated.

25 [Claim 11]

The product according to claim 9 or 10, wherein
the M component of the chemical composition is at least
one of titanium, zirconium, hafnium, vanadium, niobium and
tantalum.

5

[Claim 12]

The product according to claim 11, wherein:

in the case that the chemical composition includes the
titanium as the M component, content of the titanium is

10 0.01 to 1 mass %;

in the case that the chemical composition includes the
zirconium as the M component, content of the zirconium is
0.05 to 1.5 mass %;

15 in the case that the chemical composition includes the
hafnium as the M component, content of the hafnium is 0.01
to 0.5 mass %;

in the case that the chemical composition includes the
vanadium as the M component, content of the vanadium is
0.01 to 0.5 mass %;

20 in the case that the chemical composition includes the
niobium as the M component, content of the niobium is 0.02
to 1 mass %; and

in the case that the chemical composition includes the
tantalum as the M component, content of the tantalum is
25 0.05 to 1.5 mass %.

[Claim 13]

The product according to claim 11 or 12, wherein
the zirconium is an essential component as the M
5 component of the chemical composition.

[Claim 14]

The product according to claim 11 or 12, wherein
the M component of the chemical composition is three or
10 more of titanium, zirconium, hafnium, vanadium, niobium and
tantalum.