(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 772 544 A1

(12) # EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
10.02.2021 Bulletin 2021/06

(21) Application number: **19764769.6**

(22) Date of filing: **25.02.2019**

(51) Int Cl.:
C22F 1/10 (2006.01) ***C22C 19/05*** (2006.01)
C22F 1/00 (2006.01)

(86) International application number:
PCT/JP2019/006991

(87) International publication number:
WO 2019/172000 (12.09.2019 Gazette 2019/37)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **06.03.2018 JP 2018039400**

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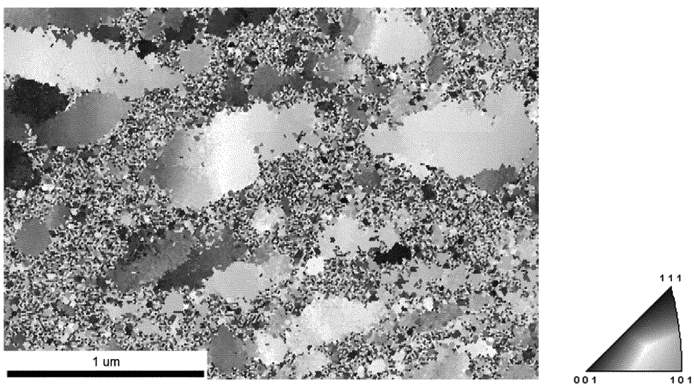
(54) **METHOD FOR MANUFACTURING SUPER-REFRACTORY NICKEL-BASED ALLOY AND SUPER-REFRACTORY NICKEL-BASED ALLOY**

(57) A method for producing a Ni-base superalloy having a composition in which the equilibrium precipitation of gamma prime at 700 ° C. is 35 mol% or more.

This method includes a preparation step of manufacturing a material having a crystal grain size of 200 μm or less by hot extrusion, and a processing step of performing cold plastic processing at a working rate of 30% or more. Cold plastic working may be a plurality of times of cold plastic working with a cumulative working rate of 30% or more, and heat treatment is not performed during a plurality of cold plastic working operations. In addition, the Ni-based super heat-resistant alloy has a composition of ≥ 35 mol% of the equilibrium precipitation of gamma prime at 700 ° C. The alloy may have linear tissue of gamma and gamma prime phases, or may have carbides aggregated linearly into an equiaxed crystal structure comprising gamma and gamma prime phases.

FIG. 4



EP 3 772 544 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a method of manufacturing a super heat resistant Ni-based alloy and to the super heat resistant Ni-based alloy. Specifically, the present invention relates to a method of manufacturing the super heat resistant Ni-based alloy having a composition such that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 35 mol% and to the super heat resistant Ni-based alloy.

BACKGROUND ART

[0002] A super heat resistant Ni-based alloy, such as an Inconel (registered trademark) 718 alloy, has been used for a heat-resistant product for an engine of an aircraft or a gas turbine for power generation. The heat-resistant product has been required to have a heat-resistance to a higher temperature due to an increase in performance and a reduction in fuel consumption of the gas turbine. In order to improve the heat resistance (or high-temperature strength) of the Ni-based alloy, it is most effective to increase an amount of gamma prime (hereinafter also referred to merely as "γ' (gamma-prime)") phase which is an intermetallic compound mainly composed of Ni_3Al and effects as a precipitation-strengthening phase. When the Ni-based alloy includes higher amounts of Al, Ti and Nb which are γ' generating elements, high-temperature strength of the Ni-based alloy can be further improved. In the future, a Ni-based alloy including a larger amount of γ' phase will be demanded in order to achieve the high heat resistance and the high-temperature strength.

[0003] However, it has been known that the Ni-based alloy including a larger amount of γ' phase has higher deformation resistance during hot working and thus has lower workability. In particular, when the amount of γ' phase in the Ni-based alloy is not less than 35- 40 mol%, the Ni-based alloy has particularly reduced workability. For example, alloys such as Inconel (registered trademark) 713C alloy, IN939, IN100 and Mar-M247 include a particularly large amount of γ' phase and thus can not be subjected to plastic working. Accordingly, these alloys are typically used as-cast, i.e. they are as-cast alloys.

[0004] As a proposal for improving hot plastic workability of such a super heat resistant Ni-based alloy, WO 2016/129485A1 discloses a method of manufacturing the super heat resistant Ni-based alloy. The Ni alloy ingot having a composition including a γ' phase of not less than 40 mol% is cold worked at a working rate of not less than 5% and less than 30%, and the cold-worked alloy is then heat treated at a temperature higher than a γ' solid solution temperature. In this method, a combination of the cold working step and the heat treatment step provides a recrystallization rate of not less than 90% at which hot working can be applied to the Ni-based alloy.

[0005] Furthermore, such cases have been increasing in recent years that a heat-resistant product of the Ni-based alloy including a large amount of γ' phase is repaired or the heat-resistant product of the Ni-based alloy is produced by three-dimensional forming. In such cases, a wire of the Ni-based alloy has been required as a raw material for the forming. The wire product can also be processed e.g. into a spring. The wire product of the Ni-based alloy has a small diameter of e.g. not more than 5 mm, or further not more than 3 mm. Such a wire product is efficiently produced, for example, by plastic-working an intermediate product of a "wire material" having a diameter of not more than 10 mm. If the "wire material" which is the intermediate product can also be produced by plastic-working, a wire product of the super heat resistant Ni-based alloy can be efficiently produced.

[0006] As a method of manufacturing such a wire product of a super heat resistant alloy, a method has been proposed (see US 4777710 A), starting from a cast wires having a diameter of not less than 5 mm and hot-extruding a bundle of the cast wires and then separate it thereafter.

CITATION LIST

PATENT LITERATURE

[0007]

PATENT LITERATURE 1: WO 2016/129485 A1
PATENT LITERATURE 2: US 4777710 A

BRIEF SUMMARY OF THE INVENTION

[0008] A super heat resistant Ni-based alloy which includes a larger amount of γ' phase has lower hot plastic workability as described above. The method of US 4777710 A is applicable to a limited composition for effectively manufacturing a wire product, but it is extremely difficult to process into a wire product by hot plastic working a super heat resistant Ni-based alloy having a composition in which an amount of γ' phase is "not less than 35 mol%" (described later). Furthermore, the method of US 4777710 A has problems since the process is complicated and takes high cost.

[0009] The method of WO 2016/129485 A1 is effective in manufacturing a super heat resistant Ni-based alloy to which hot working is applied. For the manufacturing of the Ni-based alloy, however, the ingot should be cold worked at a working rate of not less than 5% and less than 30% and then further heat treated.

[0010] An object of the present invention is to provide a method of manufacturing a super heat resistant Ni-based alloy which has excellent plastic workability by a new approach different from a conventional approach. Further object of the present invention is to provide a method of manufacturing the Ni-based alloy by plastic working at a high working rate without heat treatment during the plastic working. Further object of the present invention is to provide a new method of manufacturing a wire material and a wire product of the super heat resistant Ni-based alloy. Furthermore, further object of the present invention is to provide the super heat resistant Ni-based alloy.

[0011] According to an aspect of the present invention, provided is a method of manufacturing a super heat resistant Ni-based alloy having a composition such that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 35 mol%. The method includes:

a preparation step of manufacturing a raw material through hot extrusion, the raw material including grains having a grain size of not more than 200 μm through hot extrusion; and
a working step of subjecting the raw material to cold plastic working at a working rate of not less than 30%.

[0012] According to an embodiment, preferably, the cold plastic working is cold plastic working includes multiple workings, a cumulative working rate of the multiple workings being not less than 30%, and no heat treatment is performed between the multiple workings.

[0013] According to an embodiment, the Ni-based alloy preferably has such a composition such that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 40 mol%.

[0014] According to an embodiment, the Ni-based alloy preferably has a hardness of not less than 500 HV after the working step.

[0015] According to an embodiment, the super heat resistant Ni-based alloy has a cross-sectional structure preferably including not less than 5 grains per 1 μm^2, which grains have a maximum grain diameter of not more than 75 nm.

[0016] According to an embodiment, the method preferably includes a step of performing heat treatment after the working step of performing the cold plastic working.

[0017] According to an embodiment, the composition of the Ni-based alloy preferably includes, by mass%, 0 to 0.25% of C, 8.0 to 25.0% of Cr, 0.5 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 0 to 8% of Mo, 0 to 15.0% of W, 0 to 4.0% of Nb, 0 to 5.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 3.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

[0018] According to an embodiment, the Ni-based alloy preferably has a composition including, by mass%, 0 to 0.25% of C, 8.0 to 25.0% of Cr, 0.5 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 0 to 8% of Mo, 0 to 6.0% of W, 0 to 4.0% of Nb, 0 to 3.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 1.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

[0019] According to an aspect of the present invention, provided is a super heat resistant Ni-based alloy having such a composition that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 35 mol%. The Ni-based alloy has a banded structure of a gamma phase and a gamma prime phase. In the structure, carbides are aggregated in a banded direction of the banded structure. The Ni-based alloy may have a hardness of not less than 500 HV

[0020] According to another aspect of the present invention, provided is a super heat resistant Ni-based alloy having such a composition that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 35 mol%. The Ni-based alloy has an equiaxed structure including gamma phase and gamma prime phase. In the structure, carbides aggregate in a banded form. The Ni-based alloy may have a hardness of less than 500 HV.

[0021] According to an embodiment, these Ni-based alloys preferably have such a composition such that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 40 mol%.

[0022] According to an embodiment, these Ni-based alloys preferably have a composition including, by mass%, 0 to 0.25% of C, 8.0 to 25.0% of Cr, 0.5 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 0 to 8% of Mo, 0 to 15.0% of W, 0 to 4.0% of Nb, 0 to 5.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 3.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

[0023] According to an embodiment, these Ni-based alloys preferably have a composition including, by mass%, 0 to 0.25% of C, 8.0 to 25.0% of Cr, 0.5 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 0 to 8% of Mo, 0 to 6.0% of W, 0 to 4.0% of Nb, 0 to 3.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 1.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

[0024] The present invention can provide a method for manufacturing a super heat resistant Ni-based alloy which has excellent plastic workability and the Ni-based alloy.

[0025] Further features, advantages, and details of the present invention will be apparent from the following description of non-limiting embodiments with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026]

FIG. 1 is a schematic diagram showing a shape change of a bar material when the bar material is rolled.
FIG. 2 is a photograph of an example of a cross-sectional microstructure of a hot-extruded raw material example according to the present invention.
FIG. 3 is a photograph of a microstructure of a super heat resistant Ni-based alloy No. 1-9 as an example according to the present invention after swaging processing.
FIG. 4 is an electron backscatter diffraction (EBSD) image of the super heat resistant Ni-based alloy No. 1-9 as an example according to the present invention after swaging processing.
FIG. 5 a photograph of a microstructure of the super heat resistant Ni-based alloy No. 1-9 as an example according to the present invention after heat treatment.
FIG. 6A is a photograph in substitution for a drawing showing appearance of a lateral surface of a super heat resistant Ni-based alloy No. 2-3 as an example according to the present invention after rolling.
FIG. 6B is a photograph in substitution for a drawing showing appearance of a rolled surface of the super heat resistant Ni-based alloy No. 2-3 as an example according to the present invention after rolling.
FIG. 7A is a photograph in substitution for a drawing showing appearance of a lateral surface of a super heat resistant Ni-based alloy No. 2-7 as Comparative Example after rolling.
FIG. 7B is a photograph in substitution for a drawing showing appearance of a rolled surface of the super heat resistant Ni-based alloy No. 2-7 as Comparative Example after rolling.
FIG. 8 is an EBSD image of an example of a cross-sectional structure of a hot-extruded raw material example according to the present invention.
FIG. 9 is a diagram showing a grain size distribution of grains recognized on the EBSD image in FIG. 8.
FIG. 10 a photograph of a microstructure showing an example of a cross-sectional structure of a hot-extruded raw material example according to the present invention.
FIG. 11 a photograph of a microstructure of a super heat resistant Ni-based alloy No. 3-2 as examples according to the present invention after swaging processing.
FIG. 12 a photograph of a microstructure of a super heat resistant Ni-based alloy No. 3-3 as an example according to the present invention after swaging processing.
FIG. 13 a photograph of a microstructure of the super heat resistant Ni-based alloy No. 3-3 as an example according to the present invention of FIG. 12 after heat treatment.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The present invention provides a new method for manufacturing a super heat resistant Ni-based alloy having excellent plastic workability, by a new approach different from conventional hot plastic working.

[0028] The present inventors have studied plastic workability of a super heat resistant Ni-based alloy including a large amount of γ' phase. As a result, they have found a phenomenon that plastic workability of the Ni-based alloy is dramatically improved by subjecting a material of a super heat resistant Ni-based alloy to hot extrusion and then cold plastic working at a working rate of not less than 30%. At that time, it was found that nano-grains are generated in a structure of the Ni-based alloy by the cold plastic working at a working rate of not less than 30%. The generation of the nano-grains presumably contributes to dramatic improvement of the plastic workability of the Ni-based alloy.

[0029] Accordingly, the method according to the present invention of manufacturing a super heat resistant Ni-based alloy having a composition whose amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 35 mol% includes a preparation step of manufacturing a raw material having a grain size of not more than 200 μm through hot extrusion; and a working step for performing cold plastic working of the raw material at a working rate of not less than 30%.

[0030] The present invention is directed to the super heat resistant Ni-based alloy having a composition such that an amount of precipitated gamma prime (γ') phase in equilibrium at 700°C is not less than 35 mol%.

[0031] The amount of γ' phase of the Ni-based alloy can be indicated by a numerical indicator such as a "volume ratio" or an "area ratio" of the γ' phase. In the specification, the amount of γ' phase is indicated by "γ' mol%". The γ' mol% indicates a stable amount of precipitated gamma prime phase in equilibrium in a thermodynamic equilibrium state of the Ni-based alloy. The amount of precipitated gamma prime phase in equilibrium, expressed in "mol %", is determined by the composition of the Ni-based alloy. The amount in mol% can be obtained by analysis through thermodynamic equilibrium calculation. The amount can be obtained correctly and easily by the analysis using various kinds of thermodynamic equilibrium calculation software.

[0032] In the present invention, the γ' mol% of the Ni-based alloy is indicated by an "equilibrium precipitation amount at 700°C". High-temperature strength of the Ni-based alloy depends on the equilibrium precipitation amount of gamma prime phase in the structure. As the Ni-based alloy has higher high-temperature strength, it is more difficult to perform hot plastic working. In general, the temperature dependence on the equilibrium precipitation amount of gamma prime phase in the structure becomes small and becomes approximately constant at or below about 700°C. Thus, the equilibrium precipitation amount at "700°C" is used.

[0033] As described above, it is typically more difficult to hot-plastic-working the super heat resistant Ni-based alloy, as the Ni-based alloy has a higher γ' mol%. On the contrary according to the present invention, high γ' mol% of the Ni-based alloy greatly contributes to improvement of cold plastic workability of the Ni-based alloy. The Ni-based alloy of the present invention includes "nano-grains" in the cross-sectional structure, which dramatically improve cold plastic workability. The nano-grains are likely to be generated at an interface between an austenitic phase (gamma (γ)) which is a matrix of the Ni-based alloy, and the gamma prime phase. The high γ' mol% of the Ni-based alloy increases the phase interface, and thus contributes to the generation of the nano-grains. When the γ' mol% has reached 35%, the generation of the nano-grains is accelerated. The amount of precipitated gamma prime phase in equilibrium at 700°C is more preferably not less than 40 mol%, still more preferably not less than 50 mol%, and further still more preferably not less than 60 mol%. In particular, the amount of precipitated gamma prime phase in equilibrium is preferably not less than 63 mol%, more preferably not less than 66 mol%, and still more preferably not less than 68 mol%. While an upper limit of the amount of precipitated gamma prime phase in equilibrium at 700°C is not particularly limited, its practical value is approximately 75 mol%.

[0034] The Ni-based alloy of a precipitation strengthening type, which has the amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 35 mol%, preferably has a composition, for example, including, by mass %, 0 to 0.25% of C, 8.0 to 25.0% of Cr, 0.5 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 0 to 8% of Mo, 0 to 15.0% of W, 0 to 4.0% of Nb, 0 to 5.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 3.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

[0035] Alternatively, the Ni-based alloy preferably has a composition including, by mass %, 0 to 0.03% of C, 8.0 to 22.0% of Cr, 2.0 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 2.0 to 7.0% of Mo, 0 to 6.0% of W, 0 to 4.0% of Nb, 0 to 3.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 1.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

[0036] Each content of a preferable composition as an embodiment of the Ni-based alloy of the present invention will be described below (the content is expressed by "mass%").

Carbon (C)

[0037] Carbon is conventionally included for improving casting ability of the Ni-based alloy. In particular, since the Ni-based alloy including a large amount of γ' phase is typically produced as a cast component since it is difficult to be plastic-worked, it includes a certain amount of carbon. Carbon remains as carbides in a structure of the cast Ni-based alloy, and a part of carbon forms coarse eutectic carbides. When the Ni-based alloy is subjected to plastic working, in particular at a room temperature, the coarse eutectic carbides become a starting point and progress route of cracking, and adversely affect plastic workability of the Ni-based alloy.

[0038] Therefore, a reduction of the amount of carbon is extremely important for Ni-based alloy according to the present invention, since the present invention has an object of providing the Ni-based alloy including a large amount of γ' phase and having excellent plastic workability, not as a cast component. However, the Ni-based alloy of the present invention may include carbon in almost the same amount as that in the cast component, since it includes "nano-grains" in the cross-sectional structure to dramatically improve cold plastic workability. In the present invention, the carbon content is preferably not more than 0.25%, more preferably not more than 0.1%, still more preferably not more than 0.03%, still more preferably not more than 0.025%, further still more preferably not more than 0.02%, and particularly preferably less than 0.02%.

[0039] Carbon is an element to be limited, and thus the carbon content is preferably controlled to be lower for the Ni-based alloy of the present invention. When carbon is not intentionally added (i.e. it is inevitable impurity), a lower limit of carbon may be 0 mass%. Even if carbon is not intentionally added, approximately 0.001% for example of carbon is measured.

Chromium (Cr)

[0040] Chromium (Cr) improves oxidation resistance and corrosion resistance. However, an excessive amount of Cr results in formation of a brittle phase such as a σ (sigma) phase to deteriorate strength and hot workability during raw material production. Therefore, the Cr content is preferably 8.0 to 25.0% for example, and more preferably 8.0 to 22.0%. A lower limit of the Cr content is preferably 9.0%, more preferably 9.5%, and still more preferably 10.0%. An upper limit of the Cr content is preferably 18.0%, more preferably 16.0%, still more preferably 14.0%, and particularly preferably 12.5%.

Molybdenum (Mo)

[0041] Molybdenum (Mo) contributes to solid solution strengthening of a matrix, and has an effect of improving high-temperature strength. However, an excessive amount of Mo results in formation of an intermetallic compound phase to deteriorate high-temperature strength. Therefore, the Mo content is preferably 0 to 8% (or may be not intentionally added (i.e. inevitable impurity)), and more preferably 2.0 to 7.0%. A lower limit of the Mo content is preferably 2.5%, more preferably 3.0%, and still more preferably 3.5%. An upper limit of the Mo content is preferably 6.0%, and more preferably 5.0%.

Aluminum (Al)

[0042] Aluminum (Al) forms a γ' (Ni_3Al) phase, which is a strengthening phase, and improves high-temperature strength. However, an excessive amount of Al deteriorates hot workability during the raw material production and causes a material defect such as cracks during processing. Therefore, the Al content is preferably 0.5 to 8.0%, and more preferably 2.0 to 8.0%. A lower limit of the Al content is preferably 2.5%, more preferably 3.0%, still more preferably 4.0%, further still more preferably 4.5%, and particularly preferably 5.1%. An upper limit of the Al content is preferably 7.5%, more preferably 7.0%, and still more preferably 6.5%.

[0043] In relation to the above Cr content, when the Cr content is reduced, the Al content is allowed to be increased for complementing the reduced amount of Cr content in order to ensure hot workability during the raw material production. For example, when the upper limit of the Cr content is 13.5%, the lower limit of the Al content is preferably 3.5%.

Titanium (Ti)

[0044] Titanium (Ti) forms a γ' phase and increases high-temperature strength through solid solution strengthening of the γ' phase, similarly to Al. However, an excessive amount of Ti makes the γ' phase unstable and coarse at a high temperature and forms a harmful η (eta) phase to deteriorate hot workability during the raw material production. Therefore, the Ti content is preferably 0.4 to 7.0% for example. Considering a balance with other γ' generating elements and an Ni matrix, a lower limit of the Ti content is preferably 0.6%, more preferably 0.7%, and still more preferably 0.8%. An upper limit of the Ti content is preferably 6.5%, more preferably 6.0%, still more preferably 4.0%, and particularly preferably 2.0%.

[0045] Optional elements that may be added to the Ni-based alloy of the present invention will be described below.

Cobalt (Co)

[0046] Cobalt (Co) improves stability of the alloy structure, and can maintain hot workability during the raw material production even if the alloy includes a large amount of strengthening element Ti. On the other hand, Co is expensive and thus increases cost of the alloy. Accordingly, Co is an optional element and it may be included, for example, in a range of not more than 28.0% according to a combination with other elements. When Co is added, a lower limit of the Co content is preferably 8.0%, and more preferably 10.0%. An upper limit of the Co content is preferably 18.0%, and more preferably 16.0%. Considering a balance with γ' generating elements and a Ni matrix, if Co is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of Co is 0%.

Tungsten (W)

[0047] Tungsten (W) is an optional element which contributes to solid solution strengthening of a matrix, similarly to Mo. However, an excessive amount of W results in formation of a harmful intermetallic compound phase to deteriorate high-temperature strength. Therefore, an upper limit of the W content is, for example, 15.0%. An upper limit of the W content is preferably 13.0%, more preferably 11.0%, and still more preferably 9.0%. An upper limit of the W content may be preferably made 6.0%, 5.5%, and 5.0%. In order to more reliably achieve the above effect of W, a lower limit of the W content is preferably 1.0%. Preferably, the lower limit of the W content may be 2.0%, 3.0%, or 4.0%. Addition of both W and Mo in combination is more effective in achieving the solid solution strengthening. In the case where both W and Mo are added in combination, the W content is preferably not less than 0.8%. Due to the addition of a sufficient amount of Mo, if W is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of W is 0%.

Niobium (Nb)

[0048] Niobium (Nb) is an optional element which forms a γ' phase and increases high-temperature strength through solid solution strengthening of the γ' phase, similarly to Al and Ti. However, an excessive amount of Nb results in formation of a harmful δ (delta) phase to deteriorate hot workability during the raw material production. Therefore, an upper limit of Nb is, for example, 4.0%. The upper limit of the Nb content is preferably 3.5%, and more preferably 2.5%. In order to more reliably achieve the above effect of Nb, a lower limit of the Nb content is preferably 1.0%, and more preferably 2.0%. Due to the addition of other γ' generating elements, if Nb is not intentionally added (i.e. it is inevitable impurity), the lower limit of Nb is 0%.

Tantalum (Ta)

[0049] Tantalum (Ta) is an optical element which forms a γ' phase and increases high-temperature strength through solid solution strengthening of the γ' phase, similarly to Al and Ti. However, an excessive amount of Ta makes the γ' phase unstable and coarse at a high temperature and forms a harmful η (eta) phase to deteriorate hot workability during the raw material production. Therefore, the Ta content is, for example, not more than 5.0%. The Ta content is preferably not more than 4.0%, more preferably not more than 3.0%, and still more preferably not more than 2.5%. In order to more reliably achieve the above effect of Ta, a lower limit of the Ta content is preferably 0.3%. A lower limit of the Ta content may be preferably made 0.8%, 1.5%, and 2.0%. Considering a balance with γ' generating elements, such as Ti and Nb, and a matrix, if Ta is not intentionally added (i.e. it is inevitable impurity), the lower limit of Ta is 0%.

Iron (Fe)

[0050] Iron (Fe) is an optional element which may be used instead of expensive Ni or Co and is effective in reducing cost of the alloy. In order to achieve the effect, it is preferable to determine whether to add Fe considering a combination with other elements. However, an excessive amount of Fe results in formation of a brittle phase such as a σ (sigma) phase to deteriorate strength and hot workability during the raw material production. Therefore, an upper limit of the Fe content is, for example, 10.0%. The upper limit of the Fe content is preferably 9.0%, and more preferably 8.0%. On the other hand, considering a balance with γ' generating elements and a Ni matrix, if Fe is not intentionally added (i.e. it is inevitable impurity), a lower limit of Fe is 0%.

Vanadium (V)

[0051] Vanadium (V) is an optical element which is effective for solid solution strengthening of a matrix and generation of carbide to increase grain boundary strength. However, an excessive amount of vanadium results in formation of such a phase that is unstable at a high temperature during a manufacturing process, and adversely affects the productivity and high-temperature dynamic performance. Therefore, an upper limit of the vanadium content is, for example, 1.2%. The upper limit of the vanadium content is preferably 1.0%, and more preferably 0.8%. In order to more reliably achieve the above effect of vanadium, a lower limit of the vanadium content is preferably 0.5%. Considering a balance with other γ' generating elements in the Ni-based alloy, if vanadium is not intentionally added (i.e. it is inevitable impurity), the lower limit of vanadium is 0%.

Hafnium (Hf)

[0052] Hafnium (Hf) is an optional element which is effective for improvement of oxidation resistance of the Ni-based alloy and generation of carbide to increase grain boundary strength. However, an excessive amount of Hf results in formation of oxide, and such a phase that is unstable at a high temperature during a manufacturing process, and adversely affects the productivity and high-temperature dynamic performance. Therefore, an upper limit of the Hf content is, for example, 3.0%, preferably 2.0%, more preferably 1.5%, and still more preferably 1.0%. In order to more reliably achieve the above effect of Hf, a lower limit of the Hf content is preferably 0.1%. A lower limit of the Hf content may be preferably made 0.5%, 0.7%, and 0.8%. Considering a balance with other γ' generating elements in the Ni-based alloy, if Hf is not intentionally added (i.e. it is inevitable impurity), the lower limit of Hf is 0%.

Boron (B)

[0053] Boron (B) increases grain boundary strength and improves creep strength and ductility. However, boron has an effect of lowering a melting point. Furthermore, when boron forms coarse boride, hot workability during the raw material preparation is deteriorated. Therefore, the boron content is preferably controlled not to exceed 0.300% for example. An upper limit of the boron content is preferably 0.200%, more preferably 0.100%, still more preferably 0.050%, and particularly preferably 0.020%. In order to achieve the above effect of boron, the boron content is preferably 0.001% at minimum. The lower limit of the boron content is more preferably 0.003%, still more preferably 0.005%, and particularly preferably 0.010%. Considering a balance with other γ' generating elements in the Ni-based alloy, if boron is not intentionally added (i.e. it is inevitable impurity), the lower limit of boron is 0%.

Zirconium (Zr)

[0054] Zirconium (Zr) has an effect of increasing grain boundary strength, similarly to boron. However, an excessive amount of Zr also lowers a melting point to deteriorate high-temperature strength and hot workability during raw material preparation. Therefore, an upper limit of the Zr content is, for example, 0.300%. The upper limit of the Zr content is preferably 0.250%, more preferably 0.200%, still more preferably 0.100%, and particularly preferably 0.050%. In order to achieve the above effect of Zr, the Zr content is preferably 0.001% at minimum. The lower limit of the Zr content is more preferably 0.005%, and still more preferably 0.010%. Considering a balance with other γ' generating elements in the Ni-based alloy, if Zr is not intentionally added (i.e. it is inevitable impurity), the lower limit of Zr is 0%.
[0055] The balance of the Ni-based alloy other than the elements described above is nickel, while inevitable impurities may be included.
[0056] Next, a method of manufacturing the super heat resistant Ni-based alloy which has the above composition will be described as an embodiment of the present invention.
[0057] In the present invention, a raw material having a grain size of not more than 200 μm is manufactured through hot extrusion. A material to be subjected to the hot extrusion may be produced by a melting method in which a molten metal is poured into a mold to produce an ingot. The ingot may be produced by combining, for example, vacuum melting with a usual method such as vacuum arc remelting or electroslag remelting. Soaking (e.g., by holding at 1100°C to 1280°C for 5 to 60 hours) may be performed in order to eliminate segregation of elements in the ingot. The soaking may be performed after the material has been formed into a shape for the hot extrusion. Alternatively, the material for the hot extrusion may be produced through a powder metallurgy process for producing an alloy ingot.
[0058] Then the material is subjected to hot extrusion process to produce a bar material having a predetermined shape. The hot extrusion is preferably performed under conditions including an extrusion temperature (heating temperature of the material) of 1050°C to 1200°C, an extrusion ratio of 4 to 20, and an extrusion rate (stem speed) of 5 to 80 mm/s. The produced extruded material has a cross-sectional diameter of, for example, not less than 10 mm, more than 20 mm and, for example, not more than 200 mm. In the process, a surface of the material may be finished through machining or the like. Alternatively, the bar material may be cut out from the extruded material so as to have a predetermined size. In this case, the bar material may be produced to have a size having a cross-sectional diameter of, for example, not more than 150 mm, not more than 100 mm, not more than 50 mm, not more than 30 mm, or not more than 10 mm. The bar material can be produced to have a size having a cross-sectional diameter of, for example, not less than 3 mm, not less than 4 mm, or not less than 5 mm. The small cross-sectional diameter of the bar material is preferable since a wire material, a wire product, or the like having a further smaller cross-sectional diameter can be produced through cold plastic working (described later) with a reduced number of times of the plastic working.
[0059] Through the hot extrusion, the material has a recrystallized structure having a grain size of not more than 200 μm, preferably not more than 150 μm, more preferably not more than 100 μm, and still more preferably 50 μm. Preferably, the recrystallized structure has a grain size of not less than 0.1 μm, more preferably not less than 0.5 μm, still more preferably not less than 0.8 μm, and further still more preferably not less than 1.5 μm. The grains generated through the recrystallization have a small intragranular strain, and refining of the grains increases grain boundaries. Thus, when the cold plastic working described later is performed, a working strain at that time is applied evenly to the entire structure. Furthermore, refining of the grains is also effective to generate nano-grains described later. By the step, deformation becomes more uniform in plastic working in the next step, and an abnormal deformation or bending may be avoided during the working. Thus, a yield may be dramatically improved. On the other hand, if the plastic working is performed without the hot extrusion step, deformation or bending occurs in the working, and a defective shape of a worked product is likely to occur. In order to further improve this effect, the hot-extruded raw material may be heat-treated for removing residual stress introduced by the working.
[0060] The grain size of the raw material may be measured by observing a cross-sectional structure of the raw material. First, the cross section is etched using Kalling's reagent, and the etched cross-sectional structure is observed under an optical microscope with a predetermined magnification. The cross-sectional structure is evaluated in terms of "Grain size number G" pursuant to JIS-G-0551 (ASTM-E112). It can be converted into an "average diameter d of grains" which corresponds to the Grain size number G. In the present invention, the grain size of the raw material refers to the "average diameter **d** of grains".
[0061] Alternatively, the grain size of the raw material may be observed by using an EBSD image of the cross section of the raw material (FIG. 8). Grains may be recognized under conditions of the EBSD measurement of a scan step: 0.1

μm when a grain boundary is defined as having an orientation difference of not less than 15° and an average of maximum grain diameter may be obtained from a grain diameter distribution showing a relationship between a maximum grain diameter of each grain and a number of grains having the grain diameter (FIG. 9). The grain size distribution may be obtained from grains which are recognized as grains under the above measurement conditions and the definition, for example from grains having a maximum grain diameter of not less than 0.2 μm. Please note that the grain size of the raw material refers to the "average of maximum grain diameters" herein.

[0062] In a case where the raw material includes carbides, the carbides may be recognized on the EBSD image as the grains defined as having "an orientation difference of not less than 15°" (e.g., those indicated by arrows in FIG. 8). In this case, the carbides may be counted as the grains in the grain size distribution, and this does not adversely affect the effects of the present invention.

[0063] Even when it is not easy to observe a grain boundary in the cross-sectional structure of the raw material by presence of a γ' phase (e.g., even when it is not easy to identify a grain boundary by observation with use of the optical microscope), a grain boundary is easily identified uniquely with use of the EBSD image. Thereby, the EBSD image is preferable to obtain the average grain size of the super heat resistant Ni-based alloy which has a large amount of the γ' phase. Furthermore, the EBSD image is preferable to obtain the average grain size even when the grains of the cross-sectional structure of the raw material is fine (e.g., even when the average grain size is small such as not more than 30 μm, not more than 20 μm, or not more than 10 μm).

[0064] The raw material preferably has a low hardness in order to ensure an initial workability of the cold plastic working, when no nano-grains described later are generated in the structure. For example, the hardness is not more than 550 HV or less than 500 HV, preferably not more than 450 HV, still more preferably not more than 400 HV, and further still more preferably not more than 380 HV. While a lower limit of the hardness of the raw material is not particularly limited, its practical value is approximately 250 HV. The hardness of the raw material can be measured by observing a cross section of the material.

[0065] Next, the raw material is subjected to cold plastic working with a working rate of not less than 30%. Unlike conventional "hot" plastically worked material, the Ni-based alloy according to the present invention having excellent plastic workability can be obtained through "cold" plastic working. In particular, when the Ni-based alloy which has an amount of γ' phase of 35 mol% is cold-plastic-worked , nano-grains are generated at a phase interface (γ/γ' interface) described later between a γ (gamma) phase and a γ' (gamma prime) phase leading to a "growing effect" on plastic workability. Thereby, the above-described super heat resistant Ni-based alloy, which is difficult to be worked by hot plastic working, may be worked into a wire material or a wire product through relatively simple steps and at low cost. In order to achieve it, the cold plastic working needs to be conducted in a low temperature range since no recovery or no recrystallization is presumably caused during the plastic working.

[0066] Thus, it is preferable according to the invention that the temperature at which the plastic working is conducted is "not higher than 500°C". The temperature is more preferably not higher than 300°C, still more preferably not higher than 100°C, and further still more preferably not higher than 50°C (e.g., at a room temperature).

[0067] Apparently, the above manufacturing of the Ni-based alloy is applicable to produce a wire material, a sheet material, a strip material, or the like. Furthermore, it is also apparent that the Ni-based alloy of the present invention may be in a form of an intermediate product such as a wire material, a sheet material, or a strip material, as well as it may be in a form of an end product such as a wire product, a sheet product, or a strip product. As for the sheet material (sheet product) and the strip material (strip product), the wire diameter (diameter) of the wire material (wire product) can be replaced with a plate thickness or a strip thickness.

[0068] In particular, when the hot-extruded raw material of the Ni-based alloy is in a form of a bar material, the bar material can be compressed to reduce its cross-sectional area. In this case, the "bar material" of the Ni-based alloy is used as a starting material and is subjected to a process in which a pressure can be uniformly applied from an entire periphery of the bar material as the plastic working, i.e. "working to compress an area of a cross section perpendicular to a longitudinal direction of the bar material". The raw bar material is worked so that a cross-sectional area (bar diameter) is plastically compressed to extend a length of the bar material. In particular for producing a wire material, it is efficient to prepare a "bar material" having a larger cross-sectional area (diameter) than the wire material by plastic working. The bar material is plastically worked by compressing the cross-sectional area from a peripheral surface toward an axis of the material, at a working rate of not less than 30%. The working include swaging, cassette roller dice wire drawing, hole dice wire drawing, and the like.

[0069] On the other hand, a sheet material, a strip material, or the like of the Ni-based alloy may be produced through rolling process.

[0070] Here, the "working rate" is explained. In a case where the bar material is subjected to swaging or dice wire drawing, the working rate is indicated by an area reduction rate. The area reduction rate is calculated by the following formula, as a relationship between a cross-sectional area A_0 of a bar material before plastic working and a cross-sectional area A_1 of a wire material or a wire product after plastic working.

$$[(A_0 - A_1) / A_0] \times 100\ (\%) \tag{1}$$

[0071] On the other hand, in a case of rolling process, the working rate is indicated by a rolling reduction rate. The rolling reduction rate is calculated by the following formula, where t_0 represents a thickness of a raw material before plastic working, and t_1 represents a thickness of a sheet material, a strip material, a sheet product, or a strip product after plastic working.

$$[(t_0 - t_1) / t_0] \times 100\ (\%) \tag{2}$$

[0072] The cumulative working rate indicates a working rate of a final workpiece in relation to a raw material through multiple times or passes of the plastic working.

[0073] FIG. 1 is a schematic diagram showing changes in shape of a bar material which occur when the bar material is rolled through multiple passes (2 passes in the drawing). In FIG. 1, reference numeral 1 indicates rolling reduction directions; reference numeral 2 indicates rolled surfaces; and reference numeral 3 indicates lateral surfaces. The bar material is a work starting material and has a substantially round cross section. The bar material receives compressive force from rolling rolls from above and below in the rolling reduction directions 1 to have a flat shape. The rolled surface 2 in contact with the rolling rolls are made flat surfaces. When a diameter of the bar material is denoted as to, and a distance between top and bottom rolled surfaces at the second pass, that is a thickness of the bar material, is denoted as t_1, a working rate of the 2-pass rolling is expressed by the above-described formula (2).

[0074] In the present invention, the working rate of the cold plastic working (including "cumulative working rate" as described later) is set to a high value of "not less than 30%". If the working rate is less than 30%, a degree of the working is little, thereby effects of the cold plastic working is not obtained. The working rate is preferably not less than 40%, and more preferably not less than 60%. The working rate is more preferably not less than 70%, still more preferably not less than 80%, still more preferably not less than 85%, still more preferably not less than 90%, and particularly preferably not less than 97%.

[0075] The Ni-based alloy having been subjected to such severe working at a working rate of not less than 30% becomes able to be subjected to further working. Accordingly, it is preferable to avoid a heat treatment during the plastic working (including avoid to heat). The heat treatment herein indicates a heat treatment in a high temperature range for generating recovery or recrystallization, for example at a temperature of higher than 500°C. Thus, severe cold working multiple times continuously makes it possible to increase the cumulative working rate (area reduction rate) infinitely (such as the cumulative working rate approaches 100%) without heat treatment between the passes of the workings. Even if the Ni-based alloy is severe-worked, the alloy can be further plastic-worked while it keeps a hardness of not less than e.g. 500 HV. In a structure of the severe-worked Ni-based alloy, nano-grains are observed to be generated. This mechanism has not yet been fully known but is considered as follows.

[0076] When the Ni-based alloy is subjected to the cold working at a working rate of not less than 30%, the alloy comes to have a hardness of not less than 500 HV in the middle of the working due to working hardening. When the alloy having the hardness of not less than 500 HV is further cold-worked, nano-grains are generated at a γ/γ' interface. The inventors have experimentally found that the working rate needs to be approximately 30% at minimum (see Examples) in order to generate sufficient nano-grains. It was observed that the nano-grain is first generated preferentially at a phase interface between the y phase and the γ' phase when the bar material of the Ni-based alloy is plastically cold-worked and a cumulative working rate of the working has reached approximately 30%. Once the nano-grains are generated and the alloy (e.g., bar material or wire material) is further plastically cold-worked, the number of nano-grains is increased, and the increase in nano-grains further improves plastic workability of the Ni-based alloy (e.g., bar material or wire material). The inventors have observed a phenomenon as if "room temperature superplastic" working. That is, repeat of plastic working (i.e. increasing a cumulative working rate) increasingly improved plastic workability of the Ni-based alloy (e.g., bar material or wire material), and cold plastic working at a cumulative working rate of not less than 97% is achieved without performing heat treatment during the working.

[0077] The cold plastic working at a working rate of "not less than 30%" may be completed by the working once. However, it is preferably performed by multiple workings in order to prevent cracks, flaw, or the like in the alloy until the nano-grains are generated in the structure. In this case, the working rate of not less than 30% indicates a cumulative working rate. Since a "large strain" caused by a working rate of not less than 30% is applied to the raw material in several stages of the multiple times workings, the strain is moderately dispersed in the raw material. This is effective to uniformly cause the boundary slip and crystal rotation of the nano-grains. As a result, it is possible to generate the nano-grains uniformly and evenly in the raw material and to prevent occurrence of cracks, flaws, or the like during the working. No heat treatment is necessary between the multiple times of the plastic working.

[0078] There is no need to define an upper limit of the working rate or the cumulative working rate of not less than 30% and it may be determined appropriately according to an intermediate product form, an end product form, or the like. In a case where, for example, the Ni-based alloy to be further subjected to the plastic working later is prepared as the intermediate product, for example, the cumulative working rate may be e.g. 50%, 45%, 40%, or 35% according to a configuration or the like of the alloy material.

[0079] When the cold plastic working is performed multiple times, it is possible to set a working rate (area reduction rate) of any plastic working (pass) to be higher than a working rate (area reduction rate) of the previous plastic working (pass) to increase working efficiency. The working rate (area reduction rate) may be increased each time the plastic working (pass) is performed.

[0080] With regard to the "pass" described in the present invention, "one pass" indicates one plastic working performed by a single dice or roll (or a pair of dices or rolls) in a case of working such as swaging, dice wire drawing, or roll described above.

[0081] In a case where the raw material of the Ni-based alloy is a bar material in particular, it is presumed to be important to apply pressure uniformly and evenly from the entire periphery of the bar material during the plastic working in order to improve plastic workability. It is effective to compress a cross-sectional area of the bar material from a peripheral surface toward an axis of the bar material. At this time, a plastic working method is not limited. However, such process is advantageous which applies pressure evenly to an entire circumference of the bar material. Specific examples of such a process include swaging processing. In the swaging processing, a peripheral surface of a bar material is forged while rotating a plurality of dice surrounding an entire circumference of the bar material. Thus, the swaging processing is preferable for generating the nano-grains. Alternatively, other types of plastic working such as cassette roller dice wire drawing and hole dice wire drawing are also applicable.

[0082] In the present invention, a raw material to be subjected to the cold plastic working is manufactured through hot extrusion. Through the hot extrusion, a recrystallized structure having a grain size of not more than 200 μm is generated (from, e.g., a structure of the cast Ni-based alloy, etc.). In the recrystallized structure having the grain size of not more than 200 μm, a γ' phase is re-precipitated uniformly in a structure of the raw material. Therefore, the nano-grains are more likely to be generated in the structure after the cold plastic working. This is presumably because the phase interface between the γ phase and the γ' phase of the alloy becomes uniform, thereby the formation of nano-grains is facilitated.

[0083] The Ni-based alloy after the cold plastic working has a banded structure of the γ phase and the γ' phase extending in a worked direction (see FIG. 3). Thus, the Ni-based alloy of the present invention may have a banded structure of the γ phase and the γ' phase. Also, carbides may be aggregated in a banded direction of the banded structure (i.e., the worked direction) (see FIG. 12). However, when the Ni-based alloy having the worked predetermined size and form is supplied as an end product, the alloy may be heat-treated (e.g., held at 1000°C to 1200°C for 30 minutes to 3 hours) according to necessity to have a desired equiaxed structure (see FIG. 5). The Ni-based alloy may also have a structure in which carbides are aggregated in a banded form in the equiaxed structure as described above (see FIG. 13). For example, the Ni-based alloy may be heat-treated to have a hardness of less than 500 HV, not more than 450 HV, or not more than 420 HV, and for example, not less than 300 HV or not less than 350 HV. Thus, the end product can be bended or cut to into a form appropriate to transportation or applications.

[0084] According to the above manufacturing method, it is possible to provide an Ni-based alloy in various forms including an intermediate product form such as a wire material, a sheet material, or a strip material and an end product form such as a wire product, a sheet product, or a strip product as described above.

[0085] The super heat resistant Ni-based alloy manufactured by the method according to the present invention has excellent plastic workability and has, in particular, excellent cold plastic workability. The Ni-based alloy may have a hardness of not less than 500 HV as described above. Alternatively, the alloy may have a cross-sectional structure including grains having a maximum grain diameter of not more than 75 nm.

[0086] The super heat resistant Ni-based alloy manufactured by the method of the present invention has a cross-sectional structure including "nano-grains" having a maximum grain diameter of not more than 75 nm. Thereby, cold plastic workability is dramatically improved. This mechanism has not yet been sufficiently clear. However, as described above, the phase interface between the γ phase and the γ' phase seems to contribute to the generation of nano-grains. As a plastic working rate is increased, the number of generated nano-grains is increased, and boundary slip and crystal rotation of the nano-grains occur, which enable plastic deformation of the Ni-based alloy. Thus, there is a possibility that the deformation mechanism differs from conventional plastic deformation which is caused by slip in crystals due to occurrence and increase of dislocation. The present inventor has observed a fact suggesting the possibility of this hypothesis in cold plastic working of the Ni-based alloy. Once nano-grains generate, the number of nano-grains is increased as the alloy is further plastically worked (i.e., as increasing a plastic working rate). However, regardless of the increase in the plastic working rate (including a case where the plastic working rate is slightly increased), a hardness of the alloy is "approximately constant" (e.g., not less than 500 HV for the Ni-based alloy having a γ' mol% of not less than 35 mol%). This phenomenon suggests that the plastic working does not increase dislocation density.

[0087] Thus, it is the nano-grains having the "maximum grain diameter of not more than 75 nm" in the cross-sectional structure that contributes to improvement of plastic workability of the Ni-based alloy. The size is different from a size of conventional grains produced in a typical process. In a case of a wire material of the Ni-based alloy, for example, the cross sectional structure may be taken from a cross section of the halved surface in a longitudinal direction of the wire material (i.e., a cross section including a central axis of the wire material). The cross-sectional structure may be taken from each portion, for example, at a position near a surface of the wire material, a position at 1/4D distant from the surface toward a central axis of the wire material (D indicates a wire diameter), and a position at the central axis of the wire material. Then, it is sufficient to confirm that the nano-grains are present in one or more of the cross-sectional structures at each position.

[0088] When the Ni-based alloy is in a form other than a wire material, a cross section of the material halved in a longitudinal direction of the material may be observed similarly to the above case.

[0089] It is preferable that not less than 5 nano-grains having the maximum grain diameter of not more than 75 nm are present per 1 μm^2 of the cross-sectional structure of the Ni-based alloy manufactured by the method of the present invention. As the number of the nano-grains is increased, a medium contributing the plastic deformation is increased and it further improves plastic workability. The number of nano-grains per 1 μm^2 of the cross-sectional structure is more preferably not less than 10, still more preferably not less than 50, still more preferably not less than 100, still more preferably not less than 200, further still more preferably not less than 300, and further still more preferably not less than 400. A number density of the nano-grains may be obtained by calculating an average value of a total number of nano-grains observed in the cross-sectional structures divided by a total area of the observed field of view.

[0090] It is not necessary to particularly define a lower limit of the maximum grain size of the nano-grains having a maximum grain diameter of not more than 75 nm in the cross-sectional structure. The presence and the number of the nano-grains having a maximum grain diameter of not more than 75 nm in the cross-sectional structure can be observed by using, e.g., EBSD images as stated below. The nano-grains having a maximum grain diameter of not more than 75 nm may be recognized, and its number may be counted from grains observed under conditions of the EBSD measurement of a scan step: 0.02 μm when a grain boundary is defined as having an orientation difference of not less than 15°. For example, the presence and the number of the nano-grains having a maximum grain diameter of approximately not less than 25 nm can be observed.

[0091] As the above, the Ni-based alloy manufactured by the method of the present invention has excellent cold plastic workability, and thus may be used "for cold plastic working".

[0092] Furthermore, the Ni-based alloy of the present invention may be in a form of a "wire material", a "sheet material", or a "strip material" which is an intermediate product to be subjected to cold plastic working. For example, the wire material has a wire diameter (diameter) of not more than 10 mm, not more than 8 mm, or not more than 6 mm. Alternatively, the wire material has a small wire diameter of not more than 5 mm, not more than 4 mm, not more than 3 mm, or not more than 2 mm. For example, the sheet material or the strip material has a thickness of not more than 10 mm, not more than 8 mm, or not more than 6 mm. Alternatively, the sheet material or the strip material has a small thickness of not more than 5 mm, not more than 4 mm, not more than 3 mm, or not more than 2 mm. For example, the wire material, the sheet material, or the strip material has a large length of not less than 10 times, not less than 50 times, or not less than 100 times the above wire diameter or the thickness.

[0093] Alternatively, the Ni-based alloy may be in a form of a "wire product", a "sheet product", or a "strip product" which is an end product form produced through the cold plastic working. For example, the wire product has a wire diameter (diameter) of not more than 5 mm, not more than 4 mm, or not more than 3 mm. Alternatively, the wire product has a smaller wire diameter of not more than 2 mm or not more than 1 mm. For example, the sheet product or the strip product has a thickness of not more than 5 mm, not more than 4 mm, or not more than 3 mm. Alternatively, the sheet product or the strip product has a smaller thickness of not more than 2 mm or not more than 1 mm. For example, the wire product, the sheet product, or the strip product has a larger length of not less than 50 times, not less than 100 times, or not less than 300 times the above wire diameter or the thickness.

Example 1

[0094] A molten metal produced by vacuum melting was cast to produce a cylindrical ingot of a super heat resistant Ni-based alloy "A" with a diameter of 100 mm and a weight of 10 kg. Table 1 shows a composition of the Ni-based alloy "A" (by mass%). Table 1 also shows a "γ' mol%" of the ingot, which were calculated with use of commercially available thermodynamic equilibrium calculation software "JMatPro (Version 8.0.1, manufactured by Sente Software Ltd.)". The content of each element in Table 1 was input into the software to obtain the "γ' mol%".

[TABLE 1]

Alloy	C	Cr	Mo	Al	Ti	Nb	Fe	Zr	B	Ni	γ' mol%
A	0.0154	11.97	4.52	5.90	0.61	2.05	1.06	0.10	0.0098	balance*	69.2

*including inevitable impurities

[0095] The ingot of the Ni-based alloy "A" was heat treated at a holding temperature of 1200°C for a holding time of 8 hours, and then cooled in a furnace. Then, a cylindrical material was cut out from the ingot along a longitudinal direction of the ingot. The cylindrical material had a diameter of 60 mm and a length of 150 mm. The cylindrical material was encased in an SUS304 capsule and subjected to the hot extrusion. The hot extrusion was performed under conditions including an extrusion temperature of 1150°C, an extrusion ratio of 4, and an extrusion stem speed of 15 mm/s. An extruded material having a diameter of 27 mm was obtained by the hot extrusion. The extruded material was cut to be halved along an axis line direction of the extruded material, and a microstructure and a hardness of the cross section were evaluated. A measurement spot was set in the cross section at a position at D/4 (D is a diameter of the extruded material) distant from a surface of the extruded material toward an axis of the extruded material. In the microstructure at the position, a γ' phase was precipitated uniformly in a y structure. At this position, 5 visual fields were extracted (FIG. 2 shows an example of a structure in a visual field). A grain size were measured in the 5 visual fields in the above-described manner. An average of "average diameters d of grains" of the visual fields was used as a "grain size of the raw material". At this position, 5 spots were extracted. Hardnesses were measured at the 5 spots. An average value of the hardnesses was used as a hardness of the raw material. By this measurement method, the grain size of the raw material (average grain diameter) was 38 μm (6.5 in grain size number according to ASTM-E112), and the hardness of the raw material was 351 HV.

[0096] Next, a bar material having a diameter of 6 mm and a length of 60 mm was cut out from the extruded material. The bar material was taken so that the longitudinal direction is along the axis line direction of the extruded material. The bar material was subjected to multiple passes of the cold plastic working at a room temperature (approximately 25 °C) with use of a rotary swaging device. The cold plastic working was performed continuously without performing a heat treatment between working passes. Table 2 shows details of each pass and a cumulative area reduction rate after the multiple passes of the working. The cumulative area reduction rate was calculated by the above-described formula (1).

[TABLE 2]

Alloy No.	Diameter DO (mm) before processing	Diameter D1 (mm) after processing	Swaging processing pass (mm)	Area reduction rate (Cumulative area reduction rate) (%)	Number density (μm^{-2}) of nano-grains of not more than 75 nm	Hardness (HV) after processing	Shape of worked material	
1-1	6.0	5.5	6.0-5.5	16.0	0	492	Good	Comparative Example
1-2	6.0	5.0	6.0-5.5-5.0	30.6	21	560	Good	The present invention
1-3	6.0	4.5	6.0-5.5-5.0-4.5	43.8	110	564	Good	The present invention
1-4	6.0	4.0	6.0-5.5-5.0-4.5 -4.0	55.6	162	562	Good	The present invention
1-5	6.0	3.5	6.0-5.5-5.0-4.5 -4.0-3.5	66.0	223	560	Good	The present invention
1-6	6.0	3. 0	6.0-5.5-5.0-4.5 -4.0-3.5-3.0	75.0	276	568	Good	The present invention
1-7	6.0	2.5	6.0-5.5-5.0-4.5 -4.0-3.5-3.0-2.5	82.6	388	620	Good	The present invention
1-8	6.0	2.0	6.0-5.5-5.0-4.5 -4.0-3.5-3.0-2.5 -2.0	88.9	510	580	Good	The present invention
1-9	6.0	1.5	6.0-5.5-5.0-4.5 -4.0-3.5-3.0-2.5 -2.0-1.5	93.8	747	558	Good	The present invention

[0097] An alloy No. 1-1 has a wire diameter of 5.5 mm after the processing. A working rate (area reduction rate) was 16.0%. An alloy No. 1-2 was further subjected to swaging processing cumulatively to have a wire diameter of 5.0 mm (working rate 30.6%). The wire material of the alloy No. 1-2 was subjected to swaging processing in passes (working rate) shown in Table 2 cumulatively one by one to produce alloys No. 1-3 to No. 1-9. Thus, wire materials of the Ni-based alloys No. 1-1 to No. 1-9 having increased cumulative working rates from the bar material were produced. No heat treatment was performed between the swaging processings. The alloy samples all maintained their good shapes after the working. FIG. 3 shows an optical micrograph of a cross-sectional structure of the alloy No. 1-9 (with a magnification of 1000 times). The cross-sectional microstructure is taken from a halved wire material cut in a longitudinal direction thereof from a portion of the cross section at a position (position A) at 1/4D distant from a surface toward a central axis of the wire material (D indicates a wire diameter of the wire material). The samples were polished and then etched with use of Kalling's reagent. FIG. 3 shows a banded structure in which a γ phase and a γ' phase extend in a worked direction.

[0098] Furthermore, an EBSD image of the cross-sectional microstructure of each of the above alloy samples was evaluated. The cross-sectional microstructure was taken from a portion of the cross section at the position A. EBSD measurement was performed with use of a scanning electron microscope "JIB-4700F (manufactured by JEOL Ltd.)" equipped with an EBSD measurement system "Aztec Version 3.2 (manufactured by Oxford Instruments)". In the EBSD measurement conditions, a magnification was 10000 times, a scan step was 0.02 μm, and a grain boundary was defined by an orientation difference of not less than 15°. At this time, a smallest size (maximum length in the grain) of the nano-grain that could be observed in the EBSD image was approximately 25 nm, and the presence and the number of nano-grains having a maximum grain diameter of not less than 25 nm were observed. The wire material of the alloy No. 1-2 of the example according to the present invention included nano-grains having a maximum grain diameter of not more than 75 nm in the cross-sectional structure.

[0099] In the cross section of the wire material of the alloy No. 1-2 halved in the longitudinal direction, structures were also taken from a portion at a position (position B) at the surface of the material and a portion at a position (position C) at the central axis of the material, and the structures thereof were similarly analyzed by the EBSD. The cross-sectional structures were obtained from 6 portions in total, i.e. 2 portions were obtained from each position A, B and C. A total number of nano-grains having a maximum grain diameter of not more than 75 nm was counted in the field of view (2 μm $\times$ 3 μm). A number density of the nano-grains per unit area, which was obtained by dividing the total number of nano-grains by a total area of the fields of view (6 $\mu m^2 \times 6$), was "21 nano-grains per 1 μm^2".

[0100] A hardness of each alloy sample at the position A was measured. The wire material of the alloy No. 1-2 had a hardness of 560 HV

[0101] On the other hand, when a cross-sectional microstructure of the alloy No. 1-1 was observed in a manner similar to that of the alloy No. 1-2, no nano-grains having a maximum grain diameter of not more than 75 nm were observed. Furthermore, the alloy No. 1-1 had a hardness of 492 HV.

[0102] The wire materials of the alloy Nos. 1-3 to 1-9 also had nano-grains having a maximum grain diameter of not more than 75 nm in their cross-sectional structures. As an example, FIG. 4 shows an EBSD image (at the position A) of the alloy No. 1-9 (in FIG. 4, nano-grains can be seen as individual fine grains which can be distinguished from one another by differences in their color tones). A number density per unit area of the nano-grains in each of the cross-sectional structures of the wire materials was measured in a manner similar to that of the alloy No. 1-2. Furthermore, a hardness of the wire materials was measured. Table 2 shows measurement results of the wire materials.

[0103] The results in Table 2 show that once nano-grains had been generated in the Ni-based alloy, further cold plastic working increased the number of the nano-grains. Although the number of nano-grains was increased, the hardness of the Ni-based alloy was approximately constant regardless of the increase of the plastic working rate. Thus, the Ni-based alloy was able to be plastically cold-worked through swaging processing to produce the wire material example No. 1-9 according to the present invention having a wire diameter of 1.5 mm. When the wire material of the alloy No. 1-2 was used as a starting material (i.e., an alloy material having a hardness of not less than 500 HV and including grains having a maximum grain diameter of not more than 75 nm in a cross-sectional structure), cold plastic working was able to be performed so that a cumulative working rate from the wire material was 91% and that a cumulative working rate from the original bar material was 94%. Furthermore, even after the plastic working at the large cumulative working rate, the wire material example of the alloy No. 1-9 according to the present invention was able to be further plastically cold-worked. Since the hardness of the worked alloy example according to the present invention was approximately constant (558 HV to 620 HV) regardless of the working rate (if the working rate was not less than 85%, the hardness rather tended to be slightly decreased), a super heat resistant Ni-based alloy material in which once grains having a maximum grain diameter of not more than 75 nm have been formed and which has a hardness of not less than 500 HV can be subjected to further cold working.

[0104] After the above-described cold working, the alloy No. 1-9 was heat treated at 1200°C for 30 minutes (and then cooled in a furnace). The alloy No. 1-9 has a hardness of 365 HV after the heat treatment. FIG. 5 shows an optical micrograph of a cross-section of the alloy No. 1-9 (with a magnification of 200 times). The cross-section of the alloy No. 1-9 was polished then etched with use of Kalling's reagent and observed at the above-described position A. FIG. 5

shows that the heat treatment forms the worked structure into an equiaxed structure.

Example 2

[0105] A bar material was cut out from a hot-extruded material of the Ni-based alloy "A" (a diameter of 27 mm, an average grain size of 38 μm, and a hardness of 351 HV) produced by the method and under the conditions described in Example 1. The bar material had a diameter of 4 mm and a length of 60 mm. The bar material was taken so that the longitudinal direction is along the axis line direction of the extruded material. The bar material was subjected to multiple passes of working at a room temperature (approximately 25°C) with use of a rolling mill (FIG. 1). The cold plastic working was performed continuously without the heat treatment between working passes. Table 3 shows details of each pass and a rolling reduction rate after the multiple passes of the working. The rolling reduction rate was calculated by the above-described formula (2).

[0106] As a Comparative Example, the ingot of the Ni-based alloy "A" was heat treated at a holding temperature of 1200°C for a holding time of 8 hours, and then cooled in a furnace. Then, a bar material having a diameter of 4 mm and a length of 60 mm was cut out from the ingot. The bar material was rolled with use of a rolling mill similarly to the examples according to the present invention. That is, the raw material was produced by rolling a cast material without the hot extrusion. The bar material before the rolling process had a grain size (average grain size) of 2.8 mm and a hardness of 323 HV.

[0107] Alloy samples No. 2-2 to No. 2-5 according to the present invention all maintained their good shapes after the working (see FIG. 6A, FIG. 6B). However, alloys No. 2-6 and No. 2-7, which were not hot-extruded, caused strain during the rolling, and could not obtain a good sheet shape. Meandering or deformation was occurred (see FIGS. 7A and 7B).

[TABLE 3]

Alloy No.	Starting material	Diameter DO (mm) before processing	Plate thickness D1 (mm) after rolling	Rolling pass (mm)	Rolling reduction rate (%)	Number density (μm^{-2}) of nano-grains of not more than 75 nm	Hardness (HV) after processing	Shape of worked material	
2-1	Extruded material	4.0	3.5	4.0-3.5	12.5	0	461	Good	Comparative Example
2-2	Extruded material	4.0	2.5	4.0-3.5-3.0-2.5	37. 5	75	594	Good	The present invention
2-3	Extruded material	4.0	2.0	4.0-3.5-3.0-2.5 -2.0	50.0	213	598	Good	The present invention
2-4	Extruded material	4.0	1.5	4.0-3.5-3.0-2.5 -2.0-1. 5	62. 5	239	617	Good	The present invention
2-5	Extruded material	4.0	1.0	4.0-3.5-3.0-2.5 -2.0-1.5-1.0	75.0	441	620	Good	The present invention
2-6	Ingot	4.0	3.0	4.0-3.5-3.0	25.0	-	-	Poor	Comparative Example
2-7	Ingot	4.0	2.0	4.0-3.5-3.0-2.5 -2.0	50.0	-	-	Poor	Comparative Example

[0108] As shown in Table 3, the sheet material of an alloy No. 2-1 after the rolling process had a plate thickness of 3.5 mm, a working rate (rolling reduction rate) of 12.5%, and a hardness of 461 HV. For the sheet materials of the alloys No. 2-2 to No. 2-5, a working rate (rolling reduction rate) was not less than 30%. These Ni-based alloys each had a hardness of not less than 500 HV. Unlike the results of Example 1, however, as the working rate was increased, the hardness tended to be slightly increased. The sheet materials further subjected to the working had a hardness of not less than 600 HV

[0109] The above results show that, in the rolling process, a Ni-based alloy having a hardness of not less than 500 HV can be subjected to further cold working, similarly to Example 1.

[0110] In a cross-sectional microstructure of each of the sheet materials of the alloys No. 2-2 to No. 2-5, nano-grains having a maximum grain diameter of not more than 75 nm were observed. As the working rate was increased, a number density of the nano-grains was increased. On the other hand, in a cross-sectional microstructure of the wire material of the alloy No. 2-1, no nano-grains having a maximum grain diameter of not more than 75 nm were observed.

Example 3

[0111] A molten metal produced by vacuum melting was cast to produce a cylindrical ingot of a super heat resistant Ni-based alloy "B" with a diameter of 80 mm and a weight of 10.5 kg. Table 4 shows a composition of the Ni-based alloy "B" (by mass%). Table 4 also shows a "γ' mol%" of the ingot, which was obtained in a manner similar to that of Example 1.

[TABLE 4]

Alloy	C	Cr	Al	Ti	Co	Mo	W	Nb
B	0.1510	7.96	5.40	0.98	10.07	0.61	9.94	<0.01

Ta	Fe	V	Hf	B	Zr	Ni	γ' mol%
2.98	0.03	<0.01	1.37	0.0130	0.04	balance*	67.0%

*including inevitable impurities

[0112] The ingot of the s Ni-based alloy "B" was heat treated at a holding temperature of 1200°C for a holding time of 8 hours, and then cooled in a furnace. Then, a cylindrical material was cut out from the ingot along a longitudinal direction of the ingot. The cylindrical material had a length of 150 mm and a diameter of 66 mm. The cylindrical material was encased in an SUS304 capsule and subjected to the hot extrusion. The hot extrusion was performed under conditions including an extrusion temperature of 1150°C, an extrusion ratio of 10, and an extrusion stem speed of 15 mm/s. An extruded material having a diameter of 27 mm was obtained by the hot extrusion.

[0113] The extruded material was cut to be halved along an axis line direction of the extruded material, a microstructure and a hardness were evaluated in a cross section. FIG. 10 shows a cross-sectional microstructure of an axis portion of the cross section by observation under a scanning electron microscope (with a magnification of 2000 times). In the microstructure, various kinds of carbides (MC, M_6C, $M_{23}C_6$, and the like) were observed (dispersions in FIG. 10). The microstructure has a hardness of 496 HV.

[0114] A grain size of the raw material was evaluated on an EBSD image. A measurement spot was taken at a position of the cross-section at D/4 (D is a diameter of the extruded material) distant from a surface of the extruded material toward an axis of the extruded material. EBSD measurement was performed with use of a scanning electron microscope "JIB-4700F (manufactured by JEOL Ltd.)" equipped with an EBSD measurement system "Aztec Version 3.2 (manufactured by Oxford Instruments)". In the EBSD measurement conditions, a magnification was 2000 times; a scan step was 0.1 μm; and a grain boundary was defined by an orientation difference of not less than 15°. With regard to grains (including carbides) recognized as grains under the measurement conditions and by the definition, a grain size distribution showing a relationship between a maximum grain diameter (maximum length) of each grain and a number of grains having the grain diameter was obtained. From the grain diameter distribution, an average of the maximum grain diameter was calculated.

[0115] FIG. 8 shows the EBSD image at this time. FIG. 9 shows the grain size distribution. FIG. 9 shows grain diameters (maximum grain diameters) on its abscissa collectively every 0.2 μm width. For example, grains having maximum grain diameters of not less than 0.2 μm to less than 0.4 μm are collected in a group "0.4 μm", and grains having maximum grain diameters of not less than 0.6 μm to less than 0.8 μm are collected in a group "0.8 μm". Of the maximum grain diameters, a maximum value was 6.43 μm, and a minimum value was 0.36 μm. An average of the maximum grain diameters (i.e., a grain size of the raw material) was 1.1 μm.

[0116] Next, a bar material having a diameter of 6 mm and a length of 60 mm was cut out from the extruded material. The bar material was taken so that the longitudinal direction is along the axis line direction of the extruded material. The bar material was subjected to multiple passes of the cold plastic working at a room temperature (approximately 25 °C) with use of a rotary swaging device. The cold plastic working was performed continuously without the heat treatment between working passes. Table 5 shows details of each pass and a cumulative area reduction rate after the multiple passes of the working. The cumulative area reduction rate was calculated by the above-described formula (1).

[TABLE 5]

Alloy No.	Diameter DO (mm) before processing	Diameter D1 (mm) after processing	Swaging processing pass (mm)	Area reduction rate (Cumulative area reduction rate) (%)	Hardness (HV) after processing	Shape of worked material	
3-1	6. 0	5.5	6.0-5.5	16.0	563	Good	Comparative Example
3-2	6. 0	5.0	6.0-5.5-5.0	30.6	612	Good	The present invention
3-3	6. 0	4.5	6.0-5.5-5.0-4.5	43.8	611	Good	The present invention
3-4	6. 0	4. 0	6.0-5.5-5.0-4.5-4.0	55.6	610	Good	The present invention

[0117] As shown in Table 5, the wire materials of the alloys No. 3-2 to No. 3-4 reached a working rate (area reduction rate) of not less than 30%, but were able to be worked while maintaining their good shapes. In a cross-sectional microstructure of each of the wire materials of the alloys No. 3-2 to No. 3-4, nano-grains having a maximum grain diameter of not more than 75 nm were observed.

[0118] The wire materials of the alloys No. 3-2, No. 3-3, and No, 3-4 had a banded worked cross-sectional structure in which a γ phase and a γ' phase extend in a worked direction (a longitudinal direction of the wire material). Furthermore, carbides tended to be aggregated in the worked direction. FIGS. 11 and 12 show the above-described cross-sectional microstructures of the alloys No. 3-2 and No. 3-3 observed with a scanning electron microscope (with a magnification of 1000 times). The worked structure may be formed into an equiaxed structure by heat-treating the cold-worked alloy (e.g., at 1150°C for 30 minutes, and then cooled in a furnace). The Ni-based alloy then has a structure in which carbides are aggregated in a banded form in the equiaxed structure as described above. FIG. 13 shows a cross-sectional microstructure of the above-described equiaxed structure of the alloy No. 3-3 observed with a scanning electron microscope (with a magnification of 1000 times).

[0119] As the above, it was observed that the super heat resistant Ni-based alloys in the Examples had excellent plastic workability and that the Ni-based alloys manufactured by the method of the present invention can be processed into a wire material having any wire diameter and the like by plastically cold-working the Ni-based alloys of the present invention examples. While the wire materials or the sheet materials were manufactured in the Examples, the wire material or the sheet material may be, of course, a wire product or a sheet product which is an end product form. Since the Ni-based alloy of the present invention has excellent plastic workability, it is apparent to those skilled in the art that the Ni-based alloy of the present invention can also be plastic worked to produce forms other than the wire material or the wire product.

Claims

1. A method of manufacturing a super heat resistant Ni-based alloy having a composition such that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 35 mol%, the method comprising:

   a preparation step of manufacturing a raw material through hot extrusion, the raw material having a grain size of not more than 200 μm; and
   a working step of subjecting the raw material to cold plastic working at a working rate of not less than 30%.

2. The method according to claim 1, wherein the cold plastic working includes multiple workings, a cumulative working rate of the multiple workings being not less than 30%, and no heat treatment is performed between the multiple workings.

3. The method according to claim 1 or 2, wherein the Ni-based alloy has a composition such that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 40 mol%.

4. The method according to any one of claims 1 to 3, wherein the Ni-based alloy has a hardness of not less than 500 HV after the working step.

5. The method according to any one of claims 1 to 4, wherein the Ni-based alloy has a cross-sectional structure including not less than 5 grains per 1 μm^2 after the working step, the grains having a maximum grain diameter of not more than 75 nm .

6. The method according to any one of claims 1 to 5, further comprising a step of performing heat treatment after the working step.

7. The method according to any one of claims 1 to 6, wherein the Ni-based alloy has a composition including, by mass%, 0 to 0.25% of C, 8.0 to 25.0% of Cr, 0.5 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 0 to 8% of Mo, 0 to 15.0% of W, 0 to 4.0% of Nb, 0 to 5.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 3.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

8. The method according to claim 7, wherein the Ni-based alloy has a composition including, by mass%, 0 to 0.25% of C, 8.0 to 25.0% of Cr, 0.5 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 0 to 8% of Mo, 0 to 6.0% of W, 0 to 4.0% of Nb, 0 to 3.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 1.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

9. A super heat resistant Ni-based alloy having such a composition that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 35 mol%, and having a banded structure of gamma phase and gamma prime phase.

10. The Ni-based alloy according to claim 9, wherein carbides are aggregated in a banded direction of the banded structure.

11. The Ni-based alloy according to claim 9 or 10, having a hardness of not less than 500 HV.

12. A super heat resistant Ni-based alloy having such a composition that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 35 mol%, and having an equiaxed structure including gamma phase and gamma prime phase, the structure including carbides aggregating in a banded form.

13. The Ni-based alloy according to claim 12, having a hardness of less than 500 HV.

14. The Ni-based alloy according to any one of claims 9 to 13, wherein the Ni-based alloy has a composition such that an amount of precipitated gamma prime phase in equilibrium at 700°C is not less than 40 mol%.

15. The Ni-based alloy according to any one of claims 9 to 14, having a composition including, by mass%, 0 to 0.25% of C, 8.0 to 25.0% of Cr, 0.5 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 0 to 8% of Mo, 0 to 15.0% of W, 0 to 4.0% of Nb, 0 to 5.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 3.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

16. The Ni-based alloy according to claim 15, having a composition including, by mass%, 0 to 0.25% of C, 8.0 to 25.0% of Cr, 0.5 to 8.0% of Al, 0.4 to 7.0% of Ti, 0 to 28.0% of Co, 0 to 8% of Mo, 0 to 6.0% of W, 0 to 4.0% of Nb, 0 to 3.0% of Ta, 0 to 10.0% of Fe, 0 to 1.2% of V, 0 to 1.0% of Hf, 0 to 0.300% of B, 0 to 0.300% of Zr, and the balance of Ni and impurities.

FIG. 1

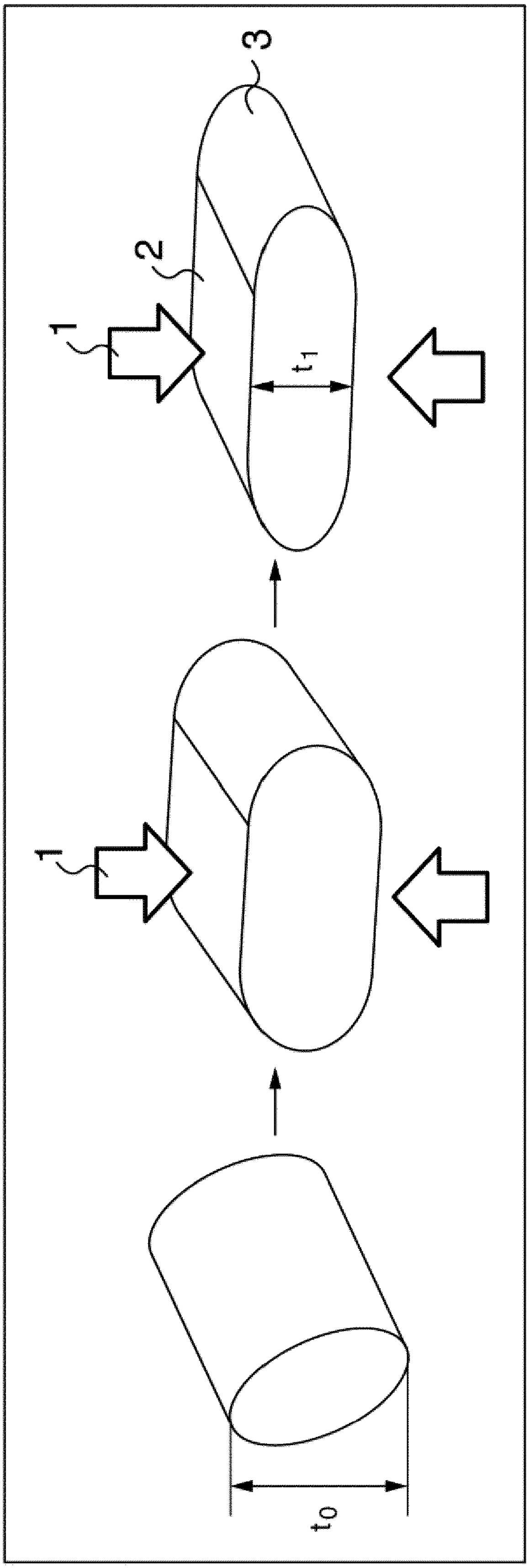
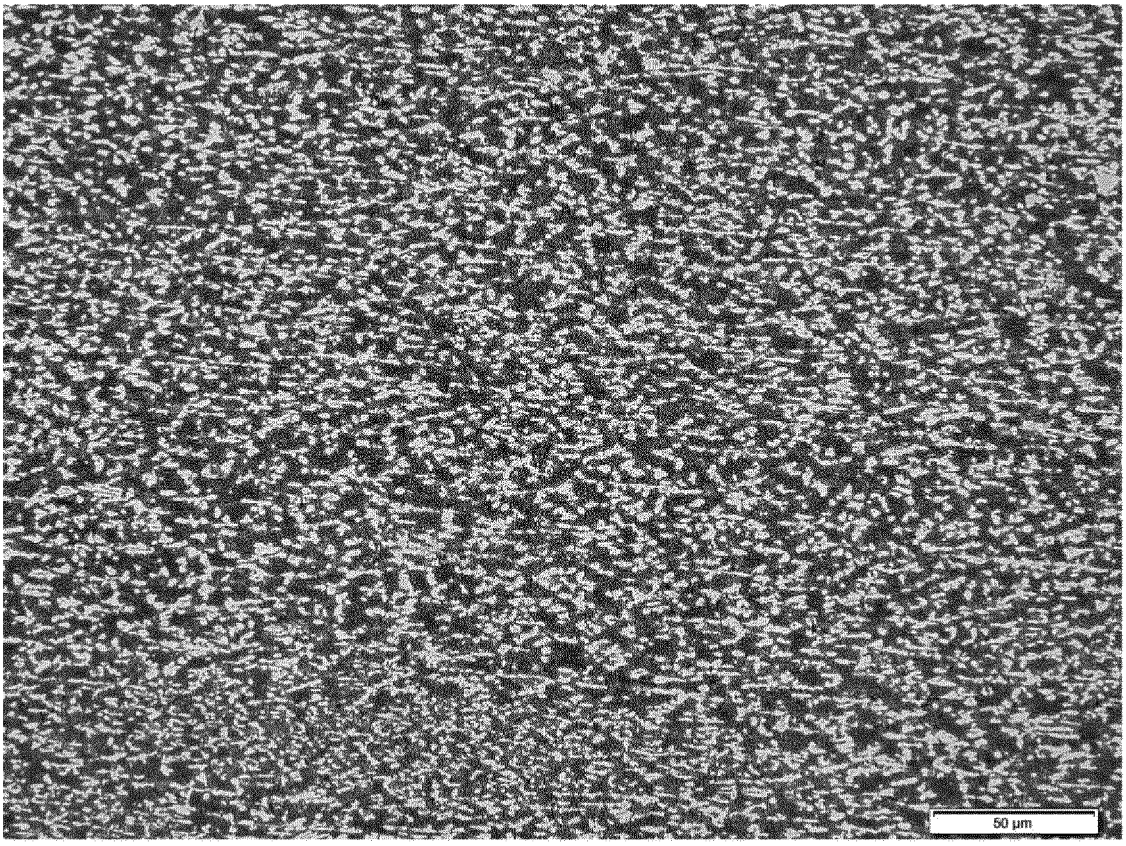
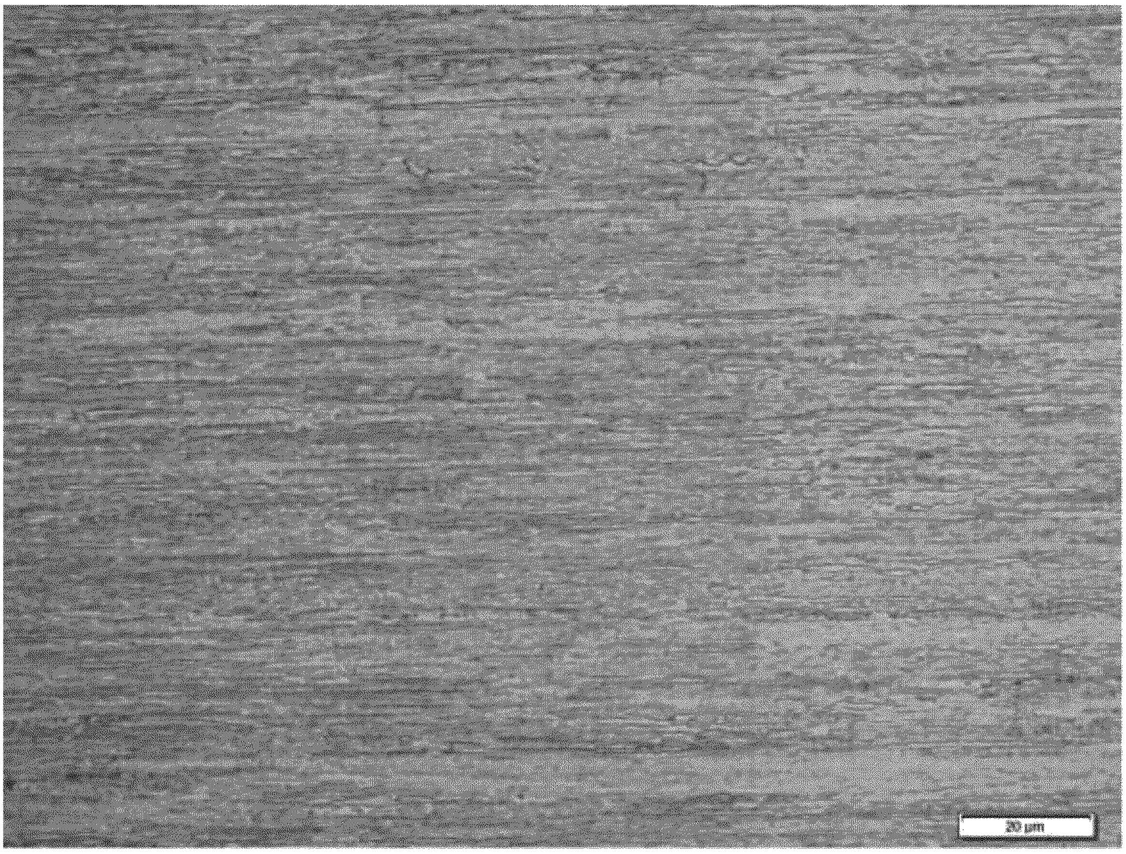


FIG. 2



50 μ m

FIG. 3



20μm

FIG. 4

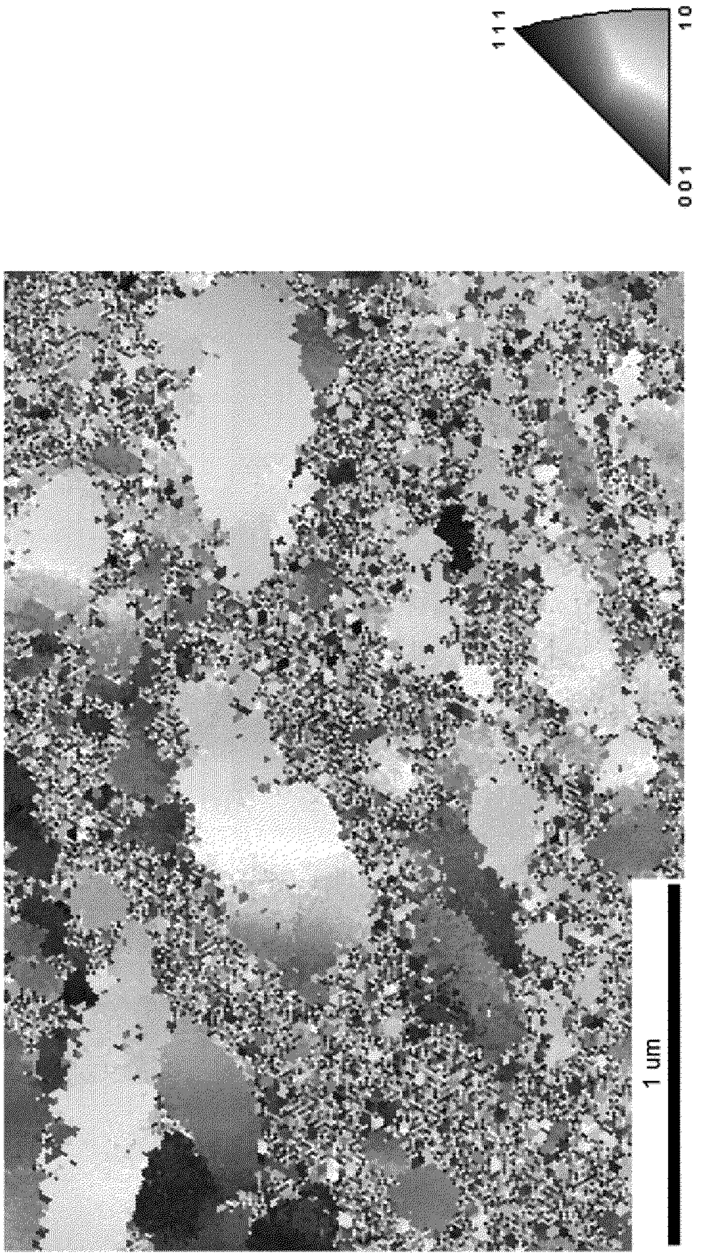
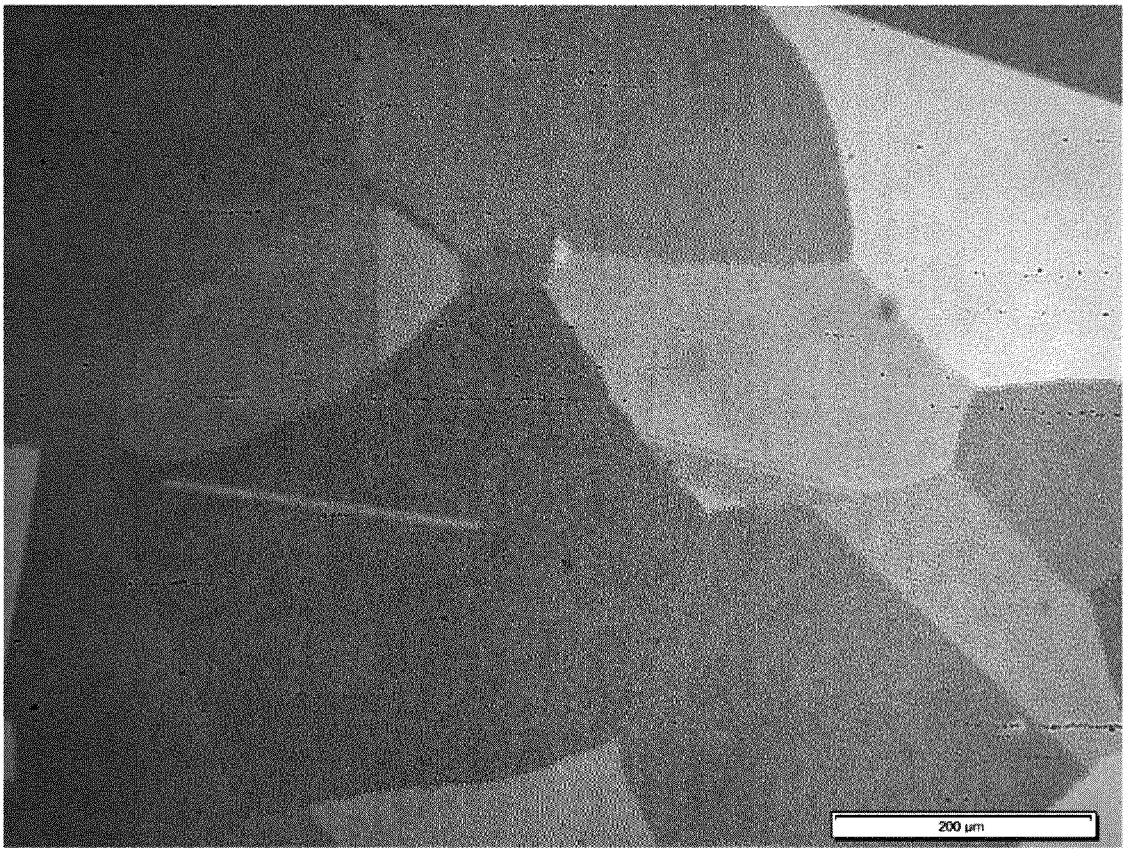


FIG. 5



200µm

FIG. 6A

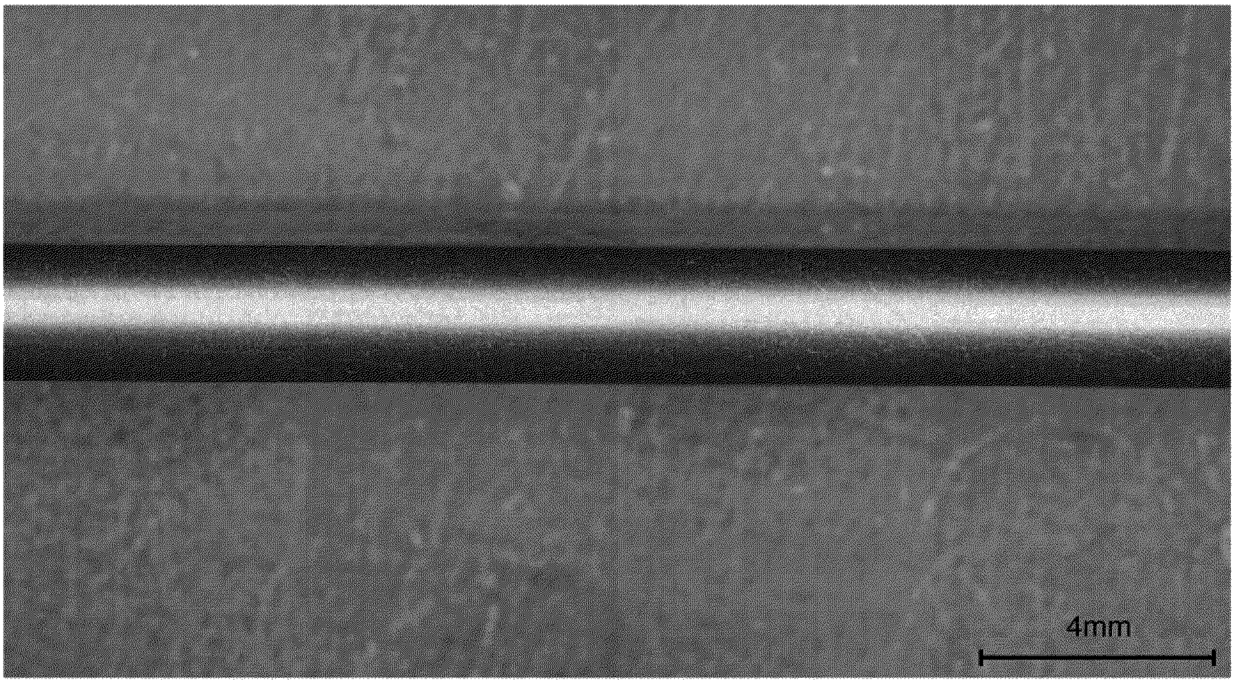


FIG. 6B

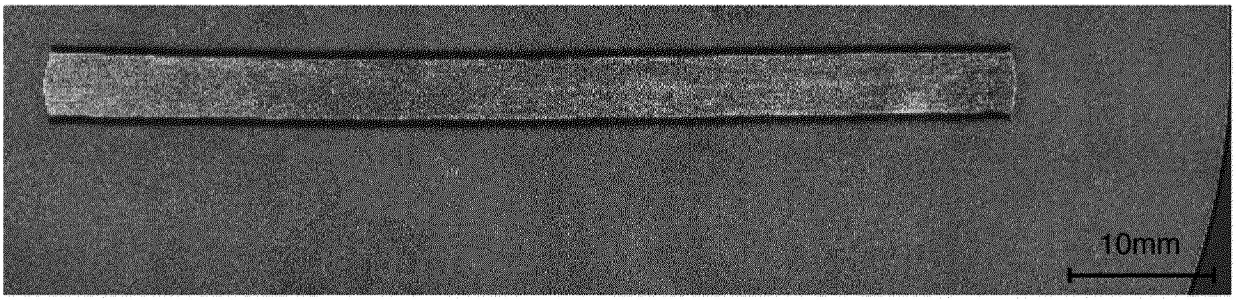


FIG. 7A

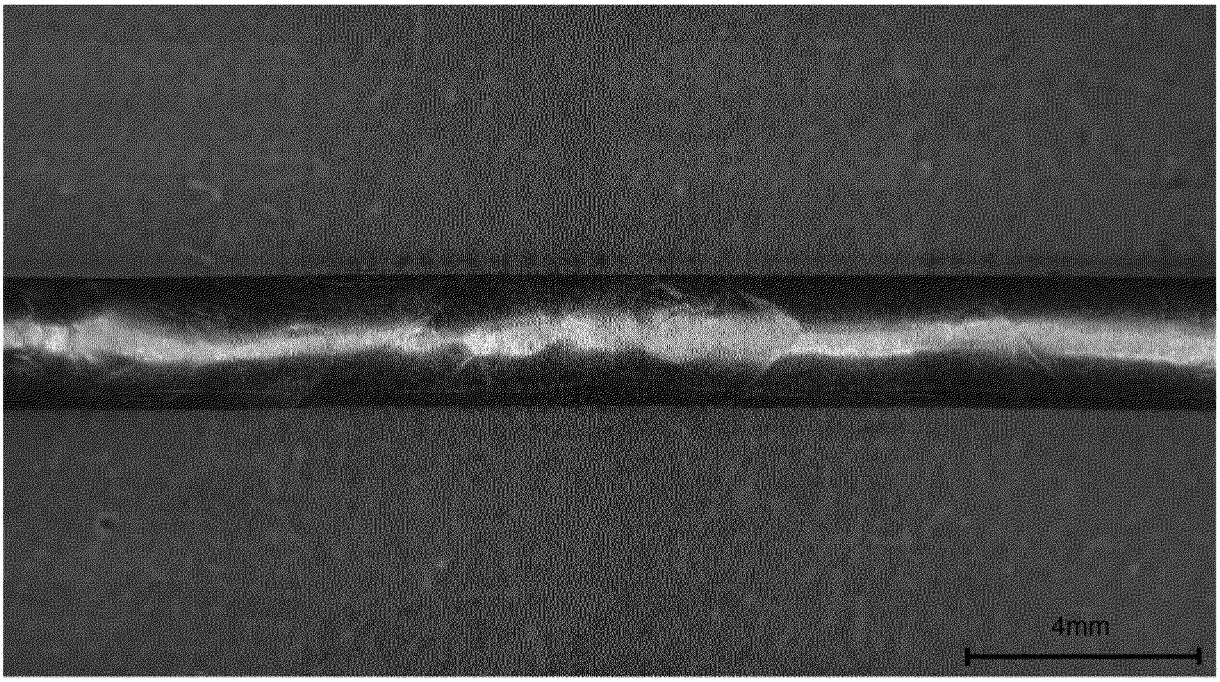


FIG. 7B

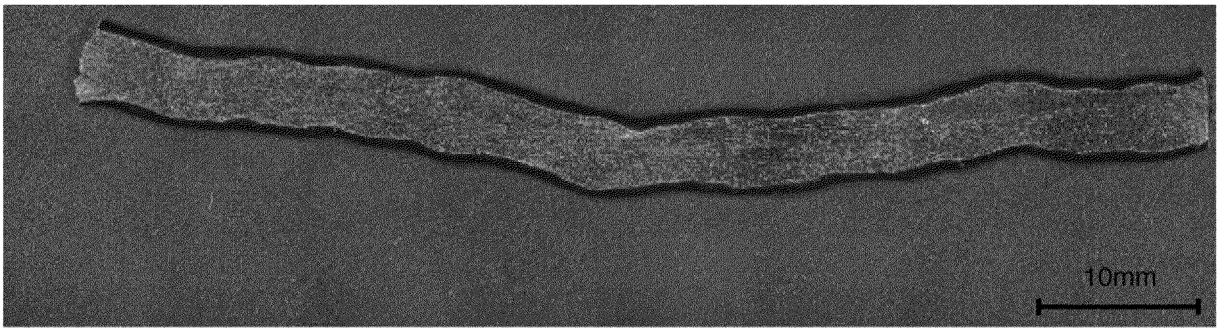


FIG. 8

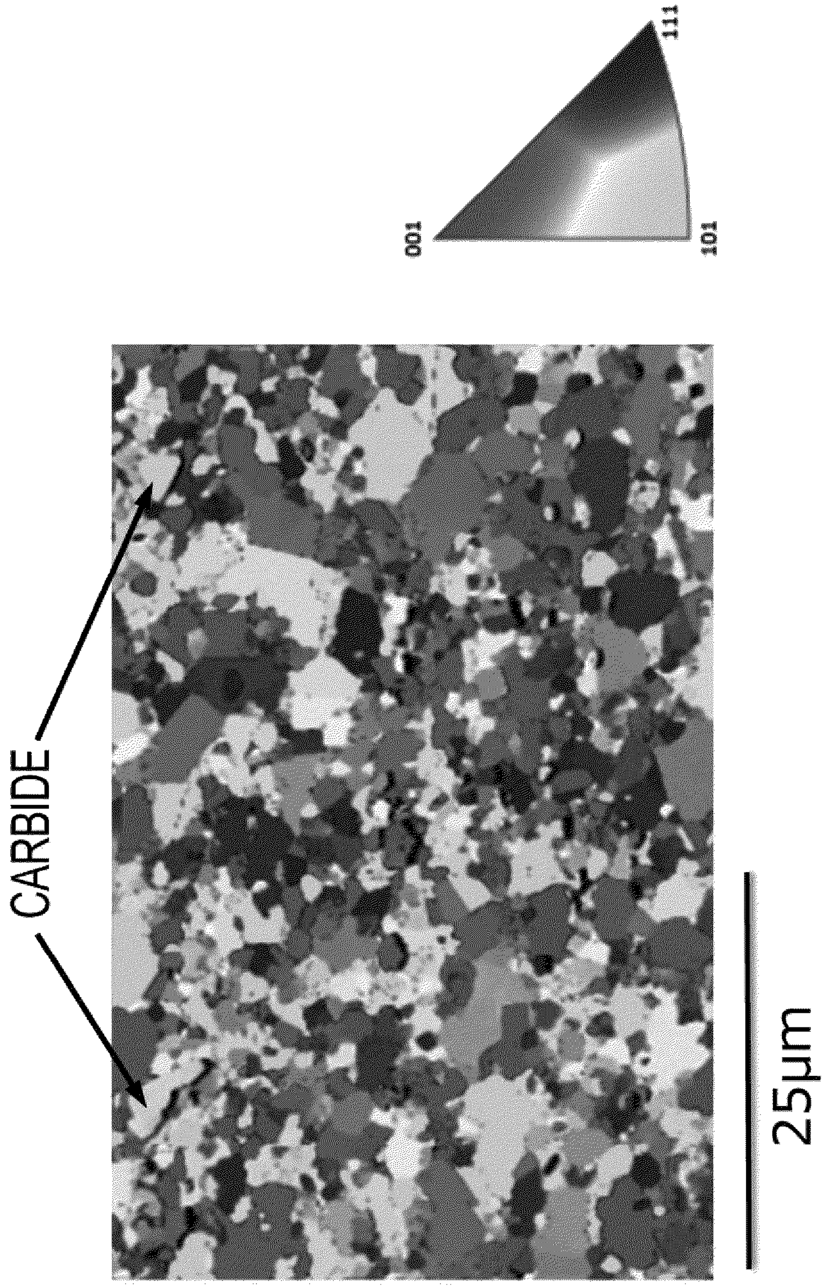


FIG. 9

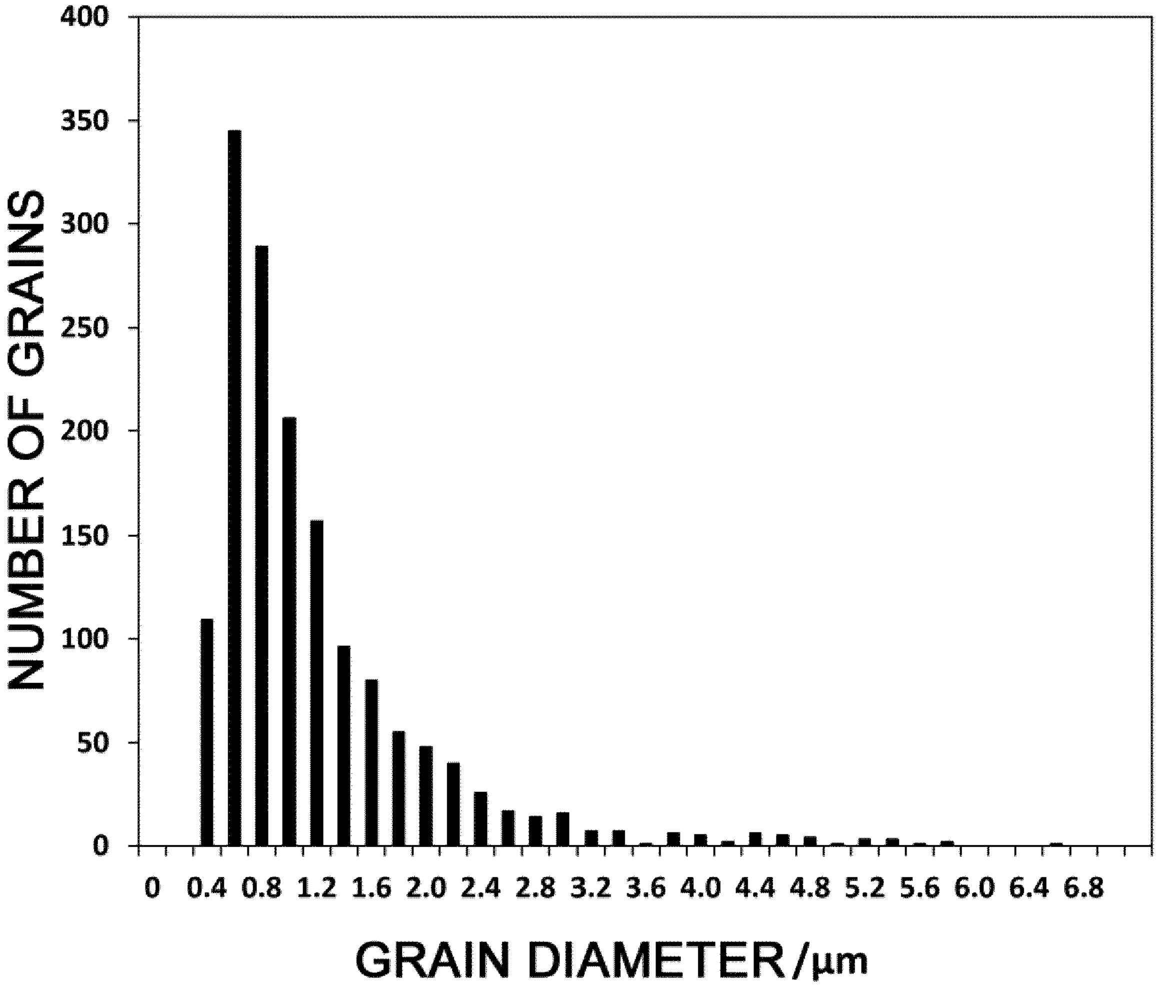
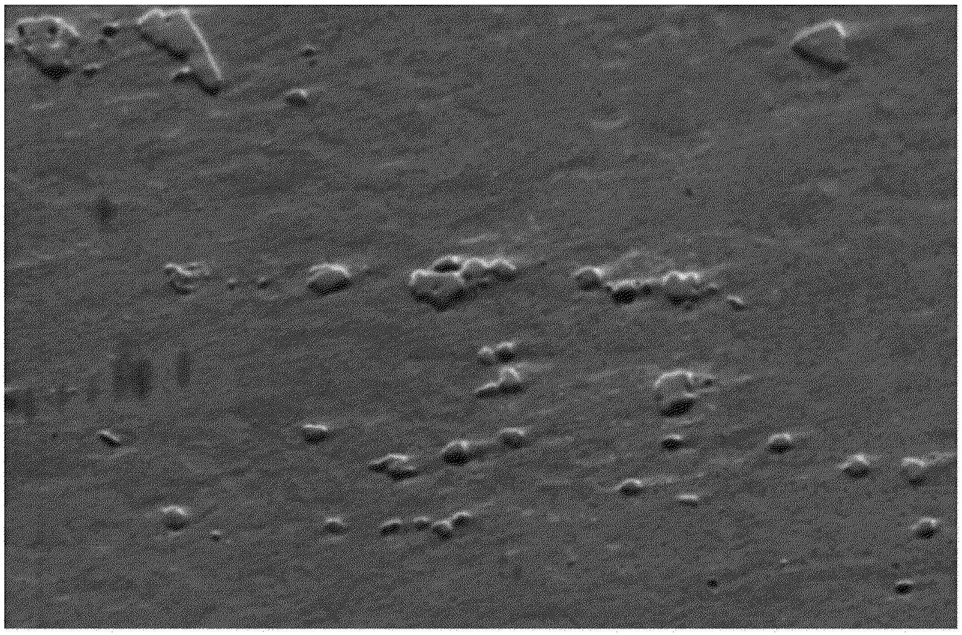
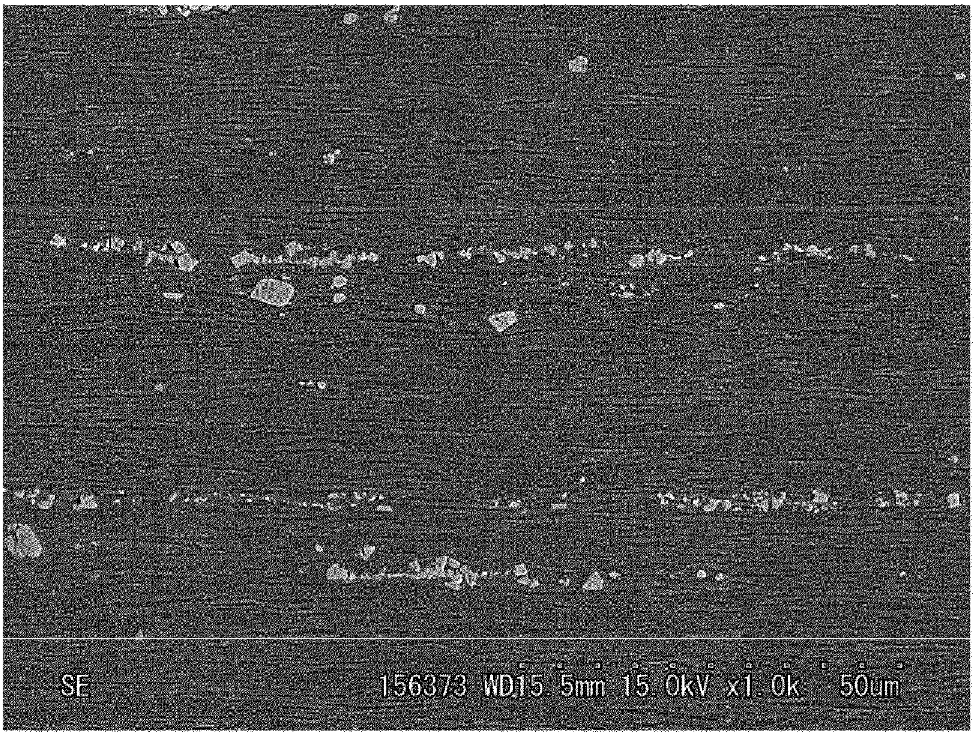

400
350
300
250
200
150
100
50
0
NUMBER OF GRAINS
0 0.4 0.8 1.2 1.6 2.0 2.4 2.8 3.2 3.6 4.0 4.4 4.8 5.2 5.6 6.0 6.4 6.8
GRAIN DIAMETER/μm

FIG. 10



25μm

FIG. 11



50μm

FIG. 12

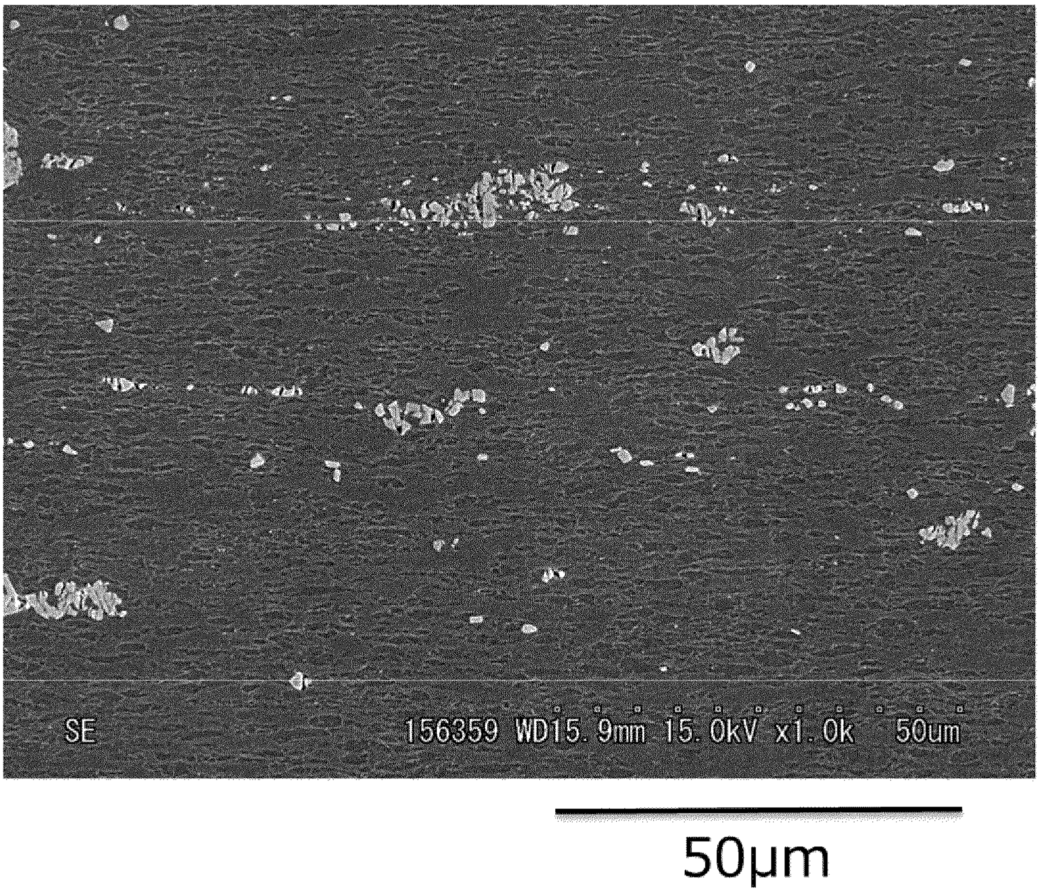
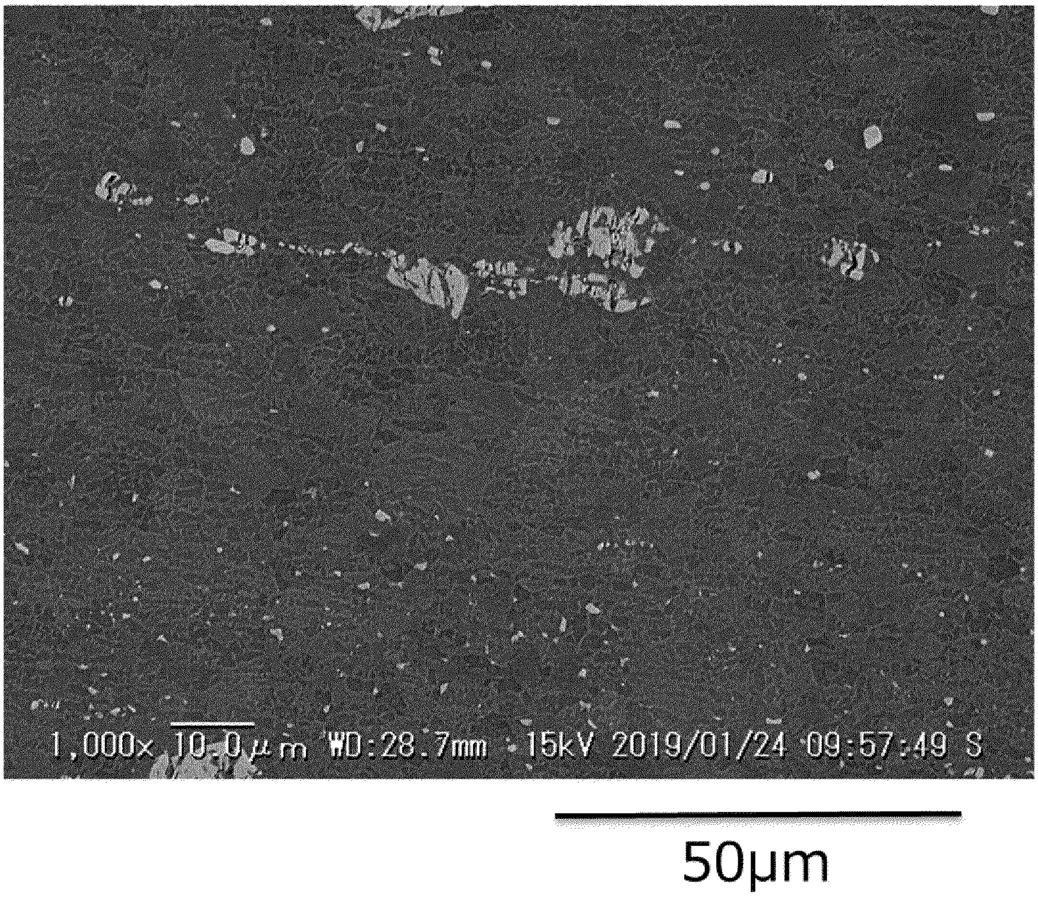


FIG. 13



INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2019/006991

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C22F1/10(2006.01)i, C22C19/05(2006.01)n, C22F1/00(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C22F1/10, C22C19/05, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	WO 2015/008343 A1 (MITSUBISHI HITACHI POWER SYSTEMS, LTD.) 22 January 2015, paragraphs [0027], [0029]-[0055], [0060]-[0080], fig. 1, 3, 6 & US 2016/0160334 A1, paragraphs [0027], [0035]-[0062], [0068]-[0086], fig. 1, 3A-3C, 6 & EP 3023509 A1 & CN 105189794 A	9, 11, 14-16 1-8 10, 12-13
Y	WO 2016/152982 A1 (HITACHI METALS, LTD.) 29 September 2016, paragraphs [0015]-[0016] & US 2018/0057921 A1, paragraphs [0054]-[0064] & EP 3287209 A1 & CN 107427896 A	1-8
P, X P, A	WO 2018/155446 A1 (HITACHI METALS, LTD.) 30 August 2018, paragraphs [0023]-[0029], [0048]-[0083], fig. 1-5 (Family: none)	9-11, 14-16 1-8, 12-13

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
14 May 2019 (14.05.2019)	28 May 2019 (28.05.2019)

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Patent documents cited in the description

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- US 4777710 A **[0006] [0007] [0008]**