



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

(43) Date of publication:
07.08.2019 Bulletin 2019/32

(51) Int Cl.:
B21C 23/00 (2006.01) **C22C 19/05** (2006.01)
C22F 1/10 (2006.01)

(21) Application number: **17855276.6**

(86) International application number:
PCT/JP2017/020143

(22) Date of filing: **30.05.2017**

(87) International publication number:
WO 2018/061317 (05.04.2018 Gazette 2018/14)

(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:
MA MD

(72) Inventors:
• **HAN, Gang**
Yasugi-shi
Shimane 692-8601 (JP)
• **KISHIGAMI, Ichirou**
Yasugi-shi
Shimane 692-8601 (JP)
• **OHTANI, Tomoiku**
Kumagaya-shi
Saitama 360-0843 (JP)

(30) Priority: **30.09.2016 JP 2016193522**

(71) Applicant: **Hitachi Metals, Ltd.**
Tokyo 108-8224 (JP)

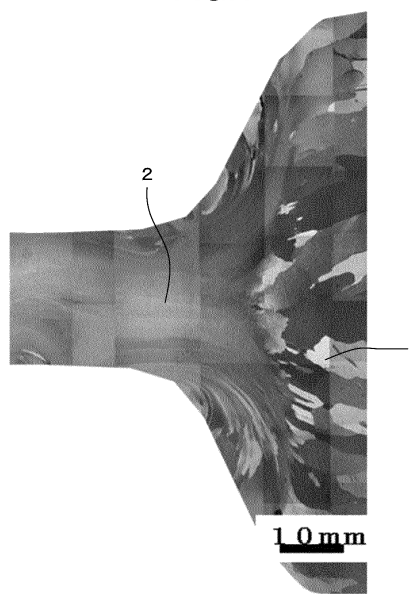
(74) Representative: **Beetz & Partner mbB**
Patentanwälte
Steinsdorfstraße 10
80538 München (DE)

(54) **METHOD OF MANUFACTURING NI-BASED SUPER HEAT RESISTANT ALLOY EXTRUDED MATERIAL, AND NI-BASED SUPER HEAT RESISTANT ALLOY EXTRUDED MATERIAL**

(57) Provided are a method of manufacturing a precipitation-strengthened Ni-based super heat resistant alloy extruded material with a high gamma prime content and an Ni-based super heat resistant alloy extruded material. This method of manufacturing an Ni-based super heat resistant alloy extruded material includes: a first step in which an ingot obtained by casting molten metal having a component composition of a precipitation-strengthened Ni-based super heat resistant alloy in which the equilibrium precipitation amount of gamma prime at 700°C is at least equal to 40 mol% is used as a billet, and the billet is heated to a hot working temperature that is at least equal to 1030°C and is less than the gamma prime solvus temperature of the Ni-based super heat resistant alloy; and a second step in which the billet that has been heated to the hot working temperature is inserted into a container, a compressive force is imparted to the billet from one end side of the container, and the billet is extruded at an extrusion rate of 10 to 300 mm/s from a hole in a die placed at the other end side of the container, to yield an Ni-based super heat resistant alloy extruded material. Furthermore, the Ni-based super heat resistant alloy extruded material has the component composition described hereinabove, with an average crystal

grain diameter in a cross-sectional structure at most equal to 20 μm in terms of an equivalent circle diameter.

FIG.1



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a method of manufacturing an extruded material of a super heat resistant Ni-based alloy, and to the extruded material of the super heat resistant Ni-based alloy.

BACKGROUND ART

10 **[0002]** A "precipitation strengthening type" super heat resistant Ni-based alloy, which has excellent heat resistance (high-temperature strength), has been used for a material for a component of e.g. an engine of an aircraft or a gas turbine for power generation. The Ni-based alloy is strengthened by "a gamma prime (γ') phase (hereinafter also referred to as "gamma prime" simply)". The gamma prime is a precipitation strengthening phase of an intermetallic compound, for example Ni_3Al , Ni_3Ti , or $\text{Ni}_3(\text{TiAl})$. It is effective to increase an amount of the gamma prime in order to further improve

15 the heat resistance of the Ni-based alloy.
[0003] Some of these components are produced by extrusion. The extrusion is a method of, for example, inserting a billet heated at a hot-working temperature into a container and applying a compressive force to the billet from one end of the container to extrude the billet through a hole of a die installed at the other end of the container to produce an extruded material. For manufacturing the extruded material of the precipitation strengthening type super heat resistant

20 Ni-based alloy, it has been proposed that an ingot produced by casting a molten metal having a composition of the Ni-based alloy is used as a billet and extruding the billet being the ingot (see Patent Literature 1).

[0004] PATENT LITERATURE 1: JP 63-125649 A

SUMMARY OF the INVENTION

25 **[0005]** In extrusion of the precipitation strengthening type super heat resistant Ni-based alloy, if a billet includes higher amount of gamma prime, deforming resistance is increased to remarkably decrease extrusion workability (i.e. hot-workability). If the billet is "an ingot" having a composition of the Ni-based alloy, segregation tends to occur during solidification in the casting and a number of brittle phases are generated in the billet. Thus, cracks tend to occur from grain boundaries of the cast structure during the extrusion and thus extrusion workability of the billet is decreased.

30 **[0006]** An object of the present invention is to provide a method of manufacturing an extruded material of a precipitation strengthening type super heat resistant Ni-based alloy, wherein a billet is an ingot having a composition of the Ni-based alloy and including a large amount of gamma prime, as well as to provide the extruded material of the Ni-based alloy.

35 **[0007]** According to the present invention, provided is a method of manufacturing an extruded material of a super heat resistant Ni-based alloy. The method includes: a first step of heating a billet made of the Ni-based alloy at a hot-working temperature; and a second step of inserting the billet heated at the hot-working temperature into a container, and applying a compressive force to the billet from one end of the container to extrude the billet through a hole of a die at the other end of the container, thereby producing the extruded material of the Ni-based alloy. The billet of the Ni-based alloy is an ingot produced by casting a molten metal having a composition of the Ni-based alloy. For the composition, an amount of precipitated gamma prime in equilibrium at 700°C is not less than 40 mol %. The hot-working temperature is not lower than 1030°C but lower than a gamma prime solvus temperature of the billet of the Ni-based alloy, and the billet is extruded at an extruding speed of 10 to 300 mm/s.

40 **[0008]** According to the present invention, an extruded material of a super heat resistant Ni-based alloy is provided. The material has a composition of a precipitation strengthening type super heat resistant Ni-based alloy. For the composition, an amount of precipitated gamma prime in equilibrium at 700°C is not less than 40 mol%. The material has an average crystal grain size in a cross-sectional structure of not more than 20 μm in an equivalent circle diameter.

45 **[0009]** According to the present invention, an extruded material having a composition of a precipitation strengthening type super heat resistant Ni-based alloy including a greater amount of gamma prime can be manufactured. In addition, an extruded material of the super heat resistant Ni-based alloy having the above composition can be provided.

50

BRIEF DESCRIPTION OF DRAWINGS

[0010]

55 FIG. 1 is a photograph showing an example of a cross-sectional structure of a portion of a billet near a die hole, which cross-sectional area is reduced by extrusion according to the present invention.

FIG. 2 shows an example of an electron beam scattering diffraction (EBSD) image of a cross-sectional microstructure of an extruded material manufactured in accordance with the present invention.

FIG. 3 shows an example of a relationship between a strain rate and a reduction of a cross-sectional area in a high-temperature tensile test on a precipitation strengthening type super heat resistant Ni-based alloy including not less than 40 mol % of precipitated gamma prime at 700°C in an equilibrium state.

DESCRIPTION OF EMBODIMENTS

[0011] In a method according to the present invention, a billet is inserted into a container and a compressive force is applied to the billet from one end of the container so that the billet is extruded from a die hole at the other end of the container. That is, "direct extrusion" is employed. The method according to the present invention by this direct extrusion has following features for manufacturing an extruded material having a composition of the precipitation strengthening type super heat resistant Ni-based alloy including a large amount of gamma prime.

(1) In the method according to the present invention, a billet is an ingot produced by casting a molten metal having the composition of the precipitation strengthening type super heat resistant Ni-based alloy including not less than 40 mol % of precipitated gamma prime in equilibrium at 700°C. Note that the ingot and the extruded material have the composition of the Ni-based alloy including not less than 40 mol % of precipitated gamma prime in equilibrium at 700°C.

[0012] A structure of the Ni-based alloy is substantially composed of a gamma phase in which alloying elements solid-solute in a Ni matrix, and gamma prime that is a precipitation strengthening phase of an intermetallic compound typically such as $\text{Ni}_3(\text{TiAl})$ or the like. The Ni-based alloy is hot-worked typically at a temperature between a solid solution temperature of the gamma prime (gamma prime solvus temperature) and a solidus temperature of the Ni-based alloy (for example, at a temperature between 900°C and 1200°C). If the alloy includes a large amount of the gamma prime during the hot working, the alloy has higher deforming resistance and thus the hot-workability of the alloy is decreased.

[0013] An amount of gamma prime in the Ni-based alloy changes depending on a temperature thereof. The equilibrium precipitation amount of gamma prime (that is an amount of gamma prime in a thermodynamic equilibrium state) increases from the minimum as a temperature decreases from the gamma prime precipitation start temperature (i.e. gamma prime solvus temperature), and the temperature dependence becomes smaller (or becomes approximately constant) below about 700°C. Therefore, an overall tendency of the precipitation amount of gamma prime can be understood based on a value at 700°C.

[0014] The billet of Ni-based alloy including not less than 40 mol % of precipitated gamma prime at 700°C in an equilibrium state includes a large amount of gamma prime and the gamma prime phase does not disappear in the temperature range, and the billet has been difficult to be extruded at a temperature of not lower than the gamma prime solvus temperature. The present invention makes it possible to extrude the billet of the super heat resistant Ni-based alloy that has been hard to be hot-worked.

[0015] In the billet that is to be extruded in the method according to the present invention, an amount of precipitated gamma prime in equilibrium at 700°C is preferably not less than 50 mol% , more preferably not less than 60 mol%. While it is not particularly necessary to define an upper limit, its practical value is about 75 mol%.

[0016] For the Ni-based alloy, the amount of precipitated gamma prime in equilibrium, expressed in "mol %", can be obtained from the composition of the alloy. The amount in "mol%" can be obtained by analysis through a thermodynamic equilibrium calculation. The amount can be obtained correctly and easily by using various kinds of thermodynamic equilibrium calculation software for the analysis.

[0017] The precipitation strengthening type super heat resistant Ni-based alloy, in which an amount of precipitated gamma prime in equilibrium at 700°C is not less than 40 mol%, has a basic composition, for example, including (by mass %, hereinafter "mass %" is simply referred to as "%") C: 0.001 to 0.25%, Cr: 8.0 to 22.0%, Mo: 2.0 to 7.0%, Al: 2.0 to 8.0%, Ti: 0.4 to 7.0%, and the balance of Ni and impurities. The alloy may further include one or more of Co: not more than 28.0%, W: not more than 6.0%, Nb: not more than 4.0%, Ta: not more than 3.0%, Fe: not more than 10.0%, V: not more than 1.2%, Hf: not more than 1.0%, B: not more than 0.300%, and Zr: not more than 0.30%. Examples of such an alloy include Alloy 713C, UDIMET720 (UDIMET is a registered trademark of Special Metals Corporation), and IN100.

[0018] With regard to the above composition, effects of each element are described below.

<C: 0.001 to 0.25%>

[0019] Carbon (C) effects to increase casting ability of the Ni-based alloy and to increase strength of grain boundaries. When an amount of carbon increases, however, coarse eutectic carbides precipitate in a last solidification portion of the cast ingot. As an amount of carbon increases, more eutectic carbides are generated and as a result, the carbides become coarse. As the coarse carbides increase, the carbides becomes cracking start points during plastic working, and ductility

of the alloy in the plastic working deteriorates. Accordingly, the carbon content is preferably 0.001 to 0.25%. More preferably, the carbon content is not more than 0.10%, further more preferably not more than 0.05%, and particularly preferably not more than 0.02%. Also, the carbon content is more preferably not less than 0.003%, further more preferably not less than 0.005%, and particularly preferably not less than 0.008%.

<Cr: 8.0 to 22.0%>

[0020] Chromium (Cr) improves oxidation resistance and corrosion resistance. However, excessive amount of Cr forms a brittle phase, such as a σ phase, to deteriorate strength and hot-workability. Therefore, the Cr content is preferably 8.0 to 22.0%. More preferably, the Cr content is not less than 9.0%, further more preferably not less 9.5%, and particularly preferably not less 10.0%. Also, the Cr content is more preferably not more than 18.0%, further more preferably not more than 16.0%, and particularly preferably not more than 14.0%.

<Mo: 2.0 to 7.0%>

[0021] Molybdenum (Mo) contributes to solid-solution strengthening of a matrix, and has an effect of improving high-temperature strength. However, excessive amount of Mo forms an intermetallic compound phase and deteriorates high-temperature strength. Therefore, the Mo content is preferably 2.0 to 7.0%. More preferably, the Mo content is not less than 2.5%, further more preferably not less than 3.0%. Also, the Mo content is more preferably not more than 6.0%, further more preferably not more than 5.5%, and particularly preferably not more than 5.0%.

<Al: 2.0 to 8.0%>

[0022] Aluminum (Al) forms the gamma prime phase and improves high-temperature strength. However, an excessive amount of Al deteriorates hot-workability and causes a material defect such as cracks during an extrusion process. Therefore, the Al content is preferably 2.0 to 8.0%. More preferably, the Al content is not less than 2.5%, further more preferably not less than 3.5%, and particularly preferably not less than 4.5%. Also, the Al content is more preferably not more than 7.5%, further more preferably not more than 7.0%, and particularly preferably not more than 6.5%.

<Ti: 0.4 to 7.0%>

[0023] Titanium (Ti) forms, similar to Al, the gamma prime and increases high-temperature strength through forming of the gamma prime. However, an excessive amount of Ti forms a harmful η (eta) phase and deteriorates hot-workability. Therefore, the Ti content is preferably 0.4 to 7.0%. More preferably, the Ti content is not less than 0.45%, and further more preferably not less than 0.5%. Also, the Ti content is more preferably not more than 5.0%, further more preferably not more than 3.0%, and particularly preferably not more than 1.0%.

<Co: not more than 28.0%>

[0024] Cobalt (Co) is an optional element that improves stability of the alloy structure, and can maintain hot-workability even if the alloy includes a large amount of strengthening element Ti. On the other hand, Co is expensive and thus increases a cost of the alloy. Therefore, even when the alloy include Co, the Co content is preferably up to 28.0%, more preferably up to 18.0%, further more preferably up to 16.0%, and particularly preferably up to 13.0%. If Co is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of Co is 0%. Furthermore, the Co content may be less than 1.0%.

[0025] In order to achieve the above effect of Co, the Co content is preferably not less than 1.0%, more preferably not less than 3.0%, further more preferably not less than 8.0%, and particularly preferably not less than 10.0%.

<W: not more than 6.0%>

[0026] Tungsten (W) is an optional element that contributes to solid-solution strengthening of a matrix, similar to Mo. However, excessive amount of W results in formation of a harmful intermetallic compound phase to decrease high-temperature strength. Therefore, even when the alloy includes W, the W content is preferably not more than 6.0%, more preferably not more than 5.5%, further more preferably not more than 5.0%, and particularly preferably not more than 4.5%. If W is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of W is 0%. Furthermore, the W content may be less than 1.0%, further less than 0.8%.

[0027] In order to achieve the above effect of W, the W content is preferably not less than 1.0%. Addition of both W and Mo is more effective in achieving the solid-solution strengthening. In the case where the alloy includes W in com-

bination with Mo, the W content is preferably not less than 0.8%.

<Nb: not more than 4.0%>

[0028] Niobium (Nb) is an optional element that forms the gamma prime and increases high-temperature strength through solid-solution strengthening of the gamma prime, similar to Al and Ti. However, excessive amount of Nb results in formation of a harmful delta δ (delta) phase to deteriorate hot-workability. Therefore, even when the alloy includes Nb, the Nb content is preferably not more than 4.0%, more preferably not more than 3.5%, further more preferably not more than 3.0%, and particularly preferably not more than 2.5%. If Nb is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of Nb is 0%. Then, the Nb content is less than 0.5%.

[0029] In order to achieve the above effect of Nb, the Nb content is preferably not less than 0.5%, more preferably not less than 1.0%, further more preferably not less than 1.5%, and particularly preferably not less than 2.0%.

<Ta: not more than 3.0%>

[0030] Tantalum (Ta) is an optional element that forms the gamma prime and increases high-temperature strength through solid-solution strengthening of the gamma prime, similar to Al and Ti. However, excessive amount of Ta makes the gamma prime phase unstable and coarse at a high temperature. Furthermore, Ta forms a harmful η (eta) phase to deteriorate hot-workability. Therefore, even when the alloy includes Ta, the Ta content is preferably not more than 3.0%, more preferably not more than 2.5%, further more preferably not more than 2.0%, and particularly preferably not more than 1.5%. In addition, if Ta is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of Ta is 0%. Then, the Ta content is less than 0.3%.

[0031] In order to achieve the above effect of Ta, the Ta content is preferably not less than 0.3%, more preferably not less than 0.5%, further more preferably not less than 0.7%, and particularly preferably not less than 1.0%.

<Fe: not more than 10.0%>

[0032] Fe is an optional element that can be included in the alloy instead of expensive Ni or Co and is effective in reducing the cost. However, excessive amount of Fe forms a brittle phase such as a σ phase to deteriorate strength and hot-workability. Therefore, even when the alloy includes Fe, the Fe content is preferably not more than 10.0%, more preferably not more than 8.0%, further more preferably not more than 6.0%, and particularly preferably not more than 3.0%. If Fe is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of Fe is 0%. Then, the Fe content is less than 0.1%.

[0033] In order to achieve the above effect of Fe, an amount of Fe that is instituted of Ni or Co is preferably not less than 0.1%, more preferably not less than 0.4%, further more preferably not less than 0.6%, and particularly preferably not less than 0.8%.

<V: not more than 1.2%>

[0034] Vanadium (V) is an optional element that is effective for solid-solution strengthening of a matrix and generation of carbide to increase grain boundary strength. However, excessive amount of V results in formation of such phase that is unstable at a high temperature during a manufacturing process, and adversely affects the productivity and high-temperature dynamic performance. Therefore, even when the alloy includes V, the V content is preferably not more than 1.2%, more preferably not more than 1.0%, further more preferably not more than 0.8%, and particularly preferably not more than 0.7%. If V is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of V is 0%. Then, the V content is less than 0.1%.

[0035] In order to achieve the above effect of V, the V content is preferably not less than 0.1%, more preferably the V content 0.2%, further more preferably the V content 0.3%, and particularly preferably the V content 0.5%.

<Hf: not more than 1.0%>

[0036] Hafnium (Hf) is an optional element that is effective for improving oxidation resistance of the alloy and generation of carbide to increase grain boundary strength. However, 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, even when the alloy includes Hf, the Hf content is preferably not more than 1.0%, more preferably not more than 0.7%, further more preferably not more than 0.5%, and particularly preferably not more than 0.3%. If Hf is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of Hf is 0%. Then, the Hf content is less than 0.02%.

[0037] In order to achieve the above effect of Hf, the Hf content is preferably not less than 0.02%, more preferably not less than 0.05%, further more preferably not less than 0.1%, and particularly preferably not less than 0.15%.

<B: not more than 0.300%>

[0038] Boron (B) is an optional element that can strengthen grain boundaries and improve creep strength and ductility. However, excessive amount of B drastically decreases a melting point of the alloy and forms coarse boride to deteriorate workability. Therefore, even when the alloy includes B, the B content is preferably not more than 0.300%, more preferably not more than 0.100%, further more preferably not more than 0.050%, and particularly preferably not more than 0.020%. If B is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of B is 0%. Then, the B content is less than 0.001%.

[0039] In order to achieve the above effect of B, the B content is preferably not less than 0.001%, more preferably not less than 0.003%, further more preferably not less than 0.005%, and particularly preferably not less than 0.007%.

<Zr: not more than 0.30%>

[0040] Zirconium (Zr) is an optional element that has an effect of improving grain boundary strength, similar to B. However, excessive amount of Zr drastically decreases a melting point of the alloy and decreases high-temperature strength and hot-workability. Therefore, even when the alloy includes Zr, the Zr content is preferably not more than 0.30%, more preferably not more than 0.25%, further more preferably not more than 0.20%, and particularly preferably not more than 0.15%. If Zr is not intentionally added (i.e. it is inevitable impurity in a raw material), the lower limit of Zr is 0%. Then, the Zr content is less than 0.001%.

[0041] In order to achieve the above effect of Zr, the Zr content is preferably not less than 0.001%, more preferably not less than 0.005%, further more preferably not less than 0.01%, and particularly preferably not less than 0.03%.

[0042] The billet that is to be extruded in the method according to present invention is "an ingot" produced by casting a molten metal having a composition of the precipitation strengthening type super heat resistant Ni-based alloy which includes gamma prime in an equilibrium precipitation amount at 700°C of not less than 40 mol%. Thus, the ingot having the above composition tends to segregate during solidification in the casting and a number of brittle phases are formed in the solidified cast structure. In the conventional extrusion, when the ingot including a number of brittle phases is used as a billet, the billet is subject to cracks from grain boundaries of the cast structure during the extrusion, and thus it has been difficult to produce the extruded material having a fine recrystallization structure. The method in accordance with the present invention makes it possible to successfully extrude such ingot of the Ni-based alloy as the billet.

[0043] (2) In the method according to the present invention, a hot-working temperature of the ingot, as the billet, is not lower than 1030°C but lower than "the gamma prime solvus temperature" of the Ni-based alloy.

[0044] It has been difficult to extrude a billet when the billet is an ingot having a composition of the precipitation strengthening type super heat resistant Ni-based alloy that includes gamma prime in an amount of not less than 40 mol% in equilibrium at 700°C and that is produced by casting. However, the present inventors have found that the ability of extrusion of such a billet is not simply determined by a deforming resistance of the billet.

[0045] In a process of the extrusion of the billet, as a hot-working temperature decreases from the gamma prime solvus temperature, an amount of precipitated gamma prime in the billet increases largely. As a result, deforming resistance of the billet increases remarkably. Furthermore, a heat generated from the deformation is not sufficient. Thus, a region near the dice hole in particular, where the billet is decreased in its cross-sectional area (cross-sectional area reducing portion), has an uneven temperature. This uneven temperature in addition to the high deforming resistance makes plastic deformation of the billet less homogeneous. As a result, an extruded material with a fine recrystallization structure is difficult to be produced.

[0046] The present inventors have found that it is effective to consider heat generated from the deformation as well as reduction of the deforming resistance for improving the possibility of extrusion of the billet. Since the deforming resistance of the billet, from which the working heat can be generated, very sensitively depends on a hot-working temperature, it is important to manage the hot-working temperature. In the method according to the present invention, the hot-working temperature is set to "not lower than 1030°C". Thereby the working heat can be used effectively. Even when the gamma prime exists in the billet (i.e. at the hot-working temperature below the gamma prime solvus temperature), the extrusion ability of the billet can be wholly improved. The hot-working temperature is preferably not lower than 1050°C, more preferably not lower than 1080°C, further more preferably not lower than 1100°C, and particularly preferably not lower than 1130°C.

[0047] As the hot-working temperature increases toward the gamma prime solvus temperature, an amount of precipitated gamma prime in the billet decreases (by solid solution) and the deforming resistance of the billet decreases. This improves the extrusion of the billet.

[0048] However, when the hot-working temperature achieves the gamma prime solvus temperature, recrystallized

grains grow to form a coarse recrystallization structure. Thus, the extruded material becomes brittle. It is important that, when the hot-working temperature is higher than the gamma prime solvus temperature, the billet of the Ni-based alloy, in which the amount of precipitated gamma prime in equilibrium at 700°C is not less than 40 mol %, becomes to have no ductility in a very narrow temperature range between the gamma prime solvus temperature and the solidus temperature. Thus, the extrusion is difficult. Therefore, the hot-working temperature is determined at a temperature lower than "the gamma prime solvus temperature" of the billet of the Ni-based alloy. Then, the extrusion of the billet is improved by utilizing the heat generated by working, and the extruded material has a fine recrystallization structure. The hot-working temperature is preferably not higher than 1180°C, more preferably not higher than 1170°C, and further more preferably not higher than 1150°C.

[0049] According to the present invention, the gamma prime solvus temperature is determined by the composition of the Ni-based alloy. The gamma prime solvus temperature can be obtained by analysis through a thermodynamic equilibrium calculation. Various type of thermodynamic equilibrium calculation software can be used for the analysis to obtain the gamma prime solvus temperature correctly and easily.

[0050] (3) In the method according to the present invention, the billet, i.e. the ingot is extruded at an extruding speed of 10 to 300 mm/s.

[0051] It is also important to adjust the extruding speed in order to improve the ability of extrusion of the billet having the composition of the precipitation strengthening type super heat resistant Ni-based alloy in which an amount of precipitated gamma prime in equilibrium at 700°C is not less than 40 mol% and that is produced by casting

[0052] FIG. 3 shows a result of tensile tests at 1150°C of Alloy 713C (an amount of precipitated gamma prime in equilibrium at 700°C is 69 mol%, and gamma prime solvus temperature is 1185°C). In the temperature range lower than the gamma prime solvus temperature, reduction of area increases as strain rate increases. Thus, it is effective to increase the working speed in order to improve the workability of the Ni-based alloy. This effective phenomenon similarly applies to the extrusion. The ductility of the Ni-based alloy is improved by increasing the extruding speed in the temperature range lower than the gamma prime solvus temperature. The extruding speed is increased, i.e. "not less than 10 mm/s" in the method according to the present invention. This extruding speed may correspond to the moving speed of a stem which pushes the billet in the extrusion. When the extruding speed is less than 10 mm/s, the ductility of the billet in the extrusion decreases and cracks may occur in the extruded material. The extruding speed is preferably not less than 12 mm/s, more preferably not less than 14 mm/s.

[0053] A mechanism of improving the ductility of the billet by increasing the extruding speed is presumed as follows. It is considered that the gamma prime in the Ni-based alloy interrupts dynamic recrystallization during the hot working and smooth deformation of the Ni-based alloy. Therefore, it is necessary to introduce higher strain energy so as to generate the dynamic recrystallization to cause the smooth deformation during the hot working of the Ni-based alloy in which the amount of the precipitated gamma prime in equilibrium at 700°C is not less than 40 mol%. It is considered that the increase of the strain rate (extruding speed) during the hot working makes the strain energy introduced into the Ni-based alloy be less relieved, and causes the sufficient dynamic recrystallization. Therefore, the smooth deformation of the Ni-based alloy becomes possible.

[0054] In the method according to the present invention, on the other hand, the extruding speed is determined to be not more than 300 mm/s. Although the increase of the extruding speed is advantageous for improving the ductility of the billet, when the extruding speed is greater than a certain value, the degree of improving the ductility slows down and is saturated. Also, it is practical that the upper limit of the extruding speed (i.e. moving speed of the stem) is about 300 mm/s in consideration of the capability of the extruding apparatus. The extruding speed is preferably not more than 280 mm/s, more preferably not more than 260 mm/s. Even if the extruding speed is not more than 100 mm/s or not more than 90 mm/s, the effect of the present invention can be obtained.

[0055] (4) In an embodiment of the present invention, the billet is preferably an ingot that has been heat-treated.

[0056] According to the present invention, even if an as-cast ingot is used as the billet, it can be extruded. However, by heating the as-cast ingot, segregation in the ingot for the billet can be reduced to improve high extrusion workability. The heat treatment is preferably conducted in a temperature range around the gamma prime solvus temperature of the Ni-based alloy. Specifically, the temperature range of 1170 to 1250°C is preferable. It is more preferably not higher than 1240°C and further more preferably not higher than 1230°C.

[0057] Too low heat treatment temperature leads to reduction of the effect. When the heat treatment temperature is higher, for example, far above the gamma prime solvus temperature, coarse grains of the gamma phase that have been formed at the casting grows further to make grain boundaries in the billet more brittle. It is supposed that the embrittlement is caused by segregation of trace elements in the grain boundaries in the billet.

[0058] A time period of the heat treatment time may be that of a typical soaking process for various kinds of ingots. For example, the time period is 3 to 30 hours, preferably not shorter than 10 hours.

[0059] In the method according to the present invention, even when the billet is the as-cast ingot having the composition of the precipitation strengthening type super heat resistant Ni-based alloy in which the amount of precipitated gamma prime in equilibrium at 700°C is not less than 40 mol%, it can be successfully extruded by employing the above hot-

working temperature and extruding speed. Even if an average grain size in a cross-section may be large, such as not less than 6.3 mm, or even not less than 7 mm in equivalent circle diameter (practically, upper limit is about 30 mm), the extrusion is possible.

[0060] The extruded material manufactured by the extrusion can have a fine recrystallization structure, for example. For example, the average grain size in the cross-sectional structure of the extruded material may be not more than 20 μm in equivalent circle diameter (practically, lower limit is about 2 μm). Furthermore, it may be not more than 15 μm , or even not more than 10 μm , in equivalent circle diameter. The average grain size in the cross-sectional structure of the extruded material can be made fine to 1/400, further to 1/1000, of the average grain size in the cross-sectional structure of the billet.

[0061] For measuring the average grain size, the billet and the extruded material are halved in an extraction direction, and a cross-sectional structure at a position of a central axis of the cross section (that is, a cross section including the central axis in the longitudinal direction of the billet or the extruded material) can be observed. Then, equivalent circle diameters of crystal grains are measured in the cross section at the position of the central axis, and an average grain size is obtained.

[0062] The extrusion ratio (a cross-sectional area of the billet / a cross-sectional area of the extruded material) of the extrusion may be that in typical extrusion. For example, the extruding ratio may be 2 to 40. The extruding ratio may be not more than 30, or not more than 20. The extruded material produced in this manner has, for example, a shape of a wire. The wire material has a diameter of, for example, 1.4 to 20 mm. The extruded material may be subjected to hot working or cold working to produce a thin wire with a diameter of 1 to 3 mm.

EXAMPLES

[0063] Molten metals having predetermined compositions were produced by vacuum melting and were cast to produce ingots with a diameter of 110 mm and a length of 120 mm. Next, each ingot was heat-treated in a furnace in an atmosphere at 1200°C for 20 hours, and then cooled in the furnace. The heat-treated ingots were machined into a shape with a diameter of 82 mm and a length of 105 mm to produce billets for extrusion. Similarly, billets for measuring average grain size were produced. A cross section of each billet at a position of the central axis in the longitudinal direction of the billet was etched with a ferric chloride solution and it was observed with an optical microscope at a magnification of 10. In a field of view of 50 mm $\times$ 40 mm, the image analysis was performed to measure an average grain size. The average grain size in equivalent circle diameter was about 10 μm .

[0064] Table 1 shows the compositions of the molten metals (that is, compositions of billet). Since Co, W, Ta, V, and Hf are impurity elements, the compositions satisfied $\text{Co} \leq 28.0\%$, $\text{W} \leq 6.0\%$, $\text{Ta} \leq 3.0\%$, $\text{V} \leq 1.2\%$, and $\text{Hf} \leq 1.0\%$. For the compositions, gamma prime solvus temperatures and amounts of gamma prime precipitated in equilibrium at 700°C were obtained with use of thermodynamic equilibrium calculation software "JMatPro (Version 8.0.1, Sente Software Ltd.)". As a result of calculating by inputting the content of each element in Table 1 into the software, the amount of gamma prime precipitated in equilibrium at 700°C was 66 to 67 mol % and the gamma prime solvus temperature was 1185 to 1188°C in the range of the compositions in Table 1.

[TABLE 1]

Sample No.	Compositions (mass%)									
	C	Cr	Mo	Al	Ti	Nb	Fe	Zr	B	Ni*
1	0.0127	12.20	4.51	5.85	0.61	2.04	1.05	0.09	0.0090	balance
2	0.0172	12.00	4.51	5.86	0.59	2.02	1.06	0.09	0.0089	balance
3	0.0135	11.97	4.50	5.86	0.59	2.00	1.06	0.09	0.0095	balance
4	0.0138	11.98	4.50	5.88	0.59	2.01	1.05	0.09	0.0097	balance
5	0.0147	12.03	4.56	5.92	0.61	2.06	1.06	0.09	0.0091	balance
6	0.0159	12.20	4.48	5.82	0.59	1.99	1.07	0.09	0.0092	balance
*including impurities ($\text{Co} \leq 28.0\%$, $\text{W} \leq 6.0\%$, $\text{Ta} \leq 3.0\%$, $\text{V} \leq 1.2\%$, and $\text{Hf} \leq 1.0\%$)										

[0065] Each billet was put into a furnace and heated at a predetermined hot-working temperature (first step). The billet was held at the hot-working temperature for two hours and was taken out from the furnace. Then, the billet was loaded into a container of an extruding apparatus and extruded directly at a predetermined extruding speed (with the predetermined moving speed of stem) (second step). This direct extrusion was started within three seconds after taken out from

the furnace. Produced extruded material was evaluated to check whether a crack was generated outside or inside the material. The results and the extruding conditions are shown in Table 2.

[TABLE 2]

Sample No.	Hot-working temperature (°C)	Extruding speed (mm/s)	Extrusion ratio	Crack	Remarks
1	1150	15	8	not present	Example according to the invention
2	1150	18	10	not present	
3	1150	36	10	not present	
4	1100	50	8	not present	
5	1250	15	8	present	Comparative example
6	1150	7.5	10	present	

[0066] The materials Nos. 1 to 4 have the composition of the precipitation strengthening type super heat resistant Ni-based alloy in which the amount of gamma prime precipitated in equilibrium at 700°C is not less than 40 mol% were produced by extruding the billets (ingots) at the hot-working temperature and the extruding speed according to the present invention. Table 2 shows that the materials Nos. 1 to 4 were not subject to cracking. In addition, the materials Nos. 1 to 4 had fine recrystallization structure.

[0067] On the other hand, the material No. 5 was extruded at a hot-working temperature higher than the gamma prime solvus temperature. Thus, its billet had low ductility in the extrusion and was cracked. In addition, the billet of the material No. 6 was extruded with a low extruding speed and has less ductility in the extrusion, thereby it was cracked. In the material No. 6, the dynamic recrystallization did not occur sufficiently and a non-recrystallized structure existed.

[0068] FIG. 1 shows a cross-sectional macro structure of a billet at a reduced cross-sectional area portion during the extrusion in the material No. 4. As shown in FIG. 1, a cast structure 1 having a coarse grain size of about 10 mm at the position of the reduced cross-sectional area portion has changed into a fine recrystallization structure 2 after the extrusion (after the cross sectional area was reduced). FIG. 2 shows an EBSD image of the cross-sectional microstructure of the material No. 4. As measurement conditions of the EBSD, a scan step was 0.1 μm and an orientation difference of not less than 15° was defined as a grain boundary. This microstructure was observed at a position of the central axis in a cross section halved in the longitudinal direction of the material. From grains counted in a field of view of 200 μm * 150 μm in FIG. 2, it is shown that the material No. 4 in accordance with the invention had a fine recrystallization structure with an average grain size of about 2.1 μm in an equivalent circle diameter. As compared with the material No. 4, the materials Nos. 1 to 3 had fine recrystallization structures with an average grain size of about not more than 20 μm in an equivalent circle diameter, as similarly measured of the average grain size, since they were extruded at a higher hot-working temperature,

[0069] Another material was produced by performing extrusion at a lower hot-working temperature of 1025°C and under the same conditions as that of the extruded material No. 1 except the hot-working temperature. As a result, the material could not have fine recrystallization structure since a deforming resistance of the billet increased drastically and sufficient heat was not generated in the extrusion.

REFERENCES LIST

[0070]

1 cast structure

2 recrystallization structure

Claims

1. A method of manufacturing an extruded material of a super heat resistant Ni-based alloy, comprising:

5 a first step of heating a billet made of the Ni-based alloy at a hot-working temperature; and
a second step of inserting the heated billet into a container, and applying a compressive force to the billet from
one end of the container to extrude the billet through a hole of a die at the other end of the container, thereby
producing the extruded material of the Ni-based alloy,
10 wherein the billet is an ingot produced by casting a molten metal, the molten metal having a composition of a
precipitation strengthening type Ni-based alloy wherein an amount of precipitated gamma prime in equilibrium
at 700°C is not less than 40 mol%; and
wherein the hot-working temperature is not lower than 1030°C but lower than a gamma prime solvus temperature
of the billet of the Ni-based alloy, and the billet is extruded at an extruding speed of 10 to 300 mm/s.

- 15 2. An extruded material of a super heat resistant Ni-based alloy, having a composition of a precipitation strengthening
type super heat resistant Ni-based alloy wherein an amount of precipitated gamma prime in equilibrium at 700°C is
not less than 40 mol%, the material having an average grain size in a cross-sectional structure of not more than 20
μm in an equivalent circle diameter.

FIG.1

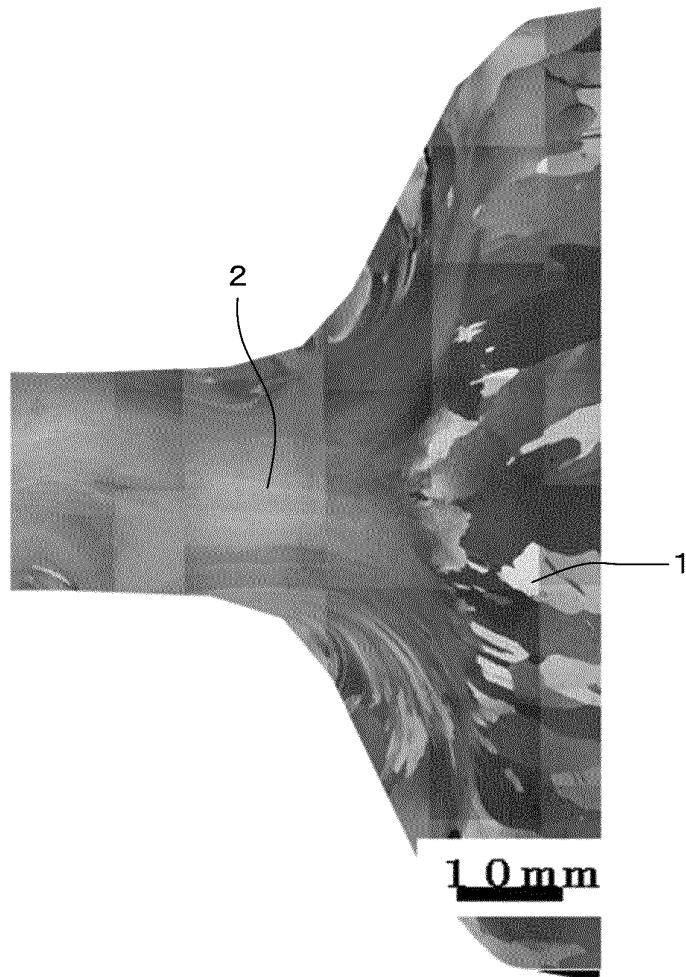


FIG.2

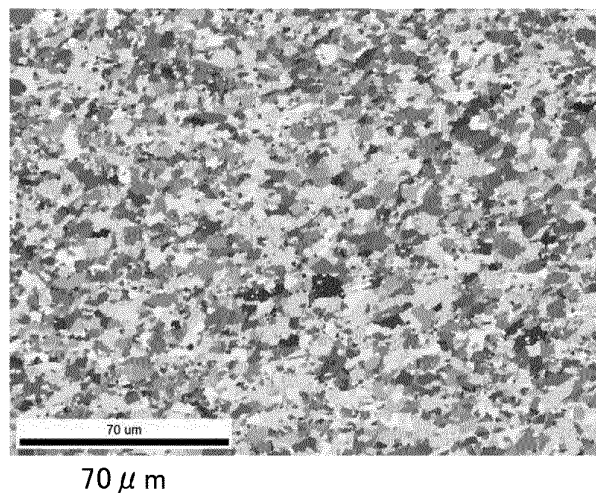
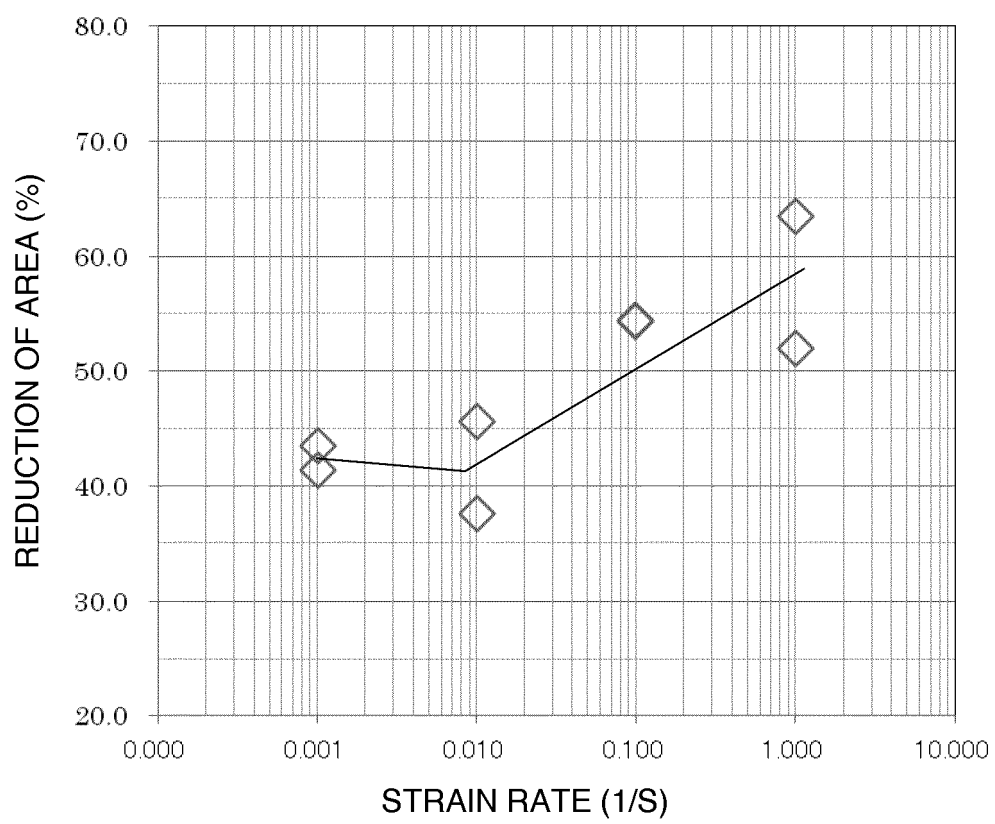


FIG.3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/020143

A. CLASSIFICATION OF SUBJECT MATTER

B21C23/00(2006.01)i, C22C19/05(2006.01)i, C22F1/10(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B21C23/00, C22C19/05, C22F1/10

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2017
 Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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.
A	JP 2013-518727 A (ATI Properties Inc.), 23 May 2013 (23.05.2013), & US 2011/0195270 A1 & WO 2011/097085 A1 & CN 102741005 A	1-2
A	WO 2009/142228 A1 (Sumitomo Metal Industries, Ltd.), 26 November 2009 (26.11.2009), & US 2011/0183151 A1 & EP 2281908 A1 & CN 102016090 A	1-2
A	JP 50-24108 A (Federal-Mogul Corp.), 15 March 1975 (15.03.1975), & US 3824097 A1 & DE 2362499 A1	1-2

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
29 June 2017 (29.06.17)Date of mailing of the international search report
11 July 2017 (11.07.17)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 63125649 A [0004]