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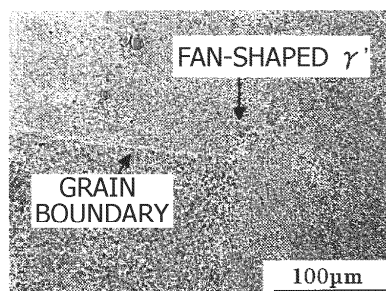
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(54) **METHOD FOR PRODUCING NI-BASED HEAT RESISTANT SUPERALLOY**

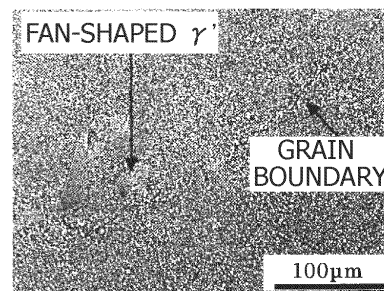
(57) A method reduces a precipitation region of a fan-shaped γ' phase in a homogenization treatment of a Ni-based heat resistant superalloy with a large amount of γ' precipitation. The method is a method for producing a Ni-based heat resistant superalloy, including at least a step of heat-treating a material having a composition of a Ni-based heat resistant superalloy having a solvus temperature of a γ' phase of at least 1080°C, wherein the heat-

treating step includes a heating step in which heating is performed at a temperature range of 1170°C to 1280°C for at least 45 hours, and a cooling step in which an average cooling rate in a temperature range from the solvus temperature of the γ' phase to the solvus temperature of the γ' phase minus 50°C satisfies [average cooling rate (°C/h)] ≥ 10 and [average cooling rate (°C/h)] $\geq 200 - 2.0 \times$ [holding time (h)].

FIG. 3



(F) No. 6



(G) No. 7

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a method for producing a Ni-based heat resistant superalloy.

BACKGROUND ART

10 **[0002]** Turbine operation at high temperatures is considered to be effective improving the efficiency of aircraft engines and power generation efficiency of gas turbines. To that end, it is important to increase the service temperature of each turbine member. In particular, for members that require a service temperature of 600°C or higher, a γ' (gamma prime) phase-precipitation strengthening Ni-based heat resistant superalloy is often used. The γ' phase is an intermetallic compound of $L1_2$ structure represented by Ni_3Al , and it is known that dissolving elements such as Ti, Nb, and Ta in the γ' phase further enhances the effect of precipitation strengthening. The γ' phase-precipitation strengthening Ni-based heat resistant superalloy is mainly composed of two phases: a matrix γ phase and a precipitation phase γ' phase, and when the amount of Ti or Nb is increased, an intermetallic compound such as an eta phase (such as Ni_3Ti) or a delta phase (such as Ni_3Nb) may be precipitated as the third phase. Furthermore, C and B are often added mainly to strengthen the grain boundary of the matrix, and trace amounts of carbides and borides may be crystallized or precipitated.

15 **[0003]** As described above, increasing the amount of Al, Ti, Nb, and Ta that form and strengthen the γ' phase is effective to enhance the high temperature strength of the Ni-based heat resistant superalloy. This increases the amount of precipitation of the γ' phase and strengthens the γ' phase itself. Examples of the high-strength Ni-based heat resistant superalloys include Udimet 720 Li (Udimet is a registered trademark of Special Metals).

20 **[0004]** Although the Ni-based heat resistant superalloy containing a large amount of Ti, Nb, and Ta is high in strength, microsegregation may easily remain even after hot working, and it is difficult to obtain a homogeneous microstructure. The main reason for the microsegregation is considered to be that the added elements in the alloy are distributed unevenly in the solid or liquid phase during the precipitation process. In particular, since the elements that contribute to the increase in precipitation amount and strengthening of the γ' phase, such as Ti, Nb, and Ta, easily concentrate at the liquid phase side during the precipitation processing of the ingot, microsegregation occurs in inside the ingot after the precipitation is completed. This microsegregation further accelerates as the precipitation rate is slower; thus, the larger the size of the ingot, the more prominent is the microsegregation. To reduce this microsegregation, a heat treatment step called homogenization treatment is generally introduced as a next step. The homogenization treatment is often applied to the ingot, and is sometimes also applied to a billet as an intermediate step in hot working.

25 **[0005]** The homogenization treatment is often performed at a temperature at or above the solvus temperature and below the melting point of the second phase such as the γ' phase. However, the appropriate conditions for the homogenization treatment, such as the required heating temperature, holding time, and cooling rate, are not necessarily determined because they vary greatly depending on not only the chemical composition, but also on the solidification rate during ingot production. In the Ni-based heat resistant superalloy with the large amount of γ' precipitation, the γ' phase is precipitated during the cooling process after the homogenization treatment. Thus, the cooling rate has a great impact on subsequent hot workability. The faster the cooling after the homogenization treatment, the finer the γ' phase precipitation. However, 30 when hot working is performed in this state, the movement of the displacement is easily inhibited by the fine γ' phase. As a result, the deformation resistance of the workpiece is significantly higher and recrystallization becomes difficult, thus hot cracking may easily occur. As a means of solving this, it is possible to coarsen the γ' phase by slowing the cooling rate after heating, and to improve the hot workability, for example, as disclosed in Patent Document 1.

35 **[0006]** Regarding the Ni-based heat resistant superalloy with a large amount of γ' precipitation after the homogenization treatment, for example, Udimet 720 Li, it is possible to obtain a uniform and fine microstructure by performing hot working in the two-phase domain of the γ phase and the γ' phase, and causing recrystallization while acting on the γ' phase that is not dissolved as pinning grains of the γ phase grain boundary. However, the uniformity of the microstructure after this hot working is strongly affected by the γ' phase distribution which acts as pinning grains. This is because, the more uneven the γ' phase distribution, the coarser the grains of the γ phase in the region having greater distances between the γ' phase grains, while the finer grains in the region having smaller distances therebetween. Thus, it is necessary to uniformly disperse the γ' phase grains to obtain a uniform microstructure after hot working. When the microstructure is non-uniform, practical undesirable events may occur, for example, fatigue failure is likely to occur due to partially coarsened grains. Thus, the grain distribution in the microstructure is desirably as uniform as possible.

40 **[0007]** When the Ni-based heat resistant superalloy is cooled, γ' phase is generally precipitated in a spherical or cubic shape in the grains. It is known, however, that when the Ni-based heat resistant superalloy with a large amount of γ' precipitation is heated to around the solvus temperature of the γ' phase or higher, and is then cooled at a slow cooling rate, a fan-shaped γ' phase (also called a fan-type γ' phase) is precipitated. This fan-shaped γ' phase is mainly precipitated from the grain boundary and grows with the movement of the grain boundary. The order of precipitation during cooling is usually 45

that the fan-shaped γ' phase is precipitated first, and then the spherical or cubic intragranular γ' phase is precipitated. Although the temperature range in which the fan-shaped γ' phase is precipitated is not uniformly determined, the precipitation is particularly significant in the temperature range of from a γ' phase solvus temperature of the respective alloy to about the γ' phase solvus temperature minus 50°C. Thus, the slower the cooling rate is in this temperature range, the larger the precipitation region of the fan-shaped γ' phase, and the smaller the precipitation region of the intragranular γ' phase. This fan-shaped γ' phase is coarse compared to the γ' phase precipitated in the grain and has an extended shape with a large aspect ratio. In other words, it can be said that the fan-shaped γ' phase is a γ' phase that is precipitated with a non-uniform distribution. However, as described above, the uniform size of the γ' phase is better for obtaining a uniform microstructure after hot working in the Ni-based heat resistant superalloy with a large amount of γ' precipitation. If a large amount of fan-shaped γ' phase is precipitated during cooling after the homogenization treatment, it becomes difficult to obtain a uniform microstructure after hot working.

REFERENCE DOCUMENT LIST

PATENT DOCUMENT

[0008] Patent Document 1: WO 2014/157144

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0009] When a Ni-based heat resistant superalloy with a large amount of γ' precipitation is subjected to a heating and cooling process that are a homogenization treatment, a large amount of fan-shaped γ' phase is precipitated during the cooling. This fan-shaped γ' phase is mainly precipitated from the grain boundary, and it is characterized by being coarse compared to the γ' phase precipitated in the grain, having a large aspect ratio, and having a non-uniform distribution. The Ni-based heat resistant superalloy with a large amount of γ' precipitation, such as Udimet 720 Li, can have a uniform and fine microstructure by performing hot working in the two-phase domain of the γ phase and the γ' phase, and causing recrystallization while acting non-solid solution γ' phase as pinning grains of the γ phase grain boundary. However, if the fan-shaped γ' phase precipitation region described above extends widely after the homogenization treatment, the size and distribution of the γ' phase as the pinning grains become uneven; thus, the size of the recrystallized grain generated during the subsequent hot working process also becomes uneven, and the resulting difficulty in obtaining a uniform microstructure is a problem.

[0010] Considering this, it is an object of the present invention to provide a method for reducing the precipitation region of the fan-shaped γ' phase in the homogenization treatment of the Ni-based heat resistant superalloy with a large amount of γ' precipitation.

MEANS FOR SOLVING THE PROBLEM

[0011] That is, the present invention is a method for producing a Ni-based heat resistant superalloy, in which the Ni-based heat resistant superalloy has a composition consisting of, in % by mass, C: 0.001 to 0.100%, Al: 1.0 to 5.0%, Ti: 3.5 to 7.0%, Cr: 8 to 20%, Co: 0 to 40%, Mo: 0 to 7.0%, W: 0 to 5.0%, Ta: 0 to 6.0%, Nb: 0 to 6.0%, B: 0.001 to 0.080%, Zr: 0 to 0.100%, Mg: 0 to 0.05%, Fe: 0 to 5.0%, and the balance of Ni with inevitable impurities, and has a solvus temperature of a γ' phase of 1080°C or higher, the method comprising at least a step of heat-treating a material having the composition, wherein the heat-treating step includes a heating step in which heating is performed in a temperature range of 1170°C to 1280°C for 45 hours or more, and a cooling step in which an average cooling rate in a temperature range from the solvus temperature of the γ' phase to the solvus temperature of the γ' phase minus 50°C satisfies [average cooling rate (°C/h)] $\geq$ 10 and [average cooling rate (°C/h)] $\geq$ 200 - 2.0 $\times$ [holding time (h)].

[0012] The heating in the heating step is preferably performed for 45 hours or more and 300 hours or less. Alternatively, the average cooling rate is preferably 800 $\geq$ [average cooling rate (°C/h)] $\geq$ 10. Alternatively, and preferably, the heating in the heating step is performed for 60 hours or more, and the average cooling rate is 100 $\geq$ [average cooling rate (°C/h)] $\geq$ 10.

EFFECTS OF THE INVENTION

[0013] According to the present invention, it is possible to efficiently reduce the precipitation region of the fan-shaped γ' phase.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

[FIG. 1] These are diagrams showing metal microstructures of the Ni-based heat resistant superalloys produced in Examples.

[FIG. 2] These are diagrams showing metal microstructures of the Ni-based heat resistant superalloys produced in Examples.

[FIG. 3] These are diagrams showing metal microstructures of the Ni-based heat resistant superalloys produced in Examples.

[FIG. 4] These are diagrams showing metal microstructures of the Ni-based heat resistant superalloys produced in Examples.

[FIG. 5] These are diagrams showing metal microstructures of the Ni-based heat resistant superalloys produced in Examples.

MODE FOR CARRYING OUT THE INVENTION

[0015] The reasons of limiting the ranges of the alloy components defined in the present invention are described below. The component values below are in % by mass.

< C: 0.001-0.100% >

[0016] C has an effect of increasing the strength of the grain boundary, and thus, the addition of 0.001% or more C is required. If C is contained in excess, a coarse carbide is formed and becomes deleterious, thus the upper limit is 0.100%. The range of C is preferably 0.005% or more, and is more preferably 0.01% or more. The range of C is also preferably 0.06% or less, and is more preferably 0.03% or less.

< Al: 1.0-5.0% >

[0017] Al is an essential element to form a γ' phase that is a strengthening phase, and it improves the high temperature strength. The present invention is directed to alloys with a large amount of γ' phase precipitation, and thus, the addition of at least 1.0% Al is required. If Al is contained in excess, the solvus temperature of the γ' phase is excessively increased, and thus, the upper limit is 5.0%. The range of Al is preferably 1.5% or more, and is more preferably 1.8% or more. The range of Al is also preferably 4.0% or less, and is more preferably 3.0% or less.

< Ti: 3.5-7.0% >

[0018] Ti is an element that is replaced by the Al site of the γ' phase and increases the strength of the γ' phase by solid-solution strengthening, and it also increases the precipitation amount of the γ' phase. In the present invention, the addition of at least 3.5% Ti is required. If Ti is added in excess, however, the γ' phase becomes unstable and the eta phase is excessively precipitated, and thus, the upper limit is 7.0%. The range of Ti is preferably 4.6% or more, and is more preferably 5.8% or more. The range of Ti is also preferably 6.8% or less, and is more preferably 6.6% or less.

< Cr: 8-20% >

[0019] Cr is an element that improves oxidation resistance and corrosion resistance. The lack of Cr amount leads to cracking due to oxidation, thus 8% or more Cr is required. If Cr is contained in excess, a brittle phase such as the sigma phase is formed, and thus, the upper limit is 20%. The range of Cr is preferably 10% or more, and is more preferably 12% or more. The range of Cr is also preferably 17% or less, and is more preferably 15% or less.

< Co: 0-40% >

[0020] Co contributes to the stability of the γ' phase, and thus, Co may be added as needed. If Co is added in excess, however, a brittle phase such as the sigma phase tends to be precipitated, and thus, the upper limit is 40%. The range of Co is preferably 35% or less, is more preferably 30% or less, and is further preferably 28% or less. When Co is added, the range of Co is preferably 5% or more, is more preferably 15% or more, and is further preferably 20% or more.

< Mo: 0-7.0% >

[0021] Mo contributes to the solid-solution strengthening of the matrix and has an effect of improving the high temperature strength and creep deformation resistance, and thus, Mo may be added as needed. If Mo is added in excess, however, the melting point is excessively reduced, and thus, the upper limit is 7.0%. The range of Mo is preferably 5.0% or less, is more preferably 3.5% or less, and is further preferably 3.0% or less. When Mo is added, the range of Mo is preferably 0.5% or more, is more preferably 1.0% or more, and is further preferably 2.0% or more.

< W: 0-5.0% >

[0022] W, like Mo, is an element that contributes to the solid-solution strengthening of the matrix, and thus, W may be added as needed. However, since W is a heavy element, diffusion in the alloy is less likely to occur, and thus, the upper limit is 5.0%. The range of W is preferably 4.0% or less, is more preferably 2.5% or less, and is further preferably 1.6% or less. When W is added, the range of W is preferably 0.5% or more, is more preferably 0.8% or more, and is further preferably 1.0% or more.

< Ta: 0-6.0% >

[0023] Ta, like Ti, is an element that is replaced by the Al site of the γ' phase to solid-solution strengthen the γ' phase, and it increases the high temperature strength. Thus, Ta may be added as needed to obtain high-strength alloys. However, excessive addition of Ta makes the γ' phase unstable and causes formation of a large amount of the eta phase and the delta phase, and thus, the upper limit is 6.0%. The range of Ta is preferably 5.0% or less, is more preferably 4.0% or less, and is further preferably 3.0% or less. When Ta is added, the range of Ta is preferably 0.5% or more, is more preferably 1.0% or more, and is further preferably 1.5% or more.

< Nb: 0-6.0% >

[0024] Nb, like Ti and Ta, is an element that is replaced by the Al site of the γ' phase to solid-solution strengthen the γ' phase, and it increases the high temperature strength. Thus, Nb may be added as needed to obtain high-strength alloys. However, excessive addition of Nb makes the γ' phase unstable and causes formation of a large amount of the eta phase and the delta phase, and thus, the upper limit is 6.0%. The range of Nb is preferably 5.0% or less, is more preferably 4.0% or less, and is further preferably 3.0% or less. When Nb is added, the range of Nb is preferably 0.5% or more, is more preferably 1.0% or more, and is further preferably 1.5% or more.

< B: 0.001-0.080% >

[0025] B is an important element for improving the grain boundary strength and improving the creep strength and high temperature ductility, and thus, the addition of 0.001% or more of B is required. If B is added in excess, however, the melting point is excessively reduced, and thus, the upper limit is 0.080%. The range of B is preferably 0.003% or more, is more preferably 0.006% or more, and is further preferably 0.010% or more. The range of B is also preferably 0.060% or less, is more preferably 0.040% or less, and is further preferably 0.030% or less.

< Zr: 0-0.100% >

[0026] Zr is believed to have an effect of improving the grain boundary strength, like B, but Zr is not necessarily required. Zr, like B, the addition in excess causes melting point reduction, and thus, the upper limit is 0.100%. The range of Zr is preferably 0.080% or less, is more preferably 0.060% or less, and is further preferably 0.050% or less. When Zr is added, the range of Zr is preferably 0.005% or more, is more preferably 0.007% or more, and is further preferably 0.010% or more.

< Mg: 0-0.05% >

[0027] Mg has an effect of improving the grain boundary strength by fixing S, an inevitable impurity causing grain boundary embrittlement, as a sulfide, and thus, Mg may be added as needed. However, if the amount of Mg added is increased, the excess Mg forms harmful intermetallic compounds, and thus, the upper limit is 0.05%. The range of Mg is preferably 0.01% or less, is more preferably 0.005% or less, and is further preferably 0.001% or less. When Mg is added, the range of Mg is preferably 0.0003% or more, and is more preferably 0.0005% or more.

< Fe: 0-5.0% >

[0028] Fe is an inexpensive element, and it is possible to reduce the raw material cost of hot workpieces by replacing some of the Ni with Fe. Thus, Fe may be included as needed. However, the excessive addition of Fe promotes the precipitation of the sigma phase, and thus, the upper limit is 5.0%. The range of Fe is preferably 4.0% or less, is more preferably 1.5% or less, and is further preferably 1.0% or less. When Fe is added, the range of Fe is preferably 0.05% or more, is more preferably 0.1% or more, and is further preferably 0.3% or more.

< Ni: Balance >

[0029] The balance is composed of Ni and inevitable impurities. Here, examples of the inevitable impurity elements include P, S, O, N, Pb, and As, but the total amount of these elements preferably does not exceed 0.05%.

[0030] The reasons of limiting the solvus temperature of the γ' phase defined in the present invention are described below.

< Solvus temperature of γ' phase >

[0031] The γ' phase solvus temperature of the Ni-based heat resistant superalloy targeted by the present invention is 1080°C or higher. This is because the growth rate of the fan-shaped γ' phase is remarkable in the high temperature range. In alloys having a γ' phase solvus temperature of less than 1080°C, a microstructure with a small precipitation region of the fan-shaped γ' phase can be obtained without using the present invention.

[0032] Next, the reasons for limiting the heating temperature and the holding time during the homogenization treatment in the heat treatment step according to the present invention are described below.

< Temperature during homogenization treatment >

[0033] The heating temperature during the homogenization treatment defined in the present invention is required to be in the temperature range of 1170°C to 1280°C. If the temperature is lower than 1170°C, diffusion in the Ni-based heat resistant superalloy is insufficient and the effect of the homogenization treatment cannot be obtained. On the other hand, if the temperature exceeds 1280°C, the local melting in the Ni-based heat resistant superalloy becomes significant, and thus, the effect of the homogenization treatment also cannot be fully obtained. Note that the heating temperature during the homogenization treatment can also be said to be a temperature that exceeds the solvus temperature of the γ' phase.

< Holding time during homogenization treatment >

[0034] The holding time during the homogenization treatment defined in the present invention is the total holding time during heating in the temperature range of 1170°C to 1280°C, which is the heating temperature described above. Accordingly, the heating time in the temperature range of less than 1170°C is not included. To obtain the effect of the present invention, it is necessary to heat and maintain in a temperature range in which sufficient diffusion occurs in the Ni-based heat resistant superalloy. However, preliminary heating treatment in a temperature range less than 1170°C may be applied as necessary, because it is effective to avoid local melting in the precipitation structure.

[0035] The holding time during the homogenization treatment defined in the present invention is required to be 45 hours or more. The holding time is preferably 60 hours or more, and is more preferably 85 hours or more. This heating and holding need not be a continuous heating, and it may be in steps. For example, a total of two homogenization treatments may be performed on an ingot. Alternatively, for example, a single homogenization treatment may be performed on an ingot, then the ingot may be subjected to a certain hot working to form a billet, and the billet may be subjected to a homogenization treatment again. The reason for defining the holding time of heating is from both the viewpoints of reducing microsegregation and of reducing the fan-shaped γ' phase precipitation region. The Ni-based heat resistant superalloy targeted by the present invention is prone to leave micro segregation and also to precipitate the fan-shaped γ' phase because a large amount of added elements such as Ti is present. However, it is possible to reduce both of these at the same time by setting the holding time to a specified value or more. The reasons of enabling reducing not only the microsegregation, but also the fan-shaped γ' phase precipitation, can be considered, although the present invention is not limited thereto, as follows. When the holding time during the homogenization treatment is long, micro segregation is reduced, and the concentration gradient of solute elements such as Al, Ti, Nb, and Ta is reduced. The lower the concentration gradient of these elements, the more uniform is the solvus temperature of the local γ' phase in the microstructure. Then, the region in which the solute element is concentrated, that is, the region in which the starting temperature of the fan-shaped γ' phase precipitation is locally high is reduced during cooling from a temperature higher than the solvus temperature of the γ' phase. Accordingly, it is possible to delay precipitation and growth. The longer the holding time during the homogenization treatment, the greater

the effect, and thus, the upper limit of the holding time is not specified. However, from the viewpoint of working time, the holding time is preferably 300 hours or less.

< Cooling rate after homogenization treatment >

[0036] The cooling rate after the homogenization treatment defined in the present invention is the average cooling rate in the temperature range of "50°C" from the γ' phase solvus temperature to the γ' phase solvus temperature minus 50°C. Increasing the cooling rate in this temperature range enables reducing the precipitation region of the fan-shaped γ' phase. The average cooling rate defined in the present invention is required to satisfy [average cooling rate (°C/h)] $\geq 200 - 2.0 \times$ [holding time (h)]. This means that the longer the holding time described above, the slower the acceptable cooling rate. The present invention is not limited by the weight of the material to be applied, but it is particularly effective in large ingots that weigh several hundred kg or more. Large ingots tend to have significant microsegregation due to slow precipitation rates, and tend to have fan-shaped γ' phase precipitation during cooling after the homogenization treatment. However, if the cooling rate after the homogenization treatment is excessively increased to avoid the fan-shaped γ' phase precipitation, the surface temperature of the ingot preferentially decreases, resulting in easily causing cooling cracking. This cracking sensitivity increases as the ingot becomes larger, and thus, specifying the cooling rate after the homogenization treatment alone is not sufficient for practical purposes. In the present invention, since the minimum required average cooling rate is determined from the holding time, an efficient homogenization treatment is possible in that the precipitation of the fan-shaped γ' phase can be reduced while avoiding the cooling cracking. The average cooling rate is required to satisfy at least 10°C/h or more, in addition to the inequality expression described above. The average cooling rate is preferably 25°C/h or more, and more preferably 40°C/h or more. The upper limit of the cooling rate is not specified, but from the viewpoint of cooling cracking and subsequent hot workability, it is preferably 800°C/h or less, and is more preferably 500°C/h or less. It is possible to reduce the precipitation region of the fan-shaped γ' phase even when the average cooling rate is reduced to 100°C/h or less by ensuring a long holding time (for example, ensuring 60 hours or more).

[0037] It should be noted that the average cooling rate is preferably maintained beyond the temperature range of "50°C", which is from the γ' phase solvus temperature to the γ' phase solvus temperature minus 50°C, even to 900.

EXAMPLES

[0038] To confirm the effect of the present invention, the homogenization treatment was tested by the following procedure. First, an electrode of the Ni-based heat resistant superalloy was prepared in a vacuum induction furnace (VIM), then the electrode was refined and dissolved by electroslag remelting (ESR), and then it was further refined and dissolved by vacuum arc remelting (VAR) to yield a VAR ingot of the Ni-based heat resistant superalloy with a weight of about 1.0 to 1.5 tons and a diameter of about 450 mm. The chemical composition of this material is shown in Table 1. The γ' phase solvus temperature of the alloy having this chemical composition is approximately 1165°C.

[Table 1]

	% by mass											
	Ni	Cr	Co	Fe	W	Mo	Al	Ti	C	B	Zr	Mg
Present invention	Bal.	13.4	24.3	0.6	1.2	2.8	2.3	6.3	0.014	0.015	0.03	0.0007
*The balance is composed of Ni and inevitable impurities.												

[0039] Next, the top side of the VAR ingot was cut, and a small piece of material of about 10 mm $\times$ 15 mm $\times$ 20 mm was cut from a location 1/4 the diameter from the surface. The top side of the VAR ingot was used because the microsegregation of this part was remarkable, and this part can be said to be a suitable material for confirming the effect of the present invention. The cut-out small piece of material was sealed in a stainless steel can, and it was then subjected to a homogenization treatment shown in Table 2. The homogenization treatment was performed with an electric furnace. In the homogenization treatment, the small piece of material was first preheated at a predetermined temperature for a predetermined holding time, was then heated to a heating temperature of the homogenization treatment, and was then retained at this heating temperature for a predetermined time. In the subsequent cooling step, the cooling rate described in Table 2 is the average cooling rate in the "temperature range from 1165°C to 1115°C". Table 2 also shows the value A calculated from $200 - 2.0 \times$ [holding time (h)]. No. 4 to No. 11 in the table satisfy the holding time and the average cooling rate defined in the present invention. The cooling rate after this homogenization treatment was maintained at least until 900°C, and then the small piece of material was continuously cooled to room temperature in the furnace at the corresponding cooling rate as it set, or it was taken out of the furnace after confirming that the temperature was 900°C or lower and cooled to room temperature.

[Table 2]

No.	Preliminary heating		Homogenization treatment					Notes
	Temperature	Holding time	Heating rate	Temperature	Holding time	Cooling rate	Value A	
	°C	h	°C/h	°C	h	°C/h		
1	1100	1	60	1200	35	60	130	Comparative example
2	1100	1	60	1200	65	25	70	Comparative example
3	1100	1	60	1200	80	25	40	Comparative example
4	1100	1	60	1200	48	200	104	Present invention
5	1100	1	60	1200	65	100	70	Present invention
6	1100	1	60	1200	120	60	-40	Present invention
7	1100	1	60	1200	200	60	-200	Present invention
8	1100	1	60	1200	300	25	-400	Present invention
9	1100	1	60	1200	80	80	40	Present invention
10	1143	30	20	1200	96	60	8	Present invention
11	1143	30	5	1200	96	60	8	Present invention

[0040] The small piece of material after the homogenization treatment was cut so that the longitudinal direction of the VAR ingot formed the observation surface. The observation surface of the small piece of material was subjected to mirror polishing, followed by electrolytic etching in 10% aqueous oxalic acid solution to facilitate the observation of the y' phase. The observation of the microstructure was performed with an optical microscope. The photographs of the microstructures of No. 1 to No. 11 in Table 2 are shown in FIGs. 1(A), 1(B), 1(C), 2(D), 2(E), 3(F), 3(G), 4(H), 4(I), 5(J), and 5(K), respectively, in this order.

[0041] First, as shown in FIGs. 1(A), 1(B) and 1(C), it was found that the microstructures of No. 1, No. 2, and No. 3 had a wide range of the fan-shaped y' phase precipitated on or near the grain boundary. These homogenization treatment conditions are beyond the scope of the present invention since the value A was greater than the cooling rate, as shown in Table 2.

[0042] Next, No. 6 and No. 7, which had the same cooling rate of 60°C/h as No. 1 and an increased holding time of 120 hours and 200 hours, respectively, were confirmed to have significantly reduced precipitation regions of the fan-shaped y' phase compared to No. 1, as shown in FIGs. 3(F) and 3(G). In addition, No. 8, which had the same cooling rate of 25°C/h as No. 2 and No. 3 and an increased holding time of 300 hours, was also confirmed to have a significantly reduced precipitation region of the fan-shaped y' phase, as shown in FIG. 4(H). From the above, it was confirmed that the homogenization treatment with long holding time as proposed by the present invention has the effect of greatly reducing the precipitation region of the fan-shaped y' phase.

[0043] Then, No. 5, which had the same holding time as No. 2 and a cooling rate of 100°C/h, was confirmed to have a small precipitation region of the fan-shaped y' phase, as shown in FIG. 2(E). In addition, No. 9, which had the same holding time as No. 3 and a cooling rate of 80°C/h, was also confirmed to have a small precipitation region of the fan-shaped y' phase, as shown in FIG. 4(I). Furthermore, No. 4, which has the shortest holding time of 48 hours but the fastest cooling rate of 200°C/h in Table 2, was confirmed to have a small precipitation region of the fan-shaped y' phase, as shown in FIG. 2(D). From the above, it was confirmed that increasing the cooling rate after the homogenization treatment as proposed by the present invention has the effect of greatly reducing the precipitation region of the fan-shaped y' phase.

[0044] In addition, the microstructures of No. 10 and No. 11, which had the different preheating temperature and subsequent heating rate, were also confirmed to have a small precipitation region of the fan-shaped γ' phase, as shown in FIGs. 5(J) and 5(K).

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Claims

1. A method for producing a Ni-based heat resistant superalloy, in which the Ni-based heat resistant superalloy has a composition consisting of, in % by mass, C: 0.001 to 0.100%, Al: 1.0 to 5.0%, Ti: 3.5 to 7.0%, Cr: 8 to 20%, Co: 0 to 40%,
 10 Mo: 0 to 7.0%, W: 0 to 5.0%, Ta: 0 to 6.0%, Nb: 0 to 6.0%, B: 0.001 to 0.080%, Zr: 0 to 0.100%, Mg: 0 to 0.05%, Fe: 0 to 5.0%, and the balance of Ni with inevitable impurities, and has a solvus temperature of a γ' phase of at least 1080°C, the method comprising a step of heat-treating a material having the composition, wherein the heat-treating step comprises a heating step in which heating is performed in a temperature range of 1170°C to 1280°C for at least 45 hours, and a cooling step in which an average cooling rate in a temperature range from the solvus temperature of the γ' phase to the solvus temperature of the γ' phase minus 50°C satisfies [average cooling rate (°C/h)] ≥ 10 and [average cooling rate (°C/h)] $\geq 200 - 2.0 \times$ [holding time (h)].
2. The method for producing a Ni-based heat resistant superalloy according to claim 1, wherein the heating in the heating step is performed for 45 hours to 300 hours.
3. The method for producing a Ni-based heat resistant superalloy according to claim 1, wherein the average cooling rate satisfies $800 \geq$ [average cooling rate (°C/h)] ≥ 10 .
4. The method for producing a Ni-based heat resistant superalloy according to claim 1, wherein the heating in the heating step is performed for at least 60 hours, and the average cooling rate satisfies $100 \geq$ [average cooling rate (°C/h)] ≥ 10 .

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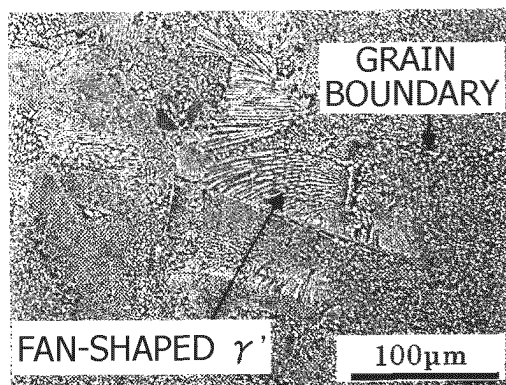
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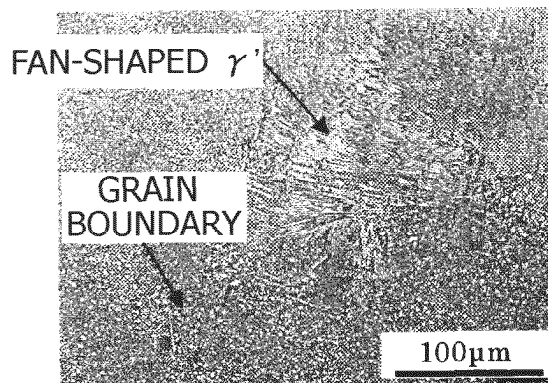
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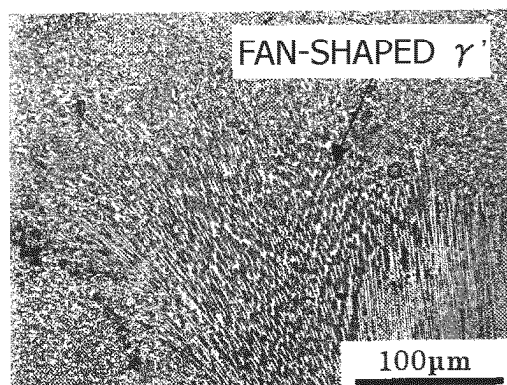
FIG. 1



(A) No. 1

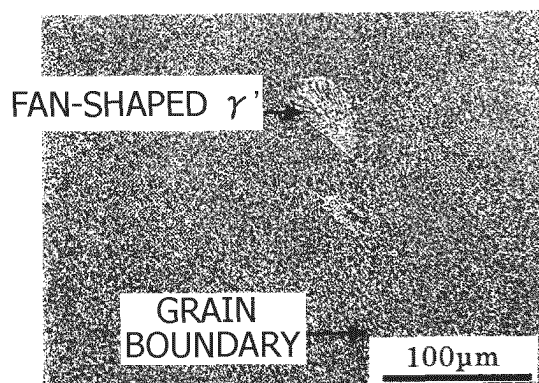


(B) No. 2

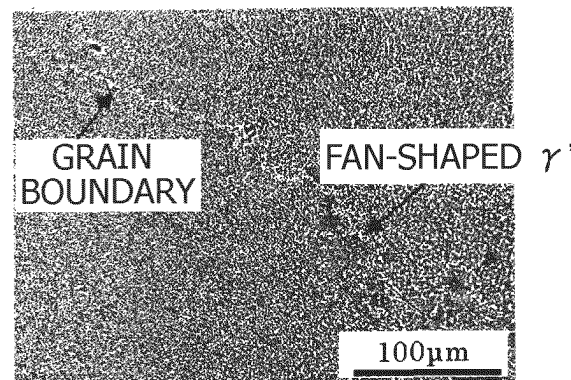


(C) No. 3

FIG. 2

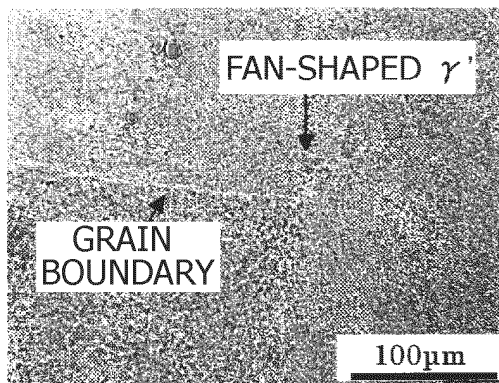


(D) No. 4

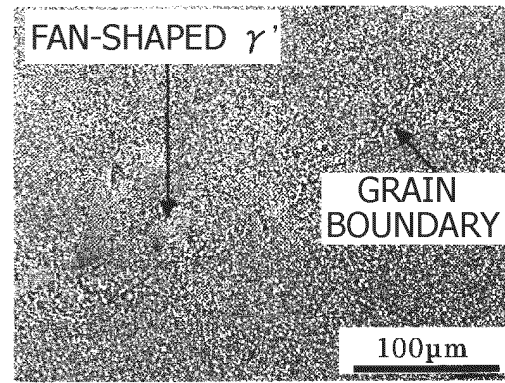


(E) No. 5

FIG. 3

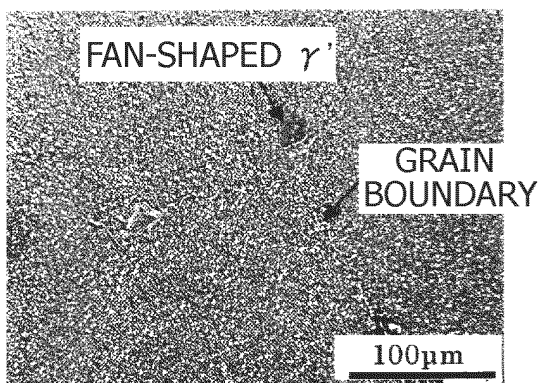


(F) No. 6

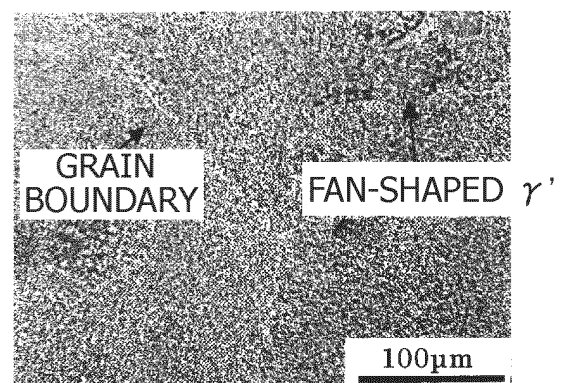


(G) No. 7

FIG. 4

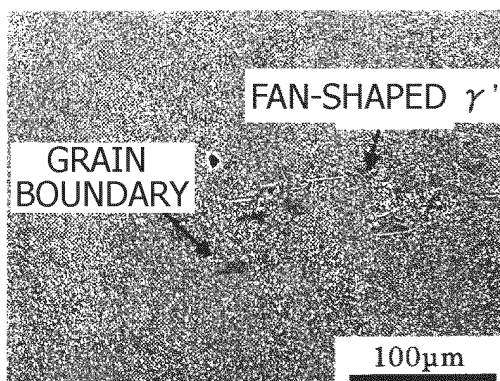


(H) No. 8

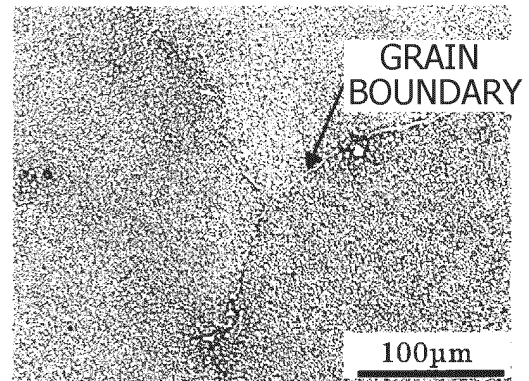


(I) No. 9

FIG. 5



(J) No. 10



(K) No. 11

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2024/009098

A. CLASSIFICATION OF SUBJECT MATTER

C22F 1/10(2006.01)i; **C22C 19/05**(2006.01)i; **C22C 30/00**(2006.01)i; **C22F 1/00**(2006.01)i; **C22F 1/16**(2006.01)i
 FI: C22F1/10 H; C22F1/10 J; C22C19/05 C; C22C30/00; C22F1/00 650A; C22F1/00 651B; C22F1/00 682; C22F1/00 691A;
 C22F1/00 691B; C22F1/00 691C; C22F1/00 692A; C22F1/00 692B; C22F1/16 Z; C22F1/10 K; C22F1/00 681

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)

C22F1/10; C22C19/05; C22C30/00; C22F1/00; C22F1/16

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 1971-2024
 Registered utility model specifications of Japan 1996-2024
 Published registered utility model applications of Japan 1994-2024

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	WO 2016/152985 A1 (HITACHI METALS LTD.) 29 September 2016 (2016-09-29)	1-4
A	WO 2016/129485 A1 (HITACHI METALS LTD.) 18 August 2016 (2016-08-18)	1-4
A	JP 2021-172852 A (MITSUBISHI POWER, LTD.) 01 November 2021 (2021-11-01)	1-4
A	US 5061324 A (GENERAL ELECTRIC COMPANY) 29 October 1991 (1991-10-29)	1-4
P, A	WO 2023/243146 A1 (MITSUBISHI HEAVY INDUSTRIES, LTD.) 21 December 2023 (2023-12-21)	1-4

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

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

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

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

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

17 May 2024

Date of mailing of the international search report

28 May 2024

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 Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2024/009098

5	Patent document cited in search report			Publication date (day/month/year)		Patent family member(s)		Publication date (day/month/year)	
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	WO	2016/129485	A1	18 August 2016		US	2018/0023176	A1	
						EP	3257963	A1	
10						CN	107250416	A	
	JP	2021-172852	A	01 November 2021		US	2021/0331239	A1	
						EP	3901297	A1	
	US	5061324	A	29 October 1991		(Family: none)			
15	WO	2023/243146	A1	21 December 2023		JP	2023-184086	A	
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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2014157144 A [0008]