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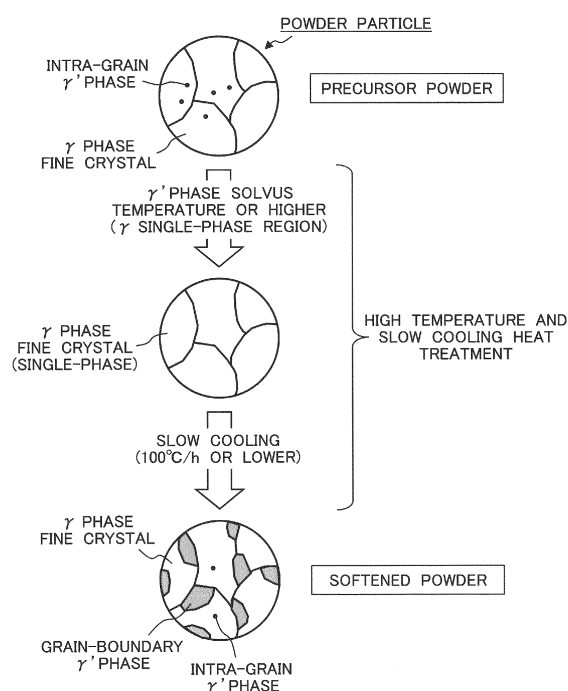
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(54) **NI-BASED ALLOY SOFTENED POWDER, AND METHOD FOR PRODUCING SAID SOFTENED POWDER**

(57) An objective of the invention is to provide an Ni-based alloy softened powder that is formed of a high precipitation-strengthened Ni-based alloy material, has better forming/molding processability than ever before, and is suitable for powder metallurgy. The Ni-based alloy softened powder has a chemical composition allowing γ' phase precipitated in γ phase as a matrix to have an equilibrium precipitation amount of 30-80 volume % at 700°C, has an average particle size of 5-500 μm , and includes particles comprising a polycrystalline body of fine crystals of the γ phase. The γ' phase is precipitated on grain boundaries of the γ phase fine crystals in an amount of 20 volume % or more. And, the particles have a Vickers hardness of 370 Hv or less at room temperature.

FIG. 3



Description**TECHNICAL FIELD OF THE INVENTION**

[0001] The present invention relates to the technology of Ni (nickel)-based alloy articles and, in particular, to a Ni-based alloy softened powder that is formed of a high precipitation-strengthened Ni-based alloy material and is suitable for powder metallurgy and a method for manufacturing the softened powder.

DESCRIPTION OF RELATED ART

[0002] In turbines (e.g., gas turbines and steam turbines) for aircrafts and thermal power plants, attaining higher temperature of the main fluid to increase thermal efficiency is now one of technological trends. Thus, improvement of mechanical properties of the turbine members at high temperatures is an important technical issue. High-temperature turbine members (e.g., turbine rotor blades, turbine stator blades, rotor disks, combustor members, and boiler members) are exposed to the severest environments and repeatedly subjected to a rotation centrifugal force and vibration during turbine operation and to thermal stress associated with the start/stop of the operation. Therefore, improvement of mechanical properties (e.g., creep properties, tensile properties, and fatigue properties) is significantly important.

[0003] In order to satisfy various mechanical properties required, precipitation-strengthened Ni-based alloy materials have been widely used for high-temperature turbine members. Specifically, in the cases where high-temperature properties are essential, a high precipitation-strengthened Ni-based alloy material is used wherein the percentage of a γ' (gamma prime) phase (e.g., $\text{Ni}_3(\text{Al}, \text{Ti})$ phase) precipitated in a γ (gamma) phase (matrix) has been increased. An example of such high precipitation-strengthened Ni-based alloy material is an Ni-based alloy material wherein at least 30 vol. % of the γ' phase has been precipitated.

[0004] As standard methods for manufacturing turbine members such as turbine rotor blades and turbine stator blades, precise casting techniques (specifically, a unidirectional solidification technique and a single-crystal solidification technique) have been conventionally used in terms of creep properties. On the other hand, a hot forging technique has been occasionally used for manufacturing turbine disks and combustor members in terms of tensile properties and fatigue properties.

[0005] However, the precipitation-strengthened Ni-based alloy material has a weak point in that if a volume percentage of the γ' phase is increased so as to increase high-temperature properties of high-temperature members, processability and formability become worse, causing a production yield of the high-temperature members to decrease (i.e., result in increase in production costs). Accordingly, along with the studies to improve properties of high-temperature members, various studies to stably produce the high-temperature members have also been carried out.

[0006] For example, Patent Literature 1 (JP Hei 9 (1997)-302450 A) discloses a method of making Ni-based superalloy articles having a controlled grain size from a forging preform. The method includes the following steps of: providing an Ni-based superalloy preform having a recrystallization temperature, a γ' -phase solvus temperature and a microstructure comprising a mixture of γ and γ' phases, wherein the γ' phase occupies at least 30% by volume of the Ni-based superalloy; hot die forging the superalloy preform at a temperature of at least approximately 1600°F, but below the γ' -phase solvus temperature and a strain rate from approximately 0.03 to approximately 10 per second to form a hot die forged superalloy work piece; isothermally forging the hot die forged superalloy workpiece to form the finished article; supersolvus heat treating the finished article to produce a substantially uniform grain microstructure of approximately ASTM 6 to 8; and cooling the article from the supersolvus heat treatment temperature.

CITATION LIST**PATENT LITERATURE**

[0007]

Patent Literature 1: JP Hei 9 (1997)-302450 A,
Patent Literature 2: JP 5869624 B2, and
Patent Literature 3: US 5,649,280 A.

SUMMARY OF THE INVENTION**PROBLEMS TO BE SOLVED BY THE INVENTION**

[0008] According to Patent Literature 1, it seems to be possible to produce a forged article at a high production yield

without cracking of the forged article even using an Ni-based alloy material in which the γ' phase occupies relatively high volume percent. However, because Patent Literature 1 conducts the hot die forging process with superplastic deformation at a low strain rate and the subsequent isothermally forging process, special production equipment as well as long work time is required (i.e., result in high equipment costs and high process costs). These would be the weak points of the technique taught in Patent Literature 1.

[0009] Since low production costs are strongly required for industrial products, it is one of high-priority issues to establish a technique to manufacture products at low costs.

[0010] For example, Patent Literature 2 (JP 5869624 B2) discloses a method for manufacturing an Ni-based alloy softened article made up of an Ni-based alloy in which the solvus temperature of the γ' phase is 1050°C or higher. The method includes a raw material preparation step to prepare an Ni-based alloy raw material to be used for the subsequent softening treatment step, and a softening treatment step to soften the Ni-based alloy raw material in order to increase processability. The softening treatment step is performed in a temperature range which is lower than the solvus temperature of the γ' phase. The softening treatment step includes a first substep to subject the Ni-based alloy raw material to hot forging at a temperature lower than the solvus temperature of the γ' phase, and a second substep to obtain an Ni-based alloy softened material containing 20 vol. % or more of incoherent γ' phase particles precipitated on grain boundaries of the γ phase (matrix of the Ni-based alloy) grains, by slowly cooling the above forged material from the temperature lower than the γ' phase solvus temperature at a cooling rate of 100°C/h or less. The technique taught in Patent Literature 2 can be said to be an epoch-making technique that enables the processing and forming of the high precipitation-strengthened Ni-based alloy material at low costs.

[0011] However, in the production of a superhigh precipitation-strengthened Ni-based alloy material such as that containing 45 vol. % or more of γ' phase (e.g., Ni-based alloy material in which 45 to 80 vol. % of γ' phase is precipitated), if a conventional forging apparatus not equipped with an especial heating and thermal keeping mechanism is used for the hot forging process performed at a temperature lower than the γ' phase solvus temperature (i.e., temperature range in which two phases, γ and γ' phases, coexist), the temperature decreases during the hot forging process (causing undesired precipitation of the γ' phase), resulting to be prone to decrease a production yield.

[0012] From the viewpoints of recent energy conservation and global environmental protection, higher temperature of the main fluid to increase thermal efficiency of turbines and higher turbine output by increasing the length of the turbine blades are expected to further progress. This means that environments where high-temperature turbine members are used could become more and more sever, and increased mechanical properties of the high-temperature turbine members will be further required. On the other hand, as stated above, achievement of low production costs (in particular, improvement of the forming/molding processability and improvement of the production yield) is one of high-priority issues concerning industrial products.

[0013] Meanwhile, one technique to manufacture a formed/molded article of a hard-to-work material at low cost is powder metallurgy using metal powder.

[0014] For example, Patent Literature 3 (US 5,649,280 A) discloses a method of making an article having a controlled grain size from an Ni-based superalloy. The method includes a forging step, a heating step and a cooling step. In the forging step, a fine-grain Ni-based superalloy preform (e.g. consolidated metal powder preform) is forged so as to impart to the preform retained strain to form a uniform fine grain-sized microstructure through complete recrystallization in a subsequent heating step. In the heating step, the forged article is subjected to an extended subsolvus heat treatment at a temperature that is higher than the recrystallization temperature and lower than the γ' phase solvus temperature. In the cooling step, the alloy article is subsequently cooled from the subsolvus temperature at a predetermined cooling rate to precipitate the γ' phase in the alloy article and control the precipitation distribution.

[0015] However, the method disclosed in Patent Literature 3 uses powder metallurgy merely as a means of reducing the grain size of the preform to be forged so as to control the grain size of the finished Ni-based superalloy article, and it contains no teaching or suggestion as to techniques to improve forming/molding processability of hard-to-work materials.

[0016] High precipitation-strengthened Ni-based alloy materials cannot be regarded as having excellent forming/molding processability. This is true even for those in powder form due to the hardness of each powder particle. Conventionally, therefore, application of powder metallurgy has inevitably required working at high temperature and/or high pressure, making it difficult to dramatically reduce the manufacturing cost of high precipitation-strengthened Ni-based alloy articles. In other words, an Ni-based alloy powder with excellent forming/molding processability suitable for powder metallurgy would dramatically reduce the manufacturing cost of high precipitation-strengthened Ni-based alloy articles.

[0017] The present invention has been made in view of the foregoing circumstances, and it has an objective to provide an Ni-based alloy softened powder that is formed of a high precipitation-strengthened Ni-based alloy material, has better forming/molding processability than ever before, and is suitable for powder metallurgy and a method for manufacturing the softened powder.

SOLUTION TO PROBLEMS

[0018]

(I) According to one aspect of the present invention, there is provided an Ni-based alloy softened powder having a chemical composition allowing γ' phase precipitated in γ phase as a matrix to have an equilibrium precipitation amount of 30 volume % or more and 80 volume % or less at 700°C. The softened powder has an average particle size of 5 μm or more and 500 μm or less. The softened powder comprises particles comprising a polycrystalline body of fine crystals of the γ phase. The γ' phase is precipitated on grain boundaries of the fine crystals of the γ phase in an amount of 20 volume % or more. And, the particles have a Vickers hardness of 370 Hv or less at room temperature.

In the above Ni-based alloy softened powder (I) of the invention, the following changes and modifications can be made.

(i) The chemical composition may include: 5 mass % or more and 25 mass % or less of Cr (chromium); more than 0 mass % and 30 mass % or less of Co (cobalt); 1 mass % or more and 8 mass % or less of Al (aluminum); the total amount of Ti (titanium), Nb (niobium) and/or Ta (tantalum) being 1 mass % or more and 10 mass % or less; 10 mass % or less of Fe (iron); 10 mass % or less of Mo (molybdenum); 8 mass % or less of W (tungsten); 0.1 mass % or less of Zr (zirconium); 0.1 mass % or less of B (boron); 0.2 mass % or less of C (carbon); 2 mass % or less of Hf (hafnium); 5 mass % or less of Re (rhenium); 0.003 mass % or more and 0.05 mass % or less of O (oxygen); and a balance being Ni and inevitable impurities.

(ii) The chemical composition may be a chemical composition that allows the γ' phase to have a solvus temperature of 1,100°C or higher.

(iii) The Ni-based alloy softened powder may have a chemical composition that allows the γ' phase to have the equilibrium precipitation amount of 45 volume % or more and 80 volume % or less at 700°C.

(iv) The particles may have a Vickers hardness of 350 Hv or less at room temperature.

(II) According to another aspect of the invention, there is provided a method for manufacturing the above-described Ni-based alloy softened powder. The method includes: a precursor powder preparation step of preparing a precursor powder that has the chemical composition and includes particles comprising a polycrystalline body of fine crystals of the γ phase; and a powder softening high temperature and slow cooling heat treatment step of subjecting the precursor powder to a high temperature and slow cooling heat treatment in which the precursor powder is heated to a temperature that is equal to or higher than the solvus temperature of the γ' phase and lower than the melting point of the γ phase (referred to as "high temperature" in the invention) to make the γ' phase solid-solve into the γ phase and subsequently cooled slowly from this temperature to a temperature lower than the solvus temperature of the γ' phase at a cooling rate of 100°C/h or less to produce the Ni-based softened powder in which the γ' phase is precipitated on grain boundaries of the fine crystals of the γ phase in an amount of 20 volume % or more.

(III) According to still another aspect of the invention, there is provided a method for manufacturing the above-described Ni-based alloy softened powder. The method includes: a single-phase precursor powder preparation step of preparing a single-phase precursor powder that has the chemical composition and includes particles comprising a polycrystalline body of single-phase fine crystals of the γ phase; and a powder softening sub-high temperature and slow cooling heat treatment step of subjecting the single-phase precursor powder to a sub-high temperature and slow cooling heat treatment in which the single-phase precursor powder is heated to a temperature that is equal to or higher than a temperature 80°C lower than the solvus temperature of the γ' phase and lower than the solvus temperature (in the invention, defining the temperature in that range as a sub-high temperature) and cooled slowly from this temperature at a cooling rate of 100°C/h or less to produce the Ni-based softened powder in which the γ' phase is precipitated on grain boundaries of the single-phase fine crystals of the γ phase in an amount of 20 volume % or more.

(IV) According to still another aspect of the invention, there is provided a method for manufacturing the above-described Ni-based alloy softened powder. The method includes: a single-phase precursor powder preparation step of preparing a single-phase precursor powder that has the chemical composition and comprises particles comprising a polycrystalline body of single-phase fine crystals of the γ phase; and a powder softening high temperature and slow cooling heat treatment step of subjecting the precursor powder to a high temperature and slow cooling heat treatment in which the single-phase precursor powder is heated to a temperature that is equal to or higher than the solvus temperature of the γ' phase and lower than the melting point of the γ phase and subsequently cooled slowly from this temperature to a temperature lower than the solvus temperature of the γ' phase at a cooling rate of 100°C/h or less to produce the Ni-based softened powder in which the γ' phase is precipitated on grain boundaries of the single-phase fine crystals of the γ phase in an amount of 20 volume % or more.

[0019] In the above methods for manufacturing the Ni-based alloy softened powder (II) to (IV) of the invention, the following changes and modifications can be made.

[0020] (v) The precursor powder preparation step or the single-phase precursor powder preparation step may include an atomization substep.

[0021] In the invention, the equilibrium precipitation amount at 700°C and the solvus temperature of the γ' phase and the melting point (solidus temperature) of the γ phase can be calculated thermodynamically based on the chemical composition of the Ni-based alloy material.

ADVANTAGES OF THE INVENTION

[0022] According to the present invention, there can be provided an Ni-based alloy softened powder that is formed of a high precipitation-strengthened Ni-based alloy material, has better forming/molding processability than ever before, and is suitable for powder metallurgy. Also, there can be provided a method for manufacturing the softened powder. Furthermore, by applying powder metallurgy using the Ni-based alloy softened powder, there can be provided a high precipitation-strengthened Ni-based alloy article at a high manufacturing yield (i.e. at lower cost than ever before).

BRIEF DESCRIPTION OF THE DRAWINGS

[0023]

FIG. 1 is schematic illustrations showing relationships between a γ phase and a γ' phase contained in a precipitation-strengthened Ni-based alloy material, (a) a case where the γ' phase particle precipitates within the γ phase grain; and (b) another case where the γ' phase particle precipitates on a boundary of the γ phase grain;

FIG. 2 is a flowchart illustrating steps of a method for manufacturing an Ni-based alloy article formed from an Ni-based alloy softened powder according to an embodiment of the present invention;

FIG. 3 is a schematic illustration showing changes in microstructure of an Ni-based alloy powder through a manufacturing method according to an embodiment of the invention;

FIG. 4 is a flowchart illustrating steps of another method for manufacturing an Ni-based alloy article formed from an Ni-based alloy softened powder according to an embodiment of the invention;

FIG. 5 is a schematic illustration showing changes in microstructure of an Ni-based alloy powder in single-phase precursor powder preparation step and powder softening sub-high temperature and slow cooling heat treatment step; and

FIG. 6 is a flowchart illustrating steps of still another method for manufacturing an Ni-based alloy article formed from an Ni-based alloy softened powder according to an embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[Basic Concept of the Invention]

[0024] The present invention is based on the precipitation-strengthening/softening mechanism in the γ' -phase precipitating Ni-based alloy material described in Patent Literature 2 (JP 5869624 B2). FIG. 1 is schematic illustrations showing relationships between a γ phase and a γ' phase contained in a precipitation-strengthened Ni-based alloy material, (a) a case where the γ' phase particle precipitates within the γ phase grain; and (b) another case where the γ' phase particle precipitates on a boundary of the γ phase grain.

[0025] As shown in FIG. 1(a), when the γ' phase particle precipitates within the γ phase grain, atoms 1 made up of a γ phase and atoms 2 made up of a γ' phase configure a coherent interface 3 (i.e., the γ' phase particle precipitates while it is lattice-matched to the γ phase grain). This type of γ' phase is referred to as an "intra-grain γ' phase" (also referred to as a "coherent γ' phase"). Because the intra-grain γ' phase particle and the γ phase crystal grain configure a coherent interface 3, it is deemed that dislocation migration within the γ phase crystal grain can be prevented by the intra-grain γ' phase particle. Accordingly, mechanical strength of the Ni-based alloy material is deemed to increase. A precipitation-strengthened Ni-based alloy article lies usually in the state of FIG. 1(a).

[0026] On the other hand, as shown in FIG. 1(b), when the γ' phase particle precipitates on a boundary of the γ phase crystal grain (in other words, between/among γ phase crystal grains), the atoms 1 made up of the γ phase and the atoms 2 made up of the γ' phase configure an incoherent interface 4 (i.e., the γ' phase particle precipitates while it is not lattice-matched to the γ phase crystal grain). This type of γ' phase is referred to as a "grain-boundary γ' phase" (also referred to as an "inter-grain γ' phase" and an "incoherent γ' phase"). Because the grain-boundary γ' phase particle and the γ phase crystal grain configure an incoherent interface 4, dislocation migration within the γ phase crystal grain is not prevented. As a result, it is deemed that the grain-boundary γ' phase does not contribute to the strengthening of the Ni-

based alloy material. Based on the above, in an Ni-based alloy body, by proactively precipitating the grain-boundary γ' phase particle instead of the intra-grain γ' phase particle, it is possible to make the Ni-based alloy body softened, thereby significantly increasing the forming/molding processability.

[0027] A major feature of the invention lies in the formation of an Ni-based alloy precursor powder/a single-phase precursor powder composed of a polycrystalline body of γ phase fine crystals or γ single-phase fine crystals and in the production of a softened powder in which the grain-boundary γ' phase is precipitated on the grain boundaries of γ phase fine crystals that constitute each powder particle in an amount of 20 volume % or more, not in the precipitation of the grain-boundary γ' phase by performing hot forging on an alloy ingot in a two-phase coexistent temperature range where the γ phase and the γ' phase are coexistent as in Patent Literature 2. The Ni-based alloy precursor powder/single-phase precursor powder can be regarded as one of the key points of the invention.

[0028] Diffusion and rearrangement of atoms configuring a γ' phase are essentially necessary for the generation/precipitation of the γ' phase. Therefore, when the γ phase crystal grains are large as those in the cast material, the γ' phase gains are deemed to preferentially precipitate within the γ phase crystal grains where the distance of diffusion and rearrangement of atoms can be short. Besides, it is not denied that the γ' phase particles precipitate on the boundaries of the γ phase crystal grains even in the cast material.

[0029] In contrast, as the γ phase crystal grain becomes finer, a distance to the crystal grain boundary becomes shorter, and the grain boundary free energy becomes higher in comparison with the volume free energy of the crystal grain. Therefore, in terms of the free energy, it is deemed to be more advantageous to diffuse atoms configuring the γ' phase along the grain boundary of the γ phase crystal grain and rearrange those atoms on the grain boundary than performing the solid-phase diffusion and rearrangement of those atoms within the γ phase crystal grain. Thus, those atoms configuring the γ' phase are deemed to preferentially and more easily diffuse and rearrange in such a manner.

[0030] Herein, in order to facilitate the formation of the γ' phase particle on the boundary of the γ phase grain, it is important to keep the γ phase grains fine in a temperature range (e.g., in the vicinity of the solvus temperature of the γ' phase) in which at least atoms configuring the γ' phase can easily diffuse. In other words, it is important to suppress the growth of the γ phase grains in the temperature range. Accordingly, the inventors intensively carried out studies of the techniques to suppress the growth of the γ phase grains even in a temperature range of slightly lower than, equal to or higher than the solvus temperature of the γ' phase.

[0031] As a result, it was found that the particles of an Ni-based alloy powder formed such that it contains an oxygen component in a controlled amount each consist of a polycrystalline body of γ phase fine crystals (i.e. the powder particles each consist of a plurality of γ phase fine crystals, in other words each powder particle contains the grain boundaries of γ phase fine crystals). It was also found that in such powder particles, the grain growth of γ phase fine crystals can be inhibited even if they are heated to a temperature near the solvus temperature of the γ' phase or equal to or higher than the solvus temperature (i.e. each powder particle does not become a γ phase single-crystalline body and remains to be a polycrystalline body) and that slowly cooling the powder from such a temperature causes precipitation and growth of the grain-boundary γ' phase on the boundaries of γ phase fine crystals. The present invention has been made based on these findings.

[0032] Preferred embodiments of the invention will be described hereinafter with reference to the accompanying drawings. However, it should be noted that the invention is not limited to the specific embodiments described below, and various combinations with known art and modifications based on known art are possible without departing from the spirit and scope of the invention where appropriate.

[Method for Manufacturing Ni-based Alloy Softened Powder]

[0033] FIG. 2 is a flowchart illustrating steps of a method for manufacturing an Ni-based alloy article formed from an Ni-based alloy softened powder according to an embodiment of the invention. As shown in FIG. 2, the method for manufacturing an Ni-based alloy article formed from an Ni-based alloy softened powder according to an embodiment of the invention roughly includes a precursor powder preparation step (S1), a powder softening high temperature and slow cooling heat treatment step (S2), a molding processing step (S3), and a solution and aging heat treatment step (S4). In the precursor powder preparation step S1, a precursor powder is prepared such that the powder has a predetermined chemical composition and each powder particle consists of a polycrystalline body of γ phase fine crystals. In the powder softening high temperature and slow cooling heat treatment step S2, the precursor powder is subjected to a predetermined high temperature and slow cooling heat treatment so as to produce an Ni-based alloy softened powder in which the grain-boundary γ' phase is precipitated in an amount of 20 volume % or more. In the molding processing step S3, a molded article having a desired shape is formed from the softened powder by a powder metallurgy technique. In the solution and aging heat treatment step S4, the molded article is subjected to a solution heat treatment to cause the grain-boundary γ' phase to enter into solid solution in the γ phase and to an aging heat treatment to precipitate the intra-grain γ' phase in crystal grains of the γ phase. The precursor powder preparation step S1 and the powder softening high temperature and slow cooling heat treatment step S2 constitute the method for manufacturing an Ni-based alloy

softened powder according to an embodiment of the invention.

[0034] Herein, the precursor powder refers to a powder whose particles are basically each formed of a polycrystalline body of γ phase fine crystals with no γ' phase precipitated on the grain boundaries of the γ phase fine crystals (at least the grain-boundary γ' phase has not been intentionally precipitated). The softened powder refers to a powder in which the grain-boundary γ' phase is precipitated in an amount of 20 volume % or more on the grain boundaries of γ phase fine crystals.

[0035] FIG. 3 is a schematic illustration showing changes in microstructure of an Ni-based alloy powder through the manufacturing method according to an embodiment of the invention. First, the Ni-based alloy precursor powder prepared in the precursor powder preparation step S1 is a powder whose particles have an average particle size of 500 μm or less and are formed of a polycrystalline body of γ phase fine crystals. Technically, since the precursor powder is strongly influenced by the temperature history (e.g. cooling rate) in the process of its formation, there may exist a mixture of γ phase fine crystals in which no γ' phase (coherent γ' phase) is precipitated and γ phase fine crystals in which the intra-grain γ' phase is partially precipitated within the γ phase fine crystals. The γ phase fine crystals with no intra-grain γ' phase precipitation and the regions in γ phase fine crystals where no intra-grain γ' phase is precipitated are considered to be oversaturated with the γ' phase or in a state of compositional fluctuation before the formation of the γ' phase.

[0036] Also, the particles of the precursor powder are basically each formed of a polycrystalline body of γ phase fine crystals, but this should not be construed as denying the possibility that some particles are formed of a γ phase single crystal. In other words, most particles of the precursor powder are composed of a polycrystalline body of γ phase fine crystals, but some particles may be formed of a γ phase single crystal.

[0037] Next, the precursor powder is heated to a temperature equal to or higher than the solvus temperature of the γ' phase but lower than the melting temperature of the γ phase. When the heating temperature becomes the γ' phase solvus temperature or higher, the entire γ' phase dissolves in the γ phase to form into a single γ phase in the viewpoint of thermal equilibrium. Herein, it is important in the invention that each powder particle is kept to consist of a polycrystalline body of γ phase fine crystals at this stage. In other words, it is important to prevent from excess coarsening of the γ phase fine crystals.

[0038] Subsequently, by slowly cooling the precursor powder from the heating temperature at a cooling rate of 100°C/h or less, it is possible to obtain a softened powder in which 20 volume % or more of grain-boundary γ' phase particles precipitate on the grain boundaries of the γ phase fine crystals. The forming/molding processability of the softened powder is significantly excellent because the precipitation-strengthening mechanism does not work due to the sufficiently small amount of precipitation of the intra-granular γ' phase particles. Here, γ' phase particles precipitated on a surface of the powder particle are also regarded as the grain-boundary γ' phase particles because the surface of powder particle can be regarded as a kind of grain boundaries of the γ phase fine crystals.

[0039] As shown in FIG. 2, the obtained softened powder is subsequently formed into a molded article with a desired shape by a powder metallurgy technique (the molding processing step S3). Because the softened powder according to an embodiment of the invention has a dramatically improved molding processability as compared to conventional high precipitation-strengthened Ni-based alloy powders, the temperature and/or pressure in the molding process can be lowered as compared to conventional ones. This means a reduced device cost and/or a reduced process cost in the molding process.

[0040] Subsequently, the molded article with a desired shape is subjected to a solution heat treatment to cause most of the grain-boundary γ' phase to solid-solve into the γ phase (e.g. the grain-boundary γ' phase is reduced in amount to 10 volume % or less) and then to an aging heat treatment to precipitate the intra-grain γ' phase in the crystal grains of the γ phase in an amount of 30 volume % or more (the solution and aging heat treatment step S4). As a result, there can be obtained a high precipitation-strengthened Ni-based alloy article that has a desired shape and is sufficiently precipitation-strengthened. The ease of molding processing achieved by using the softened powder according to an embodiment of the invention leads to a reduced device cost, a reduced process cost, and an improved manufacturing yield (i.e. a reduced cost of manufacturing an Ni-based alloy article).

[0041] The obtained Ni-based alloy article can be preferably used for next-generation high-temperature turbine members (e.g., turbine rotor blades, turbine stator blades, rotor disks, combustor members, boiler members, and heat resistant coatings).

[0042] As described before, the technique disclosed in Patent Literature 2 requires a highly accurate control for producing a softened article in which the incoherent γ' phase (grain-boundary γ' phase, inter-grain γ' phase) is precipitated while intentionally leaving the coherent γ' phase (intra-grain γ' phase) to remain. In contrast, in the technique according to an embodiment of the invention, a softened powder is produced such that the grain-boundary γ' phase is generated/precipitated after the intra-grain γ' phase is made to disappear once. According to an embodiment of the invention, a softened powder can be obtained by combining the precursor powder preparation step S1, whose industrial difficulty level is low, and the powder softening high temperature and slow cooling heat treatment step S2, whose industrial difficulty level is also low. Therefore, the technique according to the embodiment has a general versatility higher than that of the technique of Patent Literature 2, allowing cost reduction in the entire manufacturing process. It is particularly

effective in manufacturing a softened powder formed of a superhigh precipitation-strengthened Ni-based alloy material in which the γ' phase is precipitated in an amount of 45 volume % or more, for example.

[0043] Hereinafter, each of the aforementioned steps S1 and S2 will be described in more detail.

5 (Precursor Powder Preparation Step S1)

[0044] In step S1, an Ni-based alloy precursor powder having a predetermined chemical composition (specifically, a predetermined amount of oxygen component intentionally contained) is prepared. Basically, any conventional method or technique can be used to prepare the precursor powder. For example, a master alloy ingot fabrication substep (S1a) for fabricating a master alloy ingot by mixing, dissolving and casting raw materials to provide a predetermined chemical composition, and an atomization substep (S1b) for forming a precursor powder from the master alloy ingot can be performed. In addition, a classification substep (S1c) for classifying the precursor powder into an appropriate particle size range may be performed, as needed.

[0045] Control of the oxygen content can be preferably performed in the atomization substep S1b. Any conventional method or technique can be used for the atomization method except for the control of the oxygen content in the Ni-based alloy. For example, a gas atomization technique and a centrifugal force atomization technique can be preferably used while controlling the oxygen content (oxygen partial pressure) in the atomization atmosphere.

[0046] The oxygen component content (also referred to as a "content percentage") in the precursor powder is desirably equal to or more than 0.003 mass % (30 ppm) and equal to or less than 0.05 mass % (500 ppm); more desirably 0.005 mass % or more and 0.04 mass % or less; and further desirably 0.007 mass % or more and 0.02 mass % or less. If the oxygen content is less than 0.003 mass %, the growth of the γ phase fine crystals is not sufficiently suppressed; and if the oxygen content is more than 0.05 mass %, the mechanical strength and ductility of the finished Ni-based alloy member deteriorate. Meanwhile, it could be considered that oxygen atoms dissolve in the powder particles or form nuclei or embryos of oxides on the surface or the inside of the powder particles.

[0047] From the viewpoints of high precipitation-strengthening and efficient formation of the grain-boundary γ' phase particles, it is preferable that the chemical composition of the Ni-based alloy which enables the γ' phase solvus temperature to become 1020°C or higher be adopted; more preferably, the γ' phase solvus temperature become 1050°C or higher; and further more preferably, the γ' phase solvus temperature become 1110°C or higher. The chemical composition other than the oxygen component will be described in detail later.

[0048] The average particle diameter of the precursor powder is preferably from 5 μm to 500 μm ; more preferably from 10 μm to 300 μm ; and further more preferably from 20 μm to 200 μm . If the average particle diameter of the precursor powder becomes less than 5 μm , handling performance in the subsequent step S2 deteriorates and powder particles are prone to coalesce together during the step S2, making it difficult to control the average grain diameter of the softened powder. If the average particle diameter of the precursor powder becomes more than 500 μm , shape controllability and shape accuracy of the molded article in the later molding processing step S3 deteriorate. The average particle diameter of the precursor powder can be measured, for example, by means of a laser diffractometry grain-size distribution measuring apparatus.

[0049] As described before, the particles of the precursor powder are basically each formed of a polycrystalline body of γ phase fine crystals. The average grain size of the γ phase fine crystals is preferably equal to or more than 5 μm and equal to or less than 50 μm . Meanwhile, in the case of forming the precursor powder by a rapid solidification method such as atomizing, the γ' phase (e.g. eutectic γ' phase directly crystalizing from the liquid phase) do not usually precipitate on the grain boundaries of γ phase fine crystals.

(Powder Softening High Temperature and Slow Cooling Heat Treatment Step S2)

[0050] In step S2, the precursor powder prepared in the previous step S1 is heated to a temperature equal to or higher than the γ' phase solvus temperature in order to solid-solve the γ' phase particles into the γ phase grains, and then slowly cooled from that temperature to generate and increase the grain-boundary γ' phase particles, thereby producing a softened powder. In order to suppress undesired coarsening of the γ phase fine crystals as much as possible during this process, slow-cooling start temperature is preferably lower than the γ phase melting temperature (solidus temperature); more preferably at most 35°C higher than the γ' phase solvus temperature; and further preferably at most 25°C higher than the γ' phase solvus temperature.

[0051] Meanwhile, if the γ phase solidus temperature is lower than the " γ' phase solvus temperature + 35°C" or " γ' phase solvus temperature + 25°C", it is obvious that "less than the γ phase melting temperature" takes priority.

[0052] There are no particular limitations on the heat treatment atmosphere as long as it is a non-oxidizing atmosphere (an atmosphere that does not contain oxygen with an oxidizing partial pressure) to prevent undesired oxidation of the Ni-based alloy powder (oxidation that would exceed the oxygen content controlled in the previous step S1). The heat treatment atmosphere is preferably a reducing atmosphere (e.g. hydrogen gas atmosphere).

[0053] Also, this step S2 does not deny the possibility that the intra-grain γ' phase may not disappear completely as a result of the high temperature and slow cooling heat treatment and may still be present in a trace amount. For example, assuming that the grain-boundary γ' phase is precipitated in an amount of 20 volume % or more, a presence of the intra-grain γ' phase in an amount of 10 volume % or less would be permissible since it would not greatly inhibit the molding processability in the subsequent molding processing step S3. The intra-grain γ' phase should preferably be present in an amount of 5 volume % or less and more preferably 3 volume % or less.

[0054] Herein, according to the technique described in Patent Literature 2, when the Ni-based alloy forged raw material obtained through the dissolving, casting and forging processes is heated to a temperature equal to or higher than the γ' phase solvus temperature, the γ' phase particles suppressing the migration of grain boundaries of the γ phase grains disappear, causing the γ phase grains to become coarsened rapidly. As a result, even if slow-cooling is performed after the heating process at a temperature equal to or higher than the γ' phase solvus temperature as same as the step S2 of the invention, precipitation and growth of the grain-boundary γ' phase particles hardly progress.

[0055] According to the invention, in contrast, the precursor powder prepared in the precursor powder preparation step S1 contains more oxygen in its alloy composition than conventional Ni-based alloy articles (i.e. it has been controlled to contain oxygen in a larger amount). It is thought that performing a heat treatment on such a precursor powder at a temperature equal to or higher than the solvus temperature of the γ' phase causes the contained oxygen atoms to combine with metal atoms in the alloy to form local oxides.

[0056] The thus formed oxide is deemed to suppress the migration of grain boundaries of the γ phase fine crystals (i.e., suppress growth of the γ phase fine crystals). This means that even if the γ' phase is eliminated in the step S2, it is considered possible to prevent coarsening of the γ phase fine crystals.

[0057] As aforementioned, in the strengthening mechanism of precipitation-strengthened Ni-based alloy articles, formation of coherent interfaces between the γ phase and the γ' phase contributes to the strengthening, and incoherent interfaces do not contribute to the strengthening. A softened powder with an excellent molding processability can be obtained by reducing the amount of the intra-grain γ' phase (coherent γ' phase) and increasing the amount of the grain-boundary γ' phase (inter-grain γ' phase, incoherent γ' phase).

[0058] As the cooling rate in the slow-cooling process becomes lower, it is more advantageous for the precipitation and growth of the grain-boundary γ' phase particles. The cooling rate is preferably 100°C/h or less; more preferably 50°C/h or less; and further preferably 10°C/h or less. If the cooling rate is higher than 100°C/h, the intra-grain γ' phase particles preferentially precipitate, and the advantageous effects of the invention cannot be acquired adequately.

[0059] Specifically, in order to secure an excellent forming/molding processability, the slow cooling should be preferably performed until the precursor powder reaches a temperature equal to or lower than the temperature at which the grain-boundary γ' phase is precipitated in an amount of 20 volume % or more and more preferably 30 volume % or more. At the same time, the intra-grain γ' phase should preferably be precipitated in an amount of 10 volume % or less and more preferably 5 volume % or less. The precipitation amount of the γ' phase can be measured by microstructure observation and image analysis (e.g. ImageJ, a public domain program developed at the National Institutes of Health in U.S.A.).

[0060] As an exemplary end temperature of the slow-cooling process, in the case that the γ' phase solvus temperature is relatively low of 1020°C or more and less than 1100°C, the end temperature of slow-cooling process is preferably at least 50°C lower than the γ' phase solvus temperature; more preferably at least 100°C lower than the γ' phase solvus temperature; and further preferably at least 150°C lower than the γ' phase solvus temperature. In the case that the γ' phase solvus temperature is relatively high of 1110°C or more, the end temperature of slow-cooling process is preferably at least 100°C lower than the γ' phase solvus temperature; more preferably at least 150°C lower than the γ' phase solvus temperature; and further preferably at least 200°C lower than the γ' phase solvus temperature. More specifically, it is preferable that the slow-cooling process be performed down to a temperature of 1000°C or less and 800°C or more.

[0061] The cooling from the slow-cooling end temperature is preferably performed at a high cooling rate in order to suppress the precipitation of the intra-grain γ' phase particles (e.g., the precipitation amount of the intra-grain γ' phase of at most 10 volume %) during the cooling process. For example, water-cooling or gas-cooling is preferable.

[0062] As an index of forming/molding processability, it is possible to adopt a Vickers hardness (Hv) of the softened powder at a room temperature. As for the softened powder obtained through the step S2, it is possible to obtain a softened powder having the room-temperature Vickers hardness of 370 Hv or less even by using a superhigh precipitation-strengthened Ni-based alloy material in which the equilibrium amount of precipitation of the γ' phase at 700°C is 45 volume % or more. It is more preferable for better forming/molding processability that the room-temperature Vickers hardness is 350 Hv or less; and further more preferably 330 Hv or less.

[0063] FIG. 4 is a flowchart illustrating steps of another method for manufacturing an Ni-based alloy article formed from an Ni-based alloy softened powder according to an embodiment of the invention. As shown in FIG. 4, the another method for manufacturing an Ni-based alloy article formed from an Ni-based alloy softened powder according to an embodiment of the invention is different from the steps shown in FIG. 2 regarding a method for manufacturing the Ni-based alloy softened powder (the single-phase precursor powder preparation step S1' and the powder softening sub-high temperature and slow cooling heat treatment step S2'), but it is the same as the method shown in FIG. 2 regarding

the molding processing step S3 and the solution and aging heat treatment step S4. FIG. 5 is a schematic illustration showing changes in microstructure of an Ni-based alloy powder in the steps S1' and S2'.

[0064] The steps S1' to S2' (i.e. the another method for manufacturing an Ni-based alloy softened powder according to an embodiment of the invention) will be hereinafter described with reference to FIGs. 4 and 5 focusing on the difference from the steps S1 and S2 described above.

(Single-Phase Precursor Powder Preparation Step S1')

[0065] The step S1' is a step of preparing a single-phase precursor powder with a predetermined chemical composition whose particles are each formed of a polycrystalline body of γ single-phase fine crystals. In the present invention, a single-phase precursor powder means a powder that can be judged as being γ single-phase based on measurements by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) and/or X-ray diffractometry (XRD) (i.e. no γ' phase is detected). The precision level of transmission electron microscopy (TEM) or scanning transmission electron microscopy (STEM) is not required.

[0066] In the step S1', a master alloy ingot production substep (S1a) similar to that in the step S1 and an atomization substep (S1'b) for forming a single-phase precursor powder are performed. As appropriate, a classification substep (S1c) similar to that in the step S1 may be performed. For the atomization substep S1'b, an atomization method similar to the atomization substep S1b of the step S1 may be used except that the average cooling rate is controlled in a temperature range where the γ' phase easily generates/precipitates (e.g. 1,100°C to 600°C). The average cooling rate should preferably be controlled to 500°C/min or more, more preferably 1,000°C/min or more, even more preferably 1,500°C/min or more, and the most preferably 2,000°C/min or more.

[0067] As a result of the step S1' (in particular, the atomization substep S1'b), there can be obtained a single-phase precursor powder formed of a polycrystalline body of γ single-phase fine crystals, as shown in FIG. 5. The oxygen content, the average particle size, and the average grain size of the single-phase fine crystals are similar to those of the precursor powder obtained in the step S1.

(Powder Softening Sub-high Temperature and Slow Cooling Heat Treatment Step S2')

[0068] The step S2' is a step of producing an Ni-based alloy softened powder in which the grain-boundary γ' phase is precipitated in an amount of 20 volume % or more by performing a predetermined sub-high temperature and slow cooling heat treatment on the single-phase precursor powder prepared in the previous step S1'. The sub-high temperature and slow cooling heat treatment is a heat treatment to heat the single-phase precursor powder to a temperature equal to or higher than a temperature 80°C lower than the solvus temperature of the γ' phase and lower than the solvus temperature and slowly cool the precursor powder from this temperature at a cooling rate of 100°C/h or less. The heating temperature (i.e. slow cooling start temperature) should preferably be equal to or higher than a temperature 50°C lower than the solvus temperature of the γ' phase and more preferably equal to or higher than a temperature 30°C lower than the solvus temperature of the γ' phase. The cooling rate in the slow cooling process should preferably be 50°C/h or less and more preferably 10°C/h or less, as in the step S2.

[0069] Because the precursor powder to be used is single-phase, preferential nucleation and grain growth of the grain-boundary γ' phase occur (see FIG. 5). Also, the slow cooling end temperature, cooling from the slow cooling end temperature, the precipitation amount of the grain-boundary γ' phase as a result of the sub-high temperature and slow cooling heat treatment, and the amount of the intra-grain γ' phase present in the step S2' are similar to those of the softened powder obtained in the step S2.

[0070] Here, a brief discussion will be made on the reason why a softened powder similar to the softened powder obtained in the step S2 can be obtained by performing the sub-high temperature and slow cooling heat treatment on the single-phase precursor powder. Although the exact mechanism is still unclear, it is possible that the single-phase precursor powder formed of a polycrystalline body of γ single-phase fine crystals plays a key role, and the following model is conceivable.

[0071] For γ single-phase crystals (in a situation where substantially no γ' phase is present), a temperature equal to or higher than a temperature 80°C lower than the solvus temperature of the γ' phase and lower than the solvus temperature (referred to as "sub-high temperature" in the invention) is considered to be in a temperature region where the degree of undercooling is small regarding γ' phase precipitation. Also, the precipitation of the γ' phase in γ phase crystals (i.e. the intra-grain γ' phase) can be regarded as a kind of homogenous nucleation (at least a phenomenon similar to homogenous nucleation). In other words, in γ single-phase crystals, the nucleation frequency of the intra-grain γ' phase in the sub-high temperature region is considered to be extremely low.

[0072] Meanwhile, it is believed that on the grain boundaries of γ single-phase fine crystals, oxygen atoms are unevenly distributed and minute oxides are formed, as described before. In this case, the grain boundaries of fine crystals probably serve as heterogenous nucleation sites for the γ' phase. In addition, from the viewpoint of thermodynamics, it is known

that heterogenous nucleation has a much lower activation energy than homogenous nucleation and therefore has a sufficiently high nucleation frequency even with a small degree of undercooling.

[0073] Considering all these things, the sub-high temperature and slow cooling heat treatment on the single-phase precursor powder is thought to be a heat treatment to cause preferential nucleation of the heterogenous nucleation-derived grain-boundary γ' phase by having homogenous nucleation compete against heterogenous nucleation in a temperature range where the degree of undercooling of the γ' phase is small and subsequently allow for the grain growth of the generated nuclei in the slow cooling process. This model is considered to be applicable to "the preferential nucleation of the grain-boundary γ' phase and the subsequent grain growth of the grain-boundary γ' phase" in the powder softening high temperature and slow cooling step S2.

[0074] Meanwhile, it should be noted that the present invention does not deny the possibility of applying the powder softening high temperature and slow cooling heat treatment step S2 to a single-phase precursor powder. FIG. 6 is a flowchart illustrating steps of still another method for manufacturing an Ni-based alloy article formed from an Ni-based alloy softened powder according to an embodiment of the invention. As shown in FIG. 6, the still another method for manufacturing an Ni-based alloy article formed from an Ni-based alloy softened powder according to this embodiment includes the single-phase precursor powder preparation step S1' followed by the powder softening high temperature and slow cooling heat treatment step S2 in its method for manufacturing the Ni-based alloy softened powder. It may be the same as the method shown in FIG. 2 regarding the molding processing step S3 and the solution and aging heat treatment step S4.

(Chemical Composition of Ni-based Alloy Softened Powder)

[0075] Chemical composition of the Ni-based alloy material used in the invention will be described. The Ni-based alloy material has a chemical composition that allows the equilibrium amount of precipitation of the γ' phase of from 30 volume % or more and 80 volume % or less at 700°C. Specifically, a preferable chemical composition (in mass percent) is as follows: 5% to 25% of Cr; more than 0% to 30% of Co; 1% to 8% of Al; the total amount of Ti, Nb and Ta of between 1% and 10%, inclusive; 10% or less of Fe; 10% or less of Mo; 8% or less of W; 0.1% or less of Zr; 0.1% or less of B; 0.2% or less of C; 2% or less of Hf; 5% or less of Re; 0.003% to 0.05% of O; and other substances (Ni and unavoidable impurities). Hereinafter, each component will be described.

[0076] The Cr component dissolves in the γ phase and also forms an oxide (e.g., Cr_2O_3) coating on the surface of the Ni-based alloy article in an actual use environment, thereby increasing corrosion resistance and oxidation resistance. To apply this functional effect onto high-temperature turbine members, it is essential to add at least 5 mass % of Cr. However, excessive adding of the Cr accelerates the formation of a harmful phase. Therefore, the Cr content is preferably 25 mass % or less.

[0077] The Co component, which is an element similar to Ni, dissolves in the γ phase in substitution for Ni. The Co component can increase corrosion resistance as well as increasing creep strength. It can also decrease the γ' phase solvus temperature, thereby increasing the high-temperature ductility. However, excessive adding of the Co accelerates the formation of a harmful phase. Therefore, the Co content is preferably more than 0 mass % and equal to or less than 30 mass %.

[0078] The Al component is an indispensable component for forming a γ' phase that is a precipitation-strengthening phase for an Ni-based alloy. The Al component can also contribute to increase in oxidation resistance and corrosion resistance by forming an oxide (e.g., Al_2O_3) coating on the surface of the Ni-based alloy article in an actual use environment. The Al content is preferably equal to or more than 1 mass % and equal to or less than 8 mass % according to a desired amount of γ' phase precipitation.

[0079] In the same manner as the Al component, the Ti component, the Nb component and the Ta component can also form the γ' phase and increase high-temperature strength. The Ti and Nb components can also increase corrosion resistance. However, excessive adding of those components accelerates the formation of a harmful phase. Therefore, the total amount of Ti, Nb and Ta components is preferably equal to or more than 1 mass % and equal to or less than 10 mass %.

[0080] When the Fe component substitutes the Co component or the Ni component, it is possible to reduce alloy material costs. However, excessive adding of the Fe accelerates the formation of a harmful phase. Therefore, the Fe content is preferably equal to or less than 10 mass %.

[0081] The Mo component and the W component dissolve in the γ phase and can increase high-temperature strength (so-called solid solution strengthening). Therefore, it is preferable that either one component be added. The Mo component can also increase corrosion resistance. However, excessive adding of those components accelerates the formation of a harmful phase or deteriorates ductility and high-temperature strength. Therefore, the Mo content is preferably equal to or less than 10 mass %, and the W content is preferably equal to or less than 8 mass %.

[0082] The Zr component, the B component and the C component can strengthen the grain boundaries of the γ phase crystal grains (i.e., strengthening of tensile strength along the direction perpendicular to the grain boundary of the γ

phase crystal grain), thereby increasing high-temperature ductility and creep strength. However, excessive adding of those components deteriorates formability and processability. Therefore, the Zr content is preferably equal to or less than 0.1 mass %, the B content is preferably equal to or less than 0.1 mass %, and the C content is preferably equal to or less than 0.2 mass %.

[0083] The Hf component can increase oxidation resistance. However, excessive adding of the Hf accelerates the formation of a harmful phase. Therefore, the Hf content is preferably equal to or less than 2 mass %.

[0084] The Re component can contribute to the solid solution strengthening of the γ phase and increase corrosion resistance. However, excessive adding of the Re accelerates the formation of a harmful phase. Furthermore, since the Re is an expensive element, increase of the additive amount will result in increase of alloy material costs. To avoid this disadvantage, the Re content is preferably equal to or less than 5 mass %.

[0085] The O component is usually treated as an impurity and an attempt is often made to reduce the O component. However, in the invention, as stated before, the O component is an indispensable component to suppress the growth of the γ phase fine crystals and facilitate the formation of the grain-boundary γ' phase particles. The content of the O component is preferably equal to or more than 0.003 mass % and equal to or less than 0.05 mass %.

[0086] Residual components of the Ni-based alloy material are the Ni component and unavoidable impurities other than the O component. For example, unavoidable impurities are N (nitrogen), P (phosphorus), and S (sulfur).

EXAMPLES

[0087] Hereinafter, the present invention will be described in more detail with reference to a variety of experiments. However, the invention is not limited to those experiments.

[Experimental 1]

(Fabrication of Ni-based Alloy Precursor Powders PP1 to PP8 and Ni-based Alloy Single-Phase Precursor Powders PP9 and PP10)

[0088] First, master ingots (each 10 kg) were prepared by mixing, melting and casting raw materials. Melting was performed by means of a vacuum induction melting technique. Next, each of the obtained master ingots was re-molten and an Ni-based alloy powder was produced by means of a gas atomization technique while the oxygen partial pressure in the atomization atmosphere was controlled.

[0089] In the fabrication of the Ni-based alloy powders by gas atomizing, it was measured and confirmed that an average cooling rate in a temperature range from 1,100 to 600°C was 500°C/min or more in parts of the alloy powders. Also, the particles of the alloy powders observed to have been cooled at an average cooling rate of 500°C/min or more were judged as being γ single-phase because the γ' phase was not detected in microstructure observation by SEM-EDX at a magnification of 1,000. Microstructure observations were not performed on the particles of the other alloy powders for which the average cooling rates were not measured in their production by gas atomizing.

[0090] Next, each of the obtained Ni-based alloy powders was classified and sorted according into a particle size range within 25 to 150 μm to prepare Ni-based alloy precursor powders PP1 to PP8 and Ni-based alloy single-phase precursor powders PP9 and PP10. The chemical compositions of the obtained powders PP1 to PP10 are shown in Table 1.

TABLE 1 Chemical Compositions of Ni-based Alloy Precursor Powders PP1 to PP8 and Ni-based Alloy Single-phase Precursor Powders PP9 and PP10.

Precursor Powder/ Single-phase Precursor Powder	Chemical Composition (mass %)															
	Cr	Co	Al	Ti	Nb	Ta	Fe	Mo	W	Zr	B	C	Hf	Re	O	Ni
PP1	11.5	15.7	4.4	4.4	-	-	-	6.5	-	0.03	0.015	0.015	0.5	-	0.010	Bal.
PP2	13.0	20.0	3.4	3.7	0.9	2.4	-	3.8	2.1	0.05	0.020	0.050	-	-	0.011	Bal.
PP3	13.3	10.0	4.0	2.4	-	4.8	-	1.7	4.6	0.03	0.018	0.090	-	-	0.011	Bal.
PP4	15.6	14.6	2.6	5.1	-	-	-	3.0	1.2	0.03	0.030	0.008	-	-	0.013	Bal.
PP5	15.0	18.5	3.0	3.6	1.1	2.0	-	5.0	-	0.06	0.015	0.027	0.5	-	0.011	Bal.
PP6	14.0	8.0	3.5	2.5	3.5	-	-	3.5	3.5	0.05	0.010	0.16	-	-	0.014	Bal.
PP7	13.8	6.8	4.0	3.3	1.2	2.8	-	1.8	4.0	-	0.015	0.014	-	1.0	0.014	Bal.
PP8	19.6	13.5	1.3	3.0	-	-	-	4.2	-	-	0.005	0.075	-	-	0.007	Bal.
PP9	13.5	27.0	2.8	4.3	0.7	2.2	-	3.9	1.2	0.05	0.020	0.025	0.5	-	0.012	Bal.
PP10	15.7	8.4	2.3	3.4	1.1	-	4.0	3.1	2.7	-	0.011	-	-	-	0.010	Bal.
"-" indicates that the element was not intentionally included. "Bal." indicates inclusion of impurities other than O.																

[Experimental 2]

(Fabrication of Ni-based Alloy Softened Powders according to Examples 1 to 11 and Comparative Examples 1 to 12 and Evaluation of Molding Processability thereof)

[0091] The Ni-based alloy precursor powders PP1 to PP8 and the Ni-based alloy single-phase precursor powders PP9 and PP10 obtained in Experimental 1 were subjected to a powder softening treatment under the heat treatment conditions (i.e., slow-cooling start temperature, and cooling rate during the slow-cooling process) indicated in Table 2, described later, thereby fabricating the Ni-based alloy softened powders according to Examples 1 to 11 and Comparative examples 1 to 12. The slow-cooling end temperature was set to 950°C except for Comparative examples 1 and 12. Comparative examples 1 and 12 were quenched from the slow-cooling start temperature to room temperature by gas cooling.

[0092] Each of the obtained Ni-based alloy softened powders was subjected to microstructure observation (for the precipitation amount of the grain-boundary γ' phase) and Vickers hardness measurement at room temperature to evaluate molding processability.

[0093] The precipitation amount of the grain-boundary γ' phase of each softened powder was determined by electron microscope observation and image analysis (ImageJ). The room temperature Vickers hardness measurement was performed on randomly drawn 10 particles of each softened powder with a micro Vickers hardness tester (Akashi Seisakusho, Ltd., model: MVK-E). The room temperature Vickers hardness was measured for each of the 10 particles, and the average value of the 8 particles obtained after excluding the maximum and minimum values was regarded as the room temperature Vickers hardness of the softened powder. Regarding the evaluation of molding processability, a room temperature Vickers hardness of equal to or less than 370 Hv was judged as "Passed", and a room temperature Vickers hardness of more than 370 Hv was judged as "Failed".

[0094] Data and evaluation results of the Ni-based alloy softened powders of Examples 1 to 11 and Comparative examples 1 to 12 are shown in Table 2. In Table 2, the equilibrium amount of precipitation of the γ' phase at 700°C and the γ' phase solvus temperature were obtained by the thermodynamic calculation based on the alloy composition in Table 1.

TABLE 2 Data and Evaluation Results of Ni-based Alloy Softened Powders of Examples 1 to 11 and Comparative Examples 1 to 12.

Softened Powder	Precursor Powder / Single-phase Precursor Powder	Equilibrium Amount of γ' Phase Precipitation at 700°C (volume %)	γ' Phase Solvus Temperature (°C)	Slow-cooling Start Temperature based on γ' Phase Solvus Temperature (°C)	Cooling Rate During Slow-cooling Process (°C/h)	Precipitation Amount of Grain-boundary γ' Phase (volume %)	Room Temperature Vickers Hardness (Hv)	Molding Processability
Example 1	PP1	61	1193	+10	10	48	310	Passed
Example 2	PP2	53	1190	+10	50	40	308	Passed
Example 3	PP3	57	1164	+20	10	45	314	Passed
Example 4	PP4	47	1160	+20	100	34	305	Passed
Example 5	PP5	50	1173	+10	10	40	325	Passed
Example 6	PP6	53	1148	+20	50	41	338	Passed
Example 7	PP7	61	1193	+20	100	49	338	Passed
Example 8	PP9	50	1185	-15	100	34	331	Passed
Example 9	PP10	38	1102	-20	50	21	327	Passed
Example 10	PP9	50	1185	+10	100	38	303	Passed
Example 11	PP10	38	1102	+30	50	25	303	Passed
Comparative example 1	PP1	61	1193	+20	>1000	0	455	Failed
Comparative example 2	PP2	53	1190	+10	300	8	393	Failed
Comparative example 3	PP3	57	1164	+20	300	6	400	Failed
Comparative example 4	PP4	47	1160	-150	50	4	408	Failed
Comparative example 5	PP5	50	1173	-100	100	7	396	Failed
Comparative example 6	PP6	53	1148	-150	300	2	383	Failed

(continued)

Softened Powder	Precursor Powder / Single-phase Precursor Powder	Equilibrium Amount of γ' Phase Precipitation at 700°C (volume %)	γ' Phase Solvus Temperature (°C)	Slow-cooling Start Temperature based on γ' Phase Solvus Temperature (°C)	Cooling Rate During Slow-cooling Process (°C/h)	Precipitation Amount of Grain-boundary γ' Phase (volume %)	Room Temperature Vickers Hardness (Hv)	Molding Processability
Comparative example 7	PP7	61	1193	-100	200	8	391	Failed
Comparative example 8	PP8	24	1010	+10	100	2	285	Passed
Comparative example 9	PP9	50	1185	-100	100	11	396	Failed
Comparative example 10	PP10	38	1102	-100	100	6	380	Failed
Comparative example 11	PP9	50	1185	+10	200	9	388	Failed
Comparative example 12	PP10	38	1102	+30	>1000	0	403	Failed

[0095] As shown in Table 2, in the softened powders according to Comparative examples 1 and 7 in which the slow-cooling start temperature and/or the cooling rate during slow-cooling process of the high temperature and slow-cooling heat treatment are/is outside of the invention, the precipitation amount of the grain-boundary γ' phase is less than 20 volume % (instead, coarsened intra-grain γ' phase particles were detected), and the room-temperature Vickers hardness is more than 370 Hv. As a result, the molding processability properties are failed.

[0096] When the slow-cooling start temperature (i.e. heating temperature) of the high temperature and slow-cooling heat treatment is too low, or when the cooling rate during slow-cooling process is too high, the grain-boundary γ' phase rarely precipitates and grows. Therefore, it is confirmed that sufficient molding processability cannot be ensured.

[0097] In the softened powder according to Comparative example 8 in which the equilibrium amount of precipitation of the γ' phase at 700°C is outside of the invention, the equilibrium amount of the γ' phase precipitation is less than 30 volume %. This softened powder is not applicable to the high precipitation-strengthened Ni-based alloy material prescribed by the invention. However, the precipitation amount of the γ' phase is absolutely small, and the forming/molding processability does not have particular problems from the past.

[0098] Contrary to Comparative examples 1 to 8, in the softened powders according to Examples 1 to 7, any material under test have the precipitation amount of the grain-boundary γ' phase of 20 volume % or more and the room-temperature Vickers hardness of 370 Hv or less. As a result, the molding processability properties are passed. This means that one of the advantageous effects of the invention is verified.

[0099] Also, the softened powders according to Examples 8 and 9, respectively formed of the single-phase precursor powders PP9 and PP10, each has the grain-boundary γ' phase precipitation amount of 20 volume % or more and the room temperature Vickers hardness of 370 Hv or less, even though they were each obtained by the sub-high temperature and slow cooling heat treatment performed with a slow-cooling start temperature lower than the solvus temperature of the γ' phase. As a result, the molding processability properties thereof are passed. In other words, one of the advantageous effects of the invention is verified.

[0100] Moreover, the softened powders according to Examples 10 and 11, respectively obtained by applying the high temperature and slow cooling heat treatment to the single-phase precursor powders PP9 and PP10, each also has the grain-boundary γ' phase precipitation amount of 20 volume % or more and the Vickers hardness of 370 Hv or less. As a result, the molding processability properties thereof are passed. In other words, one of the advantageous effects of the invention is also verified.

[0101] In contrast, the softened powders according to Comparative Examples 9 to 12, each formed of the single-phase precursor powder PP9 or PP10 but obtained with the slow-cooling start temperature or the cooling rate in the softening treatment failing to meet the invention, each has the grain-boundary γ' phase precipitation amount of less than 20 volume % and the Vickers hardness of more than 370 Hv. As a result, the molding processability properties thereof are failed.

[0102] When the slow-cooling start temperature in the sub-high temperature and slow cooling heat treatment is too low, or when the cooling rate during the cooling process in the high temperature and slow cooling heat treatment is too high, the grain-boundary γ' phase hardly precipitates and grows. Therefore, it is confirmed that sufficient molding processability cannot be secured.

[0103] Based on the foregoing results, it has been shown that there can be obtained a softened powder that exhibits a good forming/molding processability even if the softened powder is formed of a high precipitation-strengthened Ni-based alloy material or a superhigh precipitation-strengthened Ni-based alloy material, by applying the method for manufacturing an Ni-based alloy softened powder according to embodiments of the invention. Application of powder metallurgy using this Ni-based alloy softened powder is expected to make it possible to provide a high precipitation-strengthened Ni-based alloy article at low cost.

[0104] The above-described embodiments and Examples have been specifically given in order to help with understanding on the present invention, but the invention is not limited to the described embodiments and Examples. For example, a part of an embodiment may be replaced by known art, or added with known art. That is, a part of an embodiment of the invention may be combined with known art and modified based on known art, as far as no departing from a technical concept of the invention.

LEGEND

[0105]

- 1 atom constituting γ phase;
- 2 atom constituting γ' phase;
- 3 coherent interface between γ and γ' phases; and
- 4 incoherent interface between γ and γ' phases.

Claims

1. An Ni-based alloy softened powder, having a chemical composition allowing γ' phase precipitated in γ phase as a matrix to have an equilibrium precipitation amount of 30 volume % or more and 80 volume % or less at 700°C, the softened powder having an average particle size of 5 μm or more and 500 μm or less, the softened powder comprising particles comprising a polycrystalline body of fine crystals of the γ phase, the γ' phase being precipitated on grain boundaries of the fine crystals of the γ phase in an amount of 20 volume % or more, the particles having a Vickers hardness of 370 Hv or less at room temperature.
2. The Ni-based alloy softened powder according to claim 1, wherein the chemical composition comprises:
 - 5 mass % or more and 25 mass % or less of Cr;
 - more than 0 mass % and 30 mass % or less of Co;
 - 1 mass % or more and 8 mass % or less of Al;
 the total amount of Ti, Nb and/or Ta being 1 mass % or more and 10 mass % or less;
 - 10 mass % or less of Fe;
 - 10 mass % or less of Mo;
 - 8 mass % or less of W;
 - 0.1 mass % or less of Zr;
 - 0.1 mass % or less of B;
 - 0.2 mass % or less of C;
 - 2 mass % or less of Hf;
 - 5 mass % or less of Re;
 - 0.003 mass % or more and 0.05 mass % or less of O; and a balance being Ni and inevitable impurities.
3. The Ni-based alloy softened powder according to claim 1 or 2, wherein the chemical composition is a chemical composition that allows the γ' phase to have a solvus temperature of 1,100°C or higher.
4. The Ni-based alloy softened powder according to claim 3, wherein the Ni-based alloy softened powder has a chemical composition that allows the γ' phase to have the equilibrium precipitation amount of 45 volume % or more and 80 volume % or less at 700°C.
5. The Ni-based alloy softened powder according to any one of claims 1 to 4, wherein the particles have a Vickers hardness of 350 Hv or less at room temperature.
6. A method for manufacturing an Ni-based alloy softened powder having a chemical composition allowing γ' phase precipitated in γ phase as a matrix to have an equilibrium precipitation amount of 30 volume % or more and 80 volume % or less at 700°C, the softened powder having an average particle size of 5 μm or more and 500 μm or less, the softened powder comprising particles comprising a polycrystalline body of fine crystals of the γ phase, the particles having a Vickers hardness of 370 Hv or less at room temperature, the method comprising:
 - a precursor powder preparation step of preparing a precursor powder that has the chemical composition and comprises particles comprising a polycrystalline body of fine crystals of the γ phase; and
 - a powder softening high temperature and slow cooling heat treatment step of subjecting the precursor powder to a high temperature and slow cooling heat treatment in which the precursor powder is heated to a temperature that is equal to or higher than the solvus temperature of the γ' phase and lower than the melting point of the γ phase to cause the γ' phase to enter into solid solution in the γ phase and subsequently cooled slowly from this temperature to a temperature lower than the solvus temperature of the γ' phase at a cooling rate of 100°C/h or less to produce the Ni-based softened powder in which the γ' phase is precipitated on grain boundaries of the fine crystals of the γ phase in an amount of 20 volume % or more.
7. A method for manufacturing an Ni-based alloy softened powder having a chemical composition allowing γ' phase precipitated in γ phase as a matrix to have an equilibrium precipitation amount of 30 volume % or more and 80 volume % or less at 700°C, the softened powder having an average particle size of 5 μm or more and 500 μm or less, the softened powder comprising particles comprising a polycrystalline body of fine crystals of the γ phase, the

particles having a Vickers hardness of 370 Hv or less at room temperature, the method comprising:

a single-phase precursor powder preparation step of preparing a single-phase precursor powder that has the chemical composition and comprises particles comprising a polycrystalline body of single-phase fine crystals of the γ phase; and

a powder softening sub-high temperature and slow cooling heat treatment step of subjecting the single-phase precursor powder to a sub-high temperature and slow cooling heat treatment in which the single-phase precursor powder is heated to a temperature that is equal to or higher than a temperature 80°C lower than the solvus temperature of the γ' phase and lower than the solvus temperature and cooled slowly from this temperature at a cooling rate of 100°C/h or less to produce the Ni-based softened powder in which the γ' phase is precipitated on grain boundaries of the single-phase fine crystals of the γ phase in an amount of 20 volume % or more.

8. A method for manufacturing an Ni-based alloy softened powder having a chemical composition allowing γ' phase precipitated in γ phase as a matrix to have an equilibrium precipitation amount of 30 volume % or more and 80 volume % or less at 700°C, the softened powder having an average particle size of 5 μm or more and 500 μm or less, the softened powder comprising particles comprising a polycrystalline body of fine crystals of the γ phase, the particles having a Vickers hardness of 370 Hv or less at room temperature, the method comprising:

a single-phase precursor powder preparation step of preparing a single-phase precursor powder that has the chemical composition and comprises particles comprising a polycrystalline body of single-phase fine crystals of the γ phase; and

a powder softening high temperature and slow cooling heat treatment step of subjecting the precursor powder to a high temperature and slow cooling heat treatment in which the single-phase precursor powder is heated to a temperature that is equal to or higher than the solvus temperature of the γ' phase and lower than the melting point of the γ phase and subsequently cooled slowly from this temperature to a temperature lower than the solvus temperature of the γ' phase at a cooling rate of 100°C/h or less to produce the Ni-based softened powder in which the γ' phase is precipitated on grain boundaries of the single-phase fine crystals of the γ phase in an amount of 20 volume % or more.

9. The method for manufacturing an Ni-based alloy softened powder according to any one of claims 6 to 8, wherein the chemical composition comprises:

5 mass % or more and 25 mass % or less of Cr;
more than 0 mass % and 30 mass % or less of Co;
1 mass % or more and 8 mass % or less of Al;

the total amount of Ti, Nb and/or Ta being 1 mass % or more and 10 mass % or less;

10 mass % or less of Fe;
10 mass % or less of Mo;
8 mass % or less of W;
0.1 mass % or less of Zr;
0.1 mass % or less of B;
0.2 mass % or less of C;
2 mass % or less of Hf;
5 mass % or less of Re;
0.003 mass % or more and 0.05 mass % or less of O; and a balance being Ni and inevitable impurities.

10. The method for manufacturing an Ni-based alloy softened powder according to any one of claims 6 to 9, wherein the precursor powder preparation step or the single-phase precursor powder preparation step comprises an atomization substep.

11. The method for manufacturing an Ni-based alloy softened powder according to any one of claims 6 to 10, wherein the chemical composition is a chemical composition that allows the γ' phase to have a solvus temperature of 1,100°C or higher.

12. The method for manufacturing an Ni-based alloy softened powder according to claim 11, wherein the Ni-based alloy softened powder has a chemical composition that allows the γ' phase to have an equilibrium

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precipitation amount of 45 volume % or more and 80 volume % or less at 700°C.

13. The method for manufacturing an Ni-based alloy softened powder according to any one of claims 6 to 12, wherein the particles have a Vickers hardness of 350 Hv or less at room temperature.

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FIG. 1

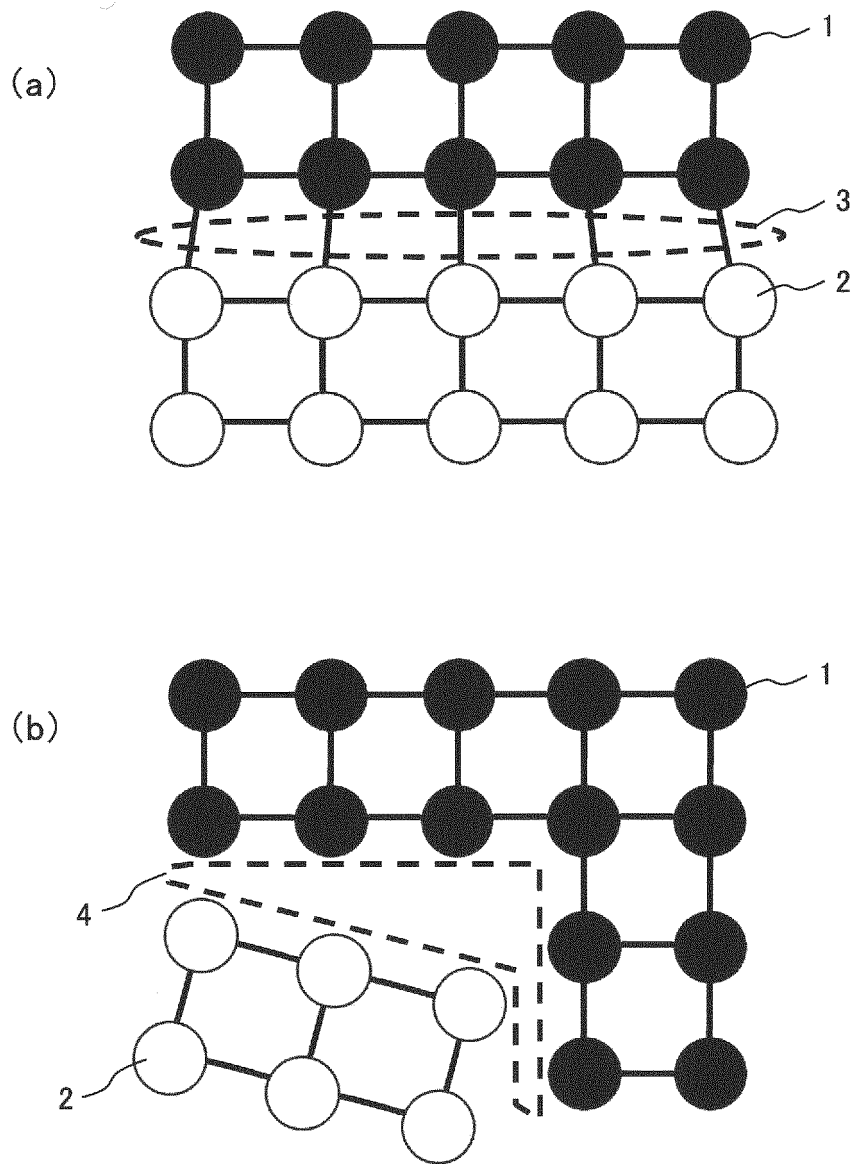


FIG. 2

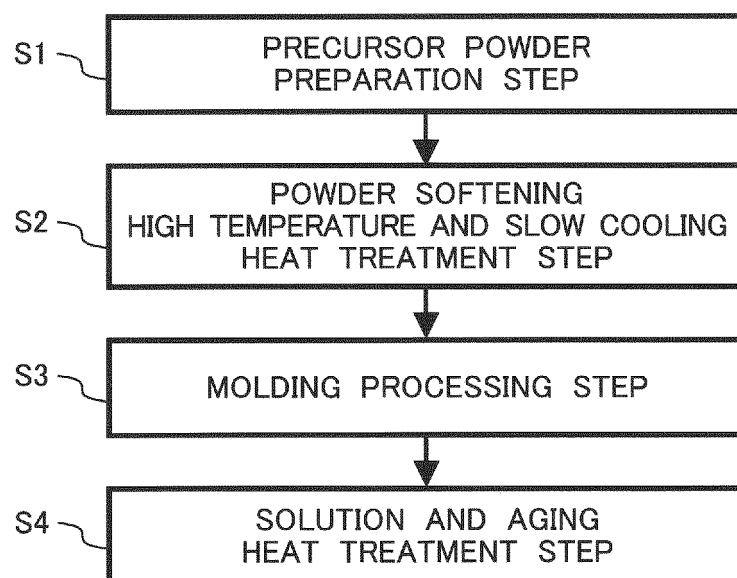


FIG. 3

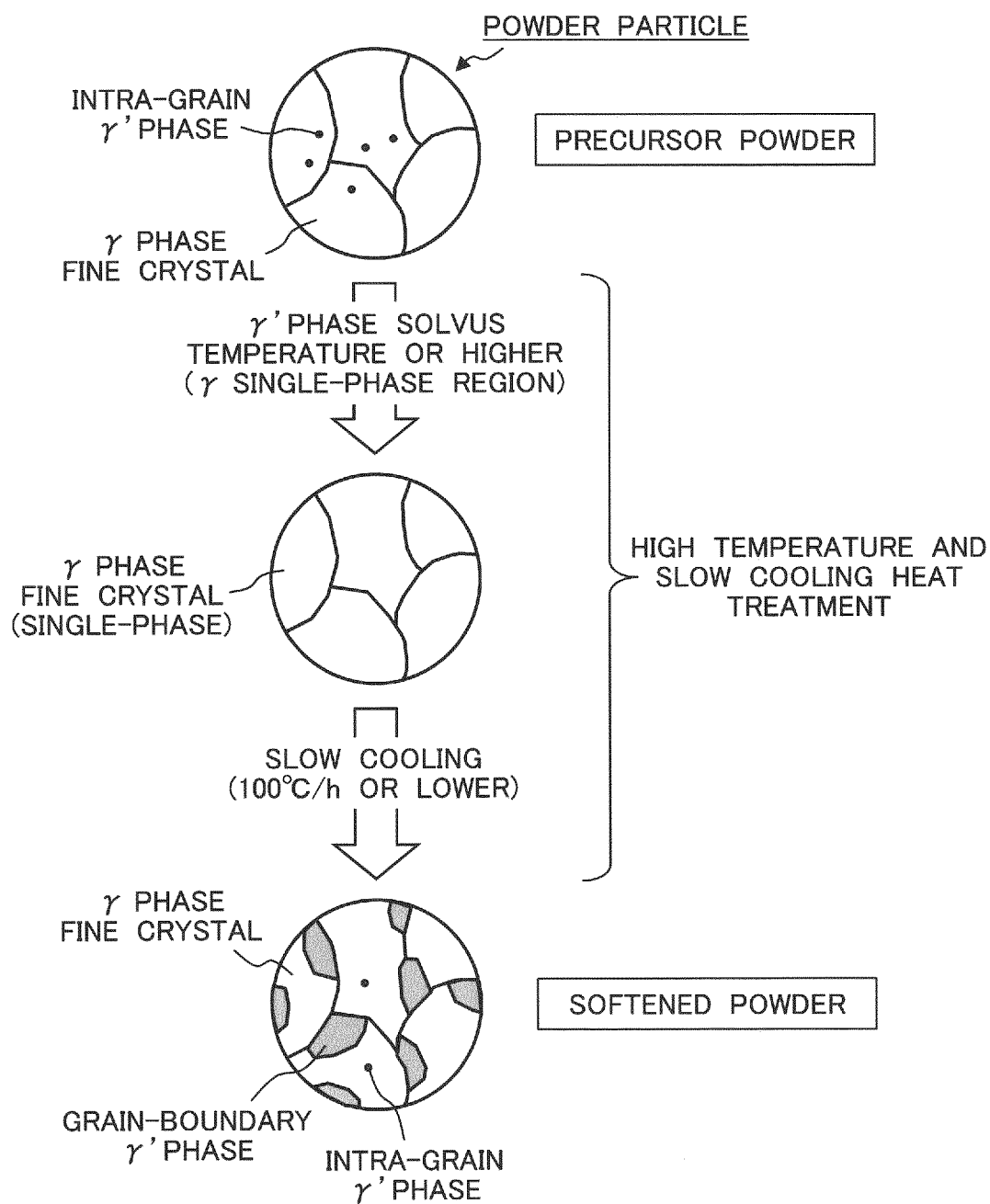


FIG. 4

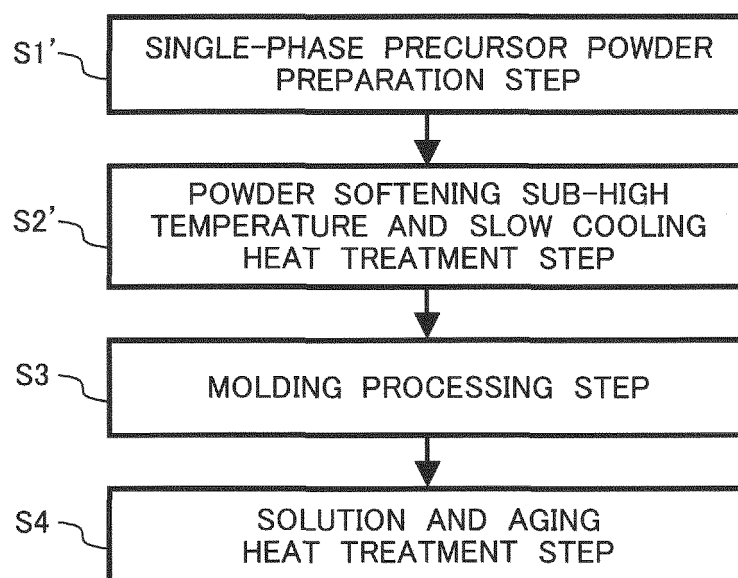


FIG. 5

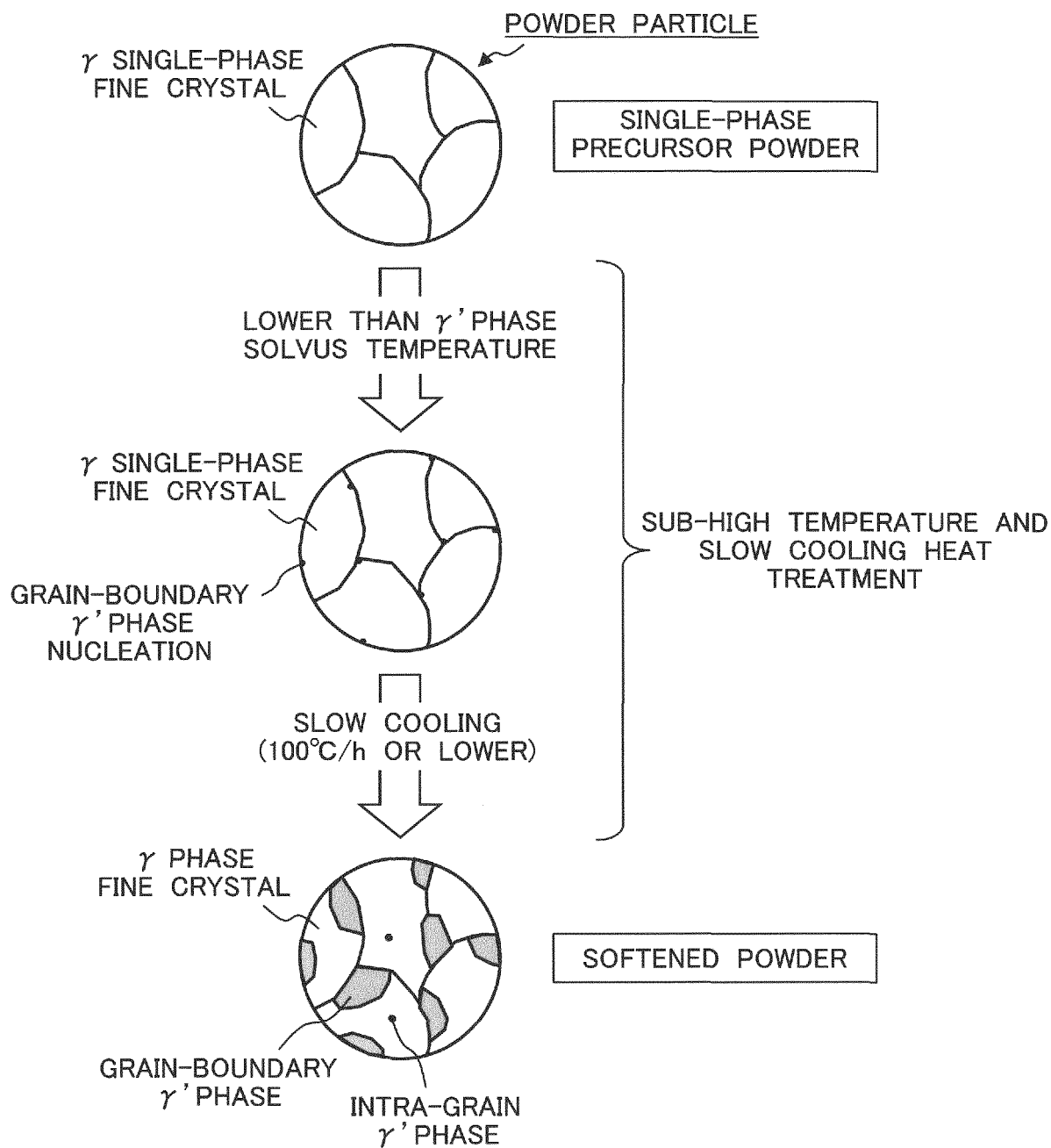
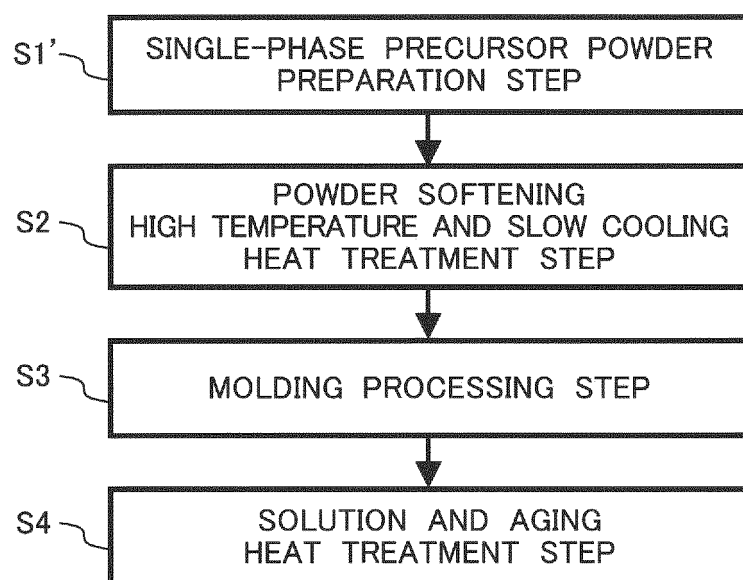


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/003833

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B22F9/20 (2006.01) i, B22F5/04 (2006.01) i, C22C19/05 (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)

Int.Cl. B22F9/20, B22F5/04, C22C19/05

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.
A	JP 2016-003374 A (MITSUBISHI HITACHI POWER SYSTEMS LTD.) 12 January 2016, entire text & US 2015/0368774 A1, entire text & CN 105200268 A	1-13
A	US 5061324 A (GENERAL ELECTRIC COMPANY) 29 October 1991, entire text (Family: none)	1-13



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search
04.03.2019Date of mailing of the international search report
12.03.2019Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/053489 A2 (GENERAL ELECTRIC COMPANY) 07 April 2016, entire text & JP 2017-532440 A & CN 106661675 A	1-13

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REFERENCES CITED IN THE DESCRIPTION

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- JP 9302450 A [0007]
- JP 5869624 B [0007] [0010] [0024]
- US 5649280 A [0007] [0014]