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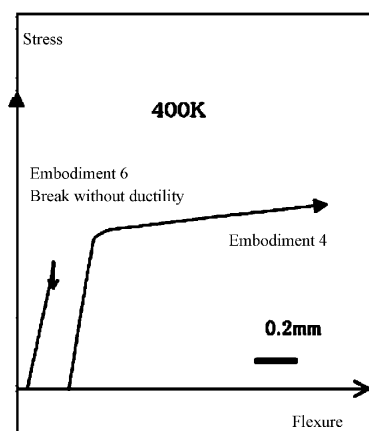
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(54) **METHOD FOR MANUFACTURING ALLOY CONTAINING TRANSITION METAL CARBIDE, TUNGSTEN ALLOY CONTAINING TRANSITION METAL CARBIDE, AND ALLOY MANUFACTURED BY SAID METHOD**

(57) The present invention relates to the development of an alloy material with significantly improved low-temperature brittleness, recrystallization brittleness, and irradiation brittleness by the introduction of a recrystallization microstructure into an alloy, particularly a tungsten material, to significantly strengthen a weak grain boundary of the recrystallization microstructure. The present invention comprises the steps of: mechanically alloying at least one species selected from a group-IVA, VA, or VIA transition metal carbide and a metallic raw material; sintering base powders obtained through the mechanically alloying step, by using a hot isostatic press; and performing plastic deformation of at least 60% on the alloy obtained through the sintering step, at a strain rate between 10^{-5}s^{-1} and 10^{-2}s^{-1} and at a temperature between 500°C and $2,000^{\circ}\text{C}$. It is therefore possible to obtain an alloy material with significantly improved low-temperature brittleness, recrystallization brittleness, and irradiation brittleness.

Fig. 5



Description{TECHNICAL FIELD}

5 **[0001]** The present invention relates to a method for manufacturing an alloy containing transition metal carbide, a tungsten alloy containing transition metal carbide, and an alloy manufactured by said method. In particular, the present invention relates to a method for manufacturing an alloy that manifests superplasticity due to grain boundary sliding when the alloy is made to undergo superplastic deformation, that exhibits high recrystallization fracture strength, that has little decrease in strength or ductility, even when heated to high temperatures due to its recrystallized structure, and
 10 which has dramatically remedied low-temperature embrittlement, recrystallization embrittlement, and neutron irradiation embrittlement, as well as an alloy that has been manufactured by this manufacturing method, in particular, a tungsten alloy.

{BACKGROUND ART}

15 **[0002]** Tungsten and tungsten alloys have melting points of as high as 3410°C which are the highest of any metal. These materials thus provide a great many advantages that are unparalleled by other metals. However, the materials have not been used for structure due to an inability to resolve problems with persisting embrittlement (low-temperature embrittlement, recrystallization embrittlement, and irradiation embrittlement), which has hampered practical use of these materials as high-temperature structural materials in extreme environments.

20 **[0003]** These embrittlement phenomena all result from very weak crystal grain boundaries and a tendency for fracture to originate from the grain boundaries which are referred to as "grain boundary embrittlement". The cause of grain boundary embrittlement is that tungsten is a metal having an extremely high degree of covalent bond character, and the grain boundaries are substantially weaker (tend to fracture) due to their high energies. Additionally, interstitial gas elements contained in air such as nitrogen and oxygen have extremely low solubility in tungsten, and thus tend to
 25 segregate and precipitate at the grain boundaries, which further weakens the grain boundaries and promotes embrittlement.

[0004] As shown in FIG. 1(a), with common metals, almost the entire temperature range is the ductile temperature region, because of the fact that plastic deformation (permanent set) occurs prior to break. On the other hand, as shown in FIG. 1(b), because tungsten has covalent bonding in which the directionality of the interatomic bonds is extremely
 30 high, the grain boundaries are substantially weaker, ductile-brittle transition occurs, and the ductile-brittle transition temperature ("DBTT" below) is also high. This phenomenon thus becomes extreme with lower temperatures at which there is a precipitous increase in the Peierls stress (yield strength) required for screw dislocations to glide in tungsten (low-temperature embrittlement), and the phenomenon is even more pronounced with recrystallized structure in which extremely weak grain boundaries are formed (recrystallization embrittlement). Moreover, when lattice defects are introduced by high-energy particle irradiation using neutrons or the like, such irradiation induced defects accumulate inside
 35 the crystal grains or at the grain boundaries and impede dislocation slip, resulting in the promotion of grain boundary embrittlement (irradiation embrittlement).

[0005] Consequently, in order to simultaneously remedy low-temperature embrittlement, recrystallization embrittlement, and irradiation embrittlement, it is necessary to introduce recrystallized microstructures containing high densities of sink sites (sinks; crystal grain boundary or dispersed particles) that can permit the material to tolerate irradiation
 40 induced defects and to convert the weak grain boundaries in the recrystallized microstructure to strong grain boundaries that resist fracture.

[0006] The inventors of the present invention, in order to resolve problems with low temperature embrittlement and embrittlement of tungsten due to neutron irradiation and recrystallization, carried out manufacture of W-TiC having ultrafine crystal grains by a hot isostatic pressing (HIP) method and by mechanical alloying (MA) in Ar and H₂ atmospheres. Effects such as an appreciable improvement in room temperature toughness were found to occur, and these results were published (non-patent documents 1, 2). However, the tungsten materials manufactured by the above methods still were not adequate for practical use.

[0007] On the other hand, a known method for improving toughness and the like of high-melting (refractory) metals has been to increase creep resistance by the introduction of 0.005 to 10 mass% of one or more types of compounds or mixtures selected from the group consisting of oxides, nitrides, carbides, borides, silicates, or aluminates with particle diameters of $\leq 1.5 \mu\text{m}$ and having melting points of 1500°C or greater into high-melting metals such as Mo, W, Nb, Ta, V, and Cr (refer to patent document 1). However, patent document 1 discloses an improvement in the heat resistance and creep resistance of high-melting metals at high temperatures, not a remedy for low-temperature embrittlement, recrystallization embrittlement, or irradiation embrittlement.
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[0008] In addition, the inventors of the present invention also applied for a patent (refer to patent document 2) based on the discovery that dispersion of 0.05 to 5 mol% of ultrafine particles of group IVa transition metal carbides with particle diameters of 10 nm or less in molybdenum alloy and restricting the crystal grain diameter to 1 μm or less enables the

strength of the molybdenum alloy to increase, less loss of strength, even when heated at high-temperature, and an alleviation of low-temperature embrittlement, recrystallization embrittlement, and neutron irradiation embrittlement. However, the molybdenum described in patent document 2 is a material that exhibits ductility at room temperature, even as a pure metal, and has completely different properties and manufacture conditions in comparison to tungsten, which is an extremely brittle material having a high melting point that is 800°C higher than that of molybdenum.

[0009] In addition, with molybdenum, it is necessary to introduce work-deformed structure by plastic working (hammering (forging), rolling, or the like) in order to improve ductility in patent document 2, resulting in a decrease in recrystallization temperature and anisotropy. With tungsten, on the other hand, the issue is ductility improvement in a recrystallized equiaxed structure that is in a recrystallized state with absolutely no work-deformed structure and therefore no anisotropy. The two cases are thus substantially different.

PRIOR ART DOCUMENTS

PATENT DOCUMENT

[0010]

Patent document 1: Japanese Laid-open Patent Publication No. 1-502680

Patent document 2: Japanese Laid-open Patent Publication No. 8-85840

NON-PATENT DOCUMENTS

[0011]

Non-patent document 1: Collected abstracts of the Japan Institute of Metals and Materials Vol. 148, p.235

Non-patent document 2: Collected abstracts of the Japan Institute of Metals and Materials Vol. 143, p.322

{DISCLOSURE OF THE INVENTION}

{Problems To Be Solved By The Invention}

[0012] The inventors of the present invention carried out painstaking investigations and discovered that, when an alloy containing transition metal carbide that has been produced by mechanical alloying (MA) and hot isostatic pressing (HIP) is additionally subjected to a strengthening treatment for the recrystallized random grain boundaries employing grain boundary sliding by superplastic deformation in order to reinforce the recrystallized grain boundaries in the alloy, the weak grain boundaries in the recrystallized microstructure can be dramatically strengthened. As a result, there is a dramatic resolution of low-temperature embrittlement, recrystallization embrittlement, and irradiation embrittlement. In addition, although the strengthening treatment for random recrystallized grain boundaries employing grain boundary sliding by superplastic deformation can be applied to any alloy that exhibits superplastic deformation due to grain boundary sliding, the novel discovery was made that this method is effective for reducing the brittleness of tungsten, which is the most brittle material among the metals. The present invention was realized based on this new knowledge.

[0013] Specifically, an aim of the present invention is to provide a method for manufacturing alloys containing transition metal carbide having dramatically resolved low-temperature embrittlement, recrystallization embrittlement, and irradiation embrittlement. An additional aim of the present invention is to provide an alloy that is manufactured by this manufacturing method. An additional aim of the present invention is to provide a tungsten alloy containing a transition metal carbide having dramatically resolved low-temperature embrittlement, recrystallization embrittlement, and irradiation embrittlement.

{Means For Resolving The Problems}

[0014] The present invention is described below and relates to a method for manufacturing an alloy containing a transition metal carbide, a tungsten alloy containing a transition metal carbide, and an alloy that is manufactured by this manufacturing method.

(1) A method for manufacturing an alloy, characterized by having a step for mechanically alloying a metal raw material and at least one selected from carbides of group IVA, VA, or VIA transition metals, a step for sintering the raw material powder obtained in the mechanical alloying step (i.e., mechanically alloyed powder) using hot isostatic pressing (HIP), and a step for subjecting the alloy obtained in the sintering step to superplastic deformation due to

grain boundary sliding of 60% or greater at 500 to 2000°C and at a strain rate of 10^{-5} to 10^{-2} s⁻¹.

(2) The method for manufacturing an alloy according to (1), characterized by having a step in which the transition metal carbide and the metal raw material are degassed by heating prior to the mechanical alloying step.

(3) A tungsten alloy comprising 0.25 to 5 mass% of at least one type selected from carbides of a group IVA, VA, or VIA transition metals, the tungsten alloy characterized in that the oxygen content is 950 ppm by mass or less, the nitrogen content is 60 ppm by mass or less, 80% or more of the tungsten phase observed in a sectioned surface area is recrystallized to equiaxed grains with grain diameters of 0.05 to 10 μ m, the ductile-brittle transition temperature determined by three-point flexure is 500K or less, and plastic deformation is possible at or above this temperature.

(4) The tungsten alloy according to (3), characterized in that 90% or greater of the azimuths of the carbide present in the tungsten alloy structure and the azimuths of the tungsten matrix are in the (Kurdjumov-Sachs) azimuth relationship: $\{111\} W // \{110\}$ transition metal carbide $<110> W // <111>$ transition metal carbide.

(5) The tungsten alloy according to (3) or (4), characterized in that the full width at half maximum for reflection of the (220) diffraction planes is 3° or less as determined by X-ray diffraction, or that there are 50 or fewer dislocations within crystal grains as determined by transmission electron microscopy.

(6) The tungsten alloy according to any of (3) to (5), characterized in that the maximum bend strength determined by three-point flexure is 1470 MPa or greater.

(7) The alloy that is manufactured by the manufacturing method according to (1) or (2).

{Effect of the Invention}

[0015] In accordance with the present invention, transition metal carbide and alloy powder are treated by mechanical alloying (MA) method and hot isostatic pressing (HIP) method, and superplastic deformation that can maximally utilize grain boundary sliding is used in order to foster and optimize carbide grain boundary precipitation and grain boundary segregation in recrystallized micrograin structures. As a result, (1) the grain boundary strength of the alloy in the recrystallized structure is significantly improved, particularly the grain boundary strength (grain boundary bond strength) of tungsten, allowing high strength and high toughness to be manifested, (2) there is little chance for recrystallization embrittlement because the material undergoes little structural change when heated at high temperatures due to the original recrystallized state, resulting in extremely little loss of strength or ductility, (3) irradiation embrittlement can be greatly resolved, and (4) effects can be obtained such as a suitable decrease in yield strength, because the tungsten alloy crystal grain diameters grow to about 0.05 to 10 μ m when tungsten is used as the metal matrix, and a tungsten alloy thus can be produced which can undergo plastic deformation, even near room temperature.

{BRIEF DESCRIPTION OF THE DRAWINGS}

[0016]

FIG. 1 shows the relationship between strength and temperature for a normal metal and tungsten;

FIG. 2 shows the principle of superplastic deformation;

FIG. 3 schematically shows plastic working with the objective of introducing work-deformed structures with dislocations as carriers, resulting in a decrease in recrystallization temperature and anisotropy;

FIG. 4 schematically shows the GSMM step;

FIG. 5 shows the three-point bending behavior at a temperature of 400 K in Embodiment 4 (DBTT: 310 K) and Embodiment 6 (DBTT: 420 K);

FIG. 6 shows the three-point bending behavior at 300 K in Embodiment 4;

FIG. 7 shows the X-ray diffraction pattern of Embodiment 2 (GSMM treated) and Comparative Example 1 (not GSMM treated);

FIG. 8 is a photograph which shows the transmission electron micrographs of Comparative Example 1 and Embodiment 2;

FIG. 9 shows the X-ray diffraction patterns of Embodiment 5 (GSMM treated) and the as-HIP prior to the GSMM treatment in Embodiment 5;

FIG. 10 is a photograph showing the transmission electron micrograph of the tungsten alloy of Embodiment 2.

{MODE FOR CARRYING OUT THE INVENTION}

[0017] The present invention is characterized in that an alloy is manufactured by a step for degassing a raw material by heating as necessary, a step for subjecting the raw material that is obtained in the degassing step to mechanical alloying (MA; also referred to as "MA step" below), a step for sintering the raw material powder obtained in the mechanical alloying step using hot isostatic pressing (HIP; also referred to below as "HIP step"), and a step for subjecting the alloy

obtained in the sintering step to a recrystallization random grain boundary strengthening treatment carried out by superplastic deformation that can maximally utilize grain boundary sliding (also referred to below as "GSMM step," where "GSMM" is an abbreviation for grain boundary sliding-based microstructure modification). In addition, the present invention is more specifically characterized in that the alloy that has been manufactured by this method is a tungsten alloy.

The present invention shall be described in greater detail below.

[0018] The raw materials that are used in the present invention will first be described. The transition metal carbide that is used in the present invention refers to a carbide of a transition metal that is selected from group IVA, VA, or VIA. Titanium carbide, zirconium carbide, niobium carbide, tantalum carbide, and the like are particularly preferred, because these transition metal elements rapidly diffuse and react with carbon and tend to form carbides before the formation of brittle W_2C , and because the carbides that are formed are thermally stable. These transition metal carbides of group IVA, VA, and VIA (referred to below simply as "transition metal carbides") may be used individually, or multiple carbides may be used in combinations.

[0019] The added amount of transition metal carbide with respect to the alloy is preferably 0.25 to 5 mass%. If the added amount of transition metal carbide is less than 0.25 mass%, then the grain boundary strengthening effects or the migration inhibitory effects of the grain boundaries at high temperatures will be poor, and the effect of an increase in recrystallization temperature or the effect of inhibiting the production of coarse crystal grains subsequent to recrystallization will be poor. There will also be insufficient remedy in low-temperature embrittlement, recrystallization embrittlement, and neutron irradiation embrittlement, as well as insufficient increase in high-temperature strength. On the other hand, the alloy will tend to have an undesirable increase in brittleness if the added amount of transition metal carbide exceeds 5 mass%.

[0020] Examples of alloy raw materials other than the transition metal carbides include one or more selected from tungsten, molybdenum, vanadium, yttrium, chrome, niobium, tantalum, titanium, zirconium, hafnium, and the like, or stainless steel, steel, and the like. However, the manufacturing method of the present invention is particularly useful for group VIA transition metals such as tungsten. The alloy raw material powder preferably has a Fischer particle diameter of 2 μm or greater. Although described in detail in the manufacturing methods presented below, the reason is that high concentrations of oxygen or nitrogen in the alloy that has been manufactured result in 1) impeding of transition metal carbide grain boundary precipitation/segregation which is necessary for dramatically resolving low-temperature embrittlement, recrystallization embrittlement, and irradiation embrittlement, 2) promotion of the formation of W_2C , which is itself brittle and acts as an origin for fracture, and 3) formation of pores by oxygen and nitrogen which act as origins for fracture. For this reason, in order to strengthen the weak grain boundaries in recrystallized microstructures within the alloy, it is essential to reduce the oxygen and nitrogen contents of the alloy raw material powder. It is preferable to carry out the degassing step described below and to provide the raw material with the particle diameter described above. However, if atmospheric control is carried out strictly so as to suppress the admixture of impurities, then this requirement of 2 μm or greater may not be needed, and 1 μm or less may be sufficient.

[0021] The respective steps of the manufacturing method of the present invention are described below. The degassing step in which the raw material powder is heated is carried out in order to decrease the final content of oxygen and nitrogen impurities in the alloy. In the raw material powder preparation stage, this is done in order to thoroughly eliminate the air (in particular moisture) contained in the raw material powder. The degree of damage caused by the nitrogen or oxygen is different depending on the metal material, and so the degassing conditions of the degassing step may be appropriately adjusted in accordance with the metal material. With vanadium, for example, the oxygen or nitrogen will be absorbed to produce a solid solution, even when heated in an ultra-high vacuum. This results in embrittlement (environmental embrittlement), and so the degassing step is carried out at a fairly low temperature or not at all. In addition, with SUS316L, there is no need to strictly carry out the step. With tungsten, on the other hand, oxygen or nitrogen that remains in the alloy precipitates or segregates at the weak recrystallized grain boundaries as described above, promoting grain boundary embrittlement (recrystallization embrittlement). Along therewith, pores are formed which act as origins of fracture. Thus, for example, when commercial tungsten powder is used as a raw material, the raw material powder is preferably placed in a container at the time of preparation of the raw material powder (a boat made of Mo or the like that is used as a powder carrier), and the raw material powder is subjected to a degassing treatment at 800 to 1500°C by evacuation to 10^{-4} Pa or less. However, the degassing step can be omitted, for example, by using an ultra-high purity W powder manufactured by PLANSEE Japan Ltd. or other tungsten raw material that already has sufficiently low oxygen and nitrogen concentrations, the raw material is sealed in an inert gas or reducing gas atmosphere (gas that has been purified to a level at which there is negligible water content or the like that contains the impurities) and an MA step or the like is carried out, thereby removing the admixed oxygen and nitrogen.

[0022] Degassing is preferably carried out using a degassing time of 120 min at 800°C or greater, or a degassing time of 90 min or greater at 950°C or greater, as a guideline. If the degassing temperature is less than 800°C, then desorption of gas will be insufficient, whereas reactions with the degassing container (boat made of Mo or the like) will tend to occur if the temperature exceeds 1500°C, resulting in initiation of aggregation of the raw material powder and additional undesirable effects in subsequent steps.

[0023] With tungsten alloy, the oxygen content in the manufactured alloy is 950 ppm or less, preferably 850 ppm or less, more preferably 300 ppm or less, and the nitrogen content is 60 ppm or less, preferably 50 ppm or less. If the oxygen and nitrogen contents of the alloy are below these values, then the production of a dense alloy will be possible. The oxygen or nitrogen content of the tungsten alloy at the raw material powder stage is about three times that of the final alloy that has been manufactured. Consequently, in regard to process management, it is preferable for process management to be carried out so that oxygen is contained at about 3000 ppm or less and nitrogen is contained at about 180 ppm or less in the raw material powder upon completion of the degassing step.

[0024] An MA step is carried out after the degassing step. With this MA step, operations extending from ball-milling of the raw material powder through sealing of the ball-milled powder in a capsule to produce a HIPed compact are preferably carried out in an inert gas or reducing gas atmosphere in order to prevent the admixture of oxygen or nitrogen. Ar, helium, neon, and the like are examples of inert gases, and hydrogen and the like are examples of reducing gasses.

[0025] The MA step is a step in which high mechanical energy is imparted to the raw material alloy powder and the transition metal carbide, thereby decomposing the transition metal carbide and bringing about solid dissolution thereof in a uniform solid solution in the matrix phase alloy structure. Simultaneously, the ultrafine powder of the mother phase (alloy) is produced. This step is carried out, for example, using a device such as a triaxial vibrating ball mill, a planetary ball mill, or an attriter. The MA treatment normally involves introducing balls and raw material powder and/or pre-alloy powder into a pot (container) and rotating or vibrating this pot on a ball mill support stand, thereby imparting high mechanical energy to the raw material powder and/or pre-alloy powder. As a result, the different element species that have been added can be forcibly solid-dissolved, even in systems in which solid dissolution will not occur under the equilibrium conditions. In addition, extremely fine crystal grains (10 to 30 nm) can be produced at around room temperature. In order to remove impurities from the ball surfaces and the inner walls of the pot which are used in the MA step, the pot and balls alone may be heated under vacuum for 3 to 10 h at 150 to 200°C prior to introducing the raw material powder into the pot.

[0026] The specific treatment conditions for the MA step, such as the treatment time, the rotation rate, the ball material and diameter, the ratio of the total ball mass to total raw material powder mass, and the ratio of total internal container volume to total ball volume, may be determined appropriately so that the transition metal carbide is uniformly mixed, decomposed and solid-dissolved in the alloy, so that ultrafine matrix phase metal crystals are produced, and so that effects of admixture of container and ball material into the raw material powder during the MA step is inhibited (suppression of admixed amounts to negligible levels, or use of materials that will not affect subsequent material characteristics, even if they become admixed).

[0027] The HIP step involves isostatic pressing of the MA powder produced in the MA step using Ar gas and carrying out sintering at a comparatively low temperature at which grain growth of the ultrafine alloy powder produced in the MA step does not easily occur, while preventing exposure to atmosphere constituted by gas impurities that are harmful to the alloy. As a result, the transition metal carbide that is forcibly solid-dissolved during the MA step segregates and precipitates, thereby preventing grain growth of the ultrafine particles due to a pinning effect, while also producing equiaxed ultrafine grains of alloy matrix phase in which transition metal carbide has segregated/precipitated at the grain boundaries without strain resulting from recrystallization. Specifically, the MA powder is sealed in the inert gas or reducing gas atmosphere described above in a metal container made of soft (mild) steel, SUS, Ti, Nb, Ta, or the like. After removing the sealed gas by producing a high vacuum (typical evacuation level of 10^{-4} to 10^{-6} Pa), the material is sintered for 1 to 5 h at 1350 to 1400°C and 100 to 1000 MPa, thereby producing an alloy having the structure described above. In order to remove impurities and the like on the inner walls of the metal container that is used in the HIP step, the metal container alone may be heated under vacuum for 1 to 3 h at 500 to 1000°C prior to introduction of the MA powder into the metal container.

[0028] The GSMM step is a step in which the weak grain boundaries in the recrystallized microstructure are replaced with strong transition metal carbide heterophase interfaces or strong grain boundaries in which the constitutive elements of the transition metal carbide have precipitated or segregated. Consequently, when the transition metal carbide precipitates or segregates at the grain boundaries, the grain boundary bond strength is increased, having the beneficial effect of increasing the fracture strength and remedying embrittlement. In addition, the GSMM step has the effect of increasing the crystal grain diameter to an appropriate size, decreasing yield strength (flow strength), and manifesting ductility(decreasing (relaxing) the grain boundary load); removing residual gas pores that tend to act as origins for fracture (1 to 3% remaining after HIP), as well as strengthening the interfaces (boundary interfaces) with different precipitates in dispersion strengthened alloys containing precipitates (e.g., vanadium or stainless steel). In the present invention, the effect of grain boundary sliding at high temperatures is used in order to promote and optimize grain boundary precipitation and segregation of the transition metal carbide. FIG. 2 is a diagram showing the principle of superplastic deformation by grain boundary sliding. Grain boundary sliding refers to crystal grain displacement/movement in a state in which the equiaxed condition is maintained, as indicated in FIG. 2 (2) → (3) → (4) when shear stress τ is applied to the crystal structure in FIG 2 (1). As a result of an extremely large number of repetitions of this type of grain boundary sliding, the transition metal carbide precipitates or segregates at the grain boundaries, having the effect of increasing

the fracture strength at the weak recrystallized grain boundaries until it surpasses the yield strength (flow strength), allowing apparent alloy deformation.

[0029] However, grain boundary sliding is non-uniform deformation that conversely promotes embrittlement along with grain boundary displacement due to crack formation at grain boundary triple points (an example being high-temperature embrittlement typically seen with copper alloys and the like). It is thus extremely important, in the present invention, for the deformation amount at break to be extremely large, and to employ superplastic deformation which can maximally utilize grain boundary sliding. As stated above, grain boundary sliding is non-uniform deformation that typically promotes embrittlement due to crack formation at grain boundary triple points in conjunction with grain boundary displacement. However, by carrying out superplastic deformation of the present invention using constant conditions described below for temperature and strain rate (a quantity obtained by dividing the speed at which a sample piece is deformed by the size of the sample piece to convert to strain), a relaxation (accommodation) mechanism operating with grain boundary sliding prevents the formation of cracks, and elongation of several hundreds of percent is produced. In order to promote and optimize transition metal carbide grain boundary precipitation and segregation, it is more effective to carry out GSMM for a longer period of time than for a shorter period of time.

[0030] As stated above, superplastic deformation is a deformation mode in which elongation of several hundreds of percent occurs due to grain boundary sliding, and equiaxed crystal grains are essentially maintained even after deformation. Thus, it is possible to "promote and optimize transition metal carbide grain boundary precipitation and segregation though relative motion or rotation of crystal grains by active grain boundary sliding over a long period of time, and to maintain an isotropic recrystallized structure with little anisotropy." This "recrystallized random grain boundary strengthening treatment carried out by superplastic deformation that can maximally utilize grain boundary sliding" is designated, in the present invention, by GSMM (grain boundary sliding-based microstructural modification).

[0031] FIG. 3 is a diagram that schematically shows the concept of "plastic working performed to introduce work-deformed structures using dislocations as a carrier, resulting in anisotropy and a decrease in recrystallization temperature," which has been widely used for increasing toughness in metals including tungsten. The term "dislocation" refers to linear lattice defects, and a characteristics of plastic working include (1) that specific crystallographic planes can perform sliding motion under small stress in specific crystallographic directions, (2) that dislocations can multiply anew through the slip process, (3) that extremely strong interactions occur with areas having an elastic strain field (e.g., the dislocations are entirely enclosed by an elastic strain field due to elastic strain that arises at around the periphery of different atomic species with different sizes). For this reason, when deformation progresses as a result of tensile stress applied to a material as shown in FIG. 3(1), 3(2), slip arises in the material as shown in FIG. 3(3), dislocations in the material multiply (specifically, the dislocation density increases), and, as a result, the stress required for the dislocations to undergo additional slipping, in other words, the stress required for plastic deformation of the alloy, increases, and reaches the fracture strength, resulting in break as shown in Fig. 3(4). "Structures in which the dislocation density has increased due to plastic deformation" are referred to as work-deformed structures or worked structures, but the increase in dislocation density amounts to an increase in the internal strain field of the material (crystal) and produces a condition of high internal energy. Thus, materials having this high internal energy tend to release this internal energy, and so when heat is applied (the temperature is increased), the internal energy is released with just a slight amount of energy (slight increase in temperature); one process for this release being recrystallization. In most cases, the upper limit of elongation by "plastic working performed to introduce deformation-processed structures using dislocations as a carrier and to produce anisotropy and a decrease in the recrystallization temperature" is approximately several tens of percentage points, and is considerably less than 100%, particularly with elongation.

[0032] On the other hand, with superplastic deformation occurring by grain boundary sliding, recrystallized structure having little strain is maintained even after deformation, and the internal energy is not substantially increased. Thus, with the GSMM treatment of the present invention, although the crystal grains grow (increase by roughly a factor of ten) because the treatment is carried out at a temperature that is higher than the HIP temperature, grain growth leads to decrease in the total area of crystal grain boundaries and hence internal energy because crystal grain boundaries are a high energy region.

[0033] As stated above, GSMM in the present invention is a new structure control technique whereby increased durability is manifested by strengthening the weak recrystallized grain boundaries which are a cause of grain boundary embrittlement. The plastic work referred to above is substantially different in principle, and the post-treatment alloy fracture strength and elongation at break are also completely different.

[0034] The GSMM step, as shown in FIG. 4 involves sandwiching the alloy that is produced in the HIP step between heat resistant, high strength ceramics or ceramics composite plates (typically BN-SiC composite material plates) and applying a pressure at a strain rate of 10^{-5} s^{-1} to 10^{-2} s^{-1} at a high temperature of 500 to 2000°C (40 to 50% or more higher than the melting points of the respective alloys measured in absolute temperature) to carry out plastic deformation due to grain boundary sliding at 60% or greater. The temperature is preferably suitably adjusted in accordance with the melting points of the respective alloys, as stated above. For example, 1200 to 2000°C is preferred for tungsten and molybdenum, but 1400 to 2000°C is additionally preferred for tungsten. In addition, a temperature of 800 to 1500°C is

preferred for vanadium and SUS316. With tungsten, there are cases where the alloy will break during compression deformation if the temperature is less than 1400°C, whereas exceeding 2000°C is undesirable because the equipment used for industrial manufacture will increase in size. In addition, if the strain rate is slower than 10^{-5} s^{-1} , effects will be obtained, but an excessively long processing time will be required, which is industrially disadvantageous. It is undesirable for the strain rate to be greater than 10^{-2} s^{-1} due to the danger of alloy fracture. Carrying out plastic deformation of 60% or greater means that the elongation (deformation) of the test piece due to plastic deformation is 60% or greater. Elongation is expressed as the elongation length of a test piece (ΔL) divided by the initial length (L), multiplied by 100 in order to obtain a percentage. The material may instead be subjected to tensile deformation, shear deformation, or the like may be used, provided that the aforementioned temperature, strain rate, and plastic deformation can be provided.

[0035] The transition metal carbide is necessary in order for the crystal grains of the alloy matrix phase to be maintained in fine grain sizes and in order to manifest superplastic deformation. In addition, the heterophase interface between the transition metal carbide and the alloy mother phase (matrix) satisfies the Kurdjumov-Sachs azimuth (orientation) relationship, and thus high-strength hetero-phase interfaces are formed. When tungsten is used as the alloy raw material, 90% or greater of the azimuths of the transition metal carbide present in the tungsten alloy structure and the azimuths of the tungsten matrix are in the (Kurdjumov-Sachs) azimuth relationship: $\{111\} \text{ W} // \{110\} \text{ transition metal carbide} <110> \text{ W} // <111> \text{ transition metal carbide}$. If 10% or more of the transition metal carbide particles do not satisfy the Kurdjumov-Sachs azimuth relationship, then it will not be possible to obtain sufficient maximum flexural strength at room temperature (approximately 1470 MPa).

[0036] In addition, with the alloy that has been manufactured by the manufacturing method of the present invention, growth occurs until the crystal particle diameter of the tungsten alloy is about 0.05 to 10 μm . As a result, an effect is produced whereby the yield strength is decreased to an optimal level, and a tungsten alloy can be produced that can undergo plastic deformation near room temperature. For tungsten alloys, when the alloy is manufactured by the manufacturing method of the present invention, the three-point bending ductile-brittle transition temperature (nil ductility temperature; DBTT) can be decreased to about 500K, and thus plastic deformation is possible at or above the ductile-brittle transition temperature.

[0037] The crystal grain diameter can be determined as the average grain diameter by using commercial image processing software (e.g., Image Pro) to carry out image processing on photographs that are typically taken by a transmission electron microscope from the center part of a sample cross section. The average grain diameter can be determined only for the tungsten matrix phase. Because averaged data could be obtained by counting the tungsten crystal grains over a surface area ratio of 80% or greater, statistical determinations were carried out.

[0038] For less than 20% of the surface area, counting the tungsten crystal grains was difficult (the grains were fine and too numerous, and it was difficult to determine where the crystal grain boundaries were, because it was difficult to see the borders of the crystal grains constituting the crystal grain boundaries). However, if the average grain diameter for tungsten is calculated over a region constituting 80% or more of the surface area, then the characteristics of the various materials can be elucidated. The crystal grain diameter can be calculated as a stable average grain diameter by counting 300 or more tungsten crystal grains and calculating the surface area. As necessary, the crystal grain diameter can be measured over a broad region of 80% or more of the total field of numerous photographs taken with a transmission electron microscope. As a result, 80% or more of the crystal grains that can be measured should be in the grain diameter range of 0.05 to 10 μm .

[0039] If the average grain diameter is less than 0.05 μm , plastic deformation will be extremely difficult, because the yield strength will become extremely high, resulting in decreased work and manufacture yields, which is industrially disadvantageous. On the other hand, if the average grain diameter exceeds 10 μm , superplastic deformation will not readily occur. In order to allow plastic deformation in the vicinity of room temperature, it is necessary to carry out suitable adjustments so that a suitable work ratio is produced during plastic deformation (in other words, during GSMM treatment) that is carried out in order to increase toughness. The temperature during the GSMM treatment may be decreased in order to produce a smaller average grain diameter, or the temperature during GSMM treatment may be increased in order to produce a larger average grain diameter.

[0040] One point that should be noted in regard to the description of the present invention is that superior characteristics (e.g., fracture strength and ductility) can be obtained in a structure in which thorough (full) recrystallization has occurred, because equiaxed crystal grains that are not anisotropic are produced in the metal structure. The term "equiaxed crystal grains" in the present invention means that the aspect ratio (ratio of the longitudinal and transverse crystal grain lengths) is 2 or less regardless of the cross-section when the metal structure is viewed two-dimensionally.

Embodiments

[0041] With the methods for manufacturing the alloys and the manufactured alloys of the embodiments described below, as shown in FIG. 4, simple compressive deformation was carried out along one axis, but deformation is not restricted to simple compression, provided that superplastic deformation allowing maximal utilization of grain boundary

sliding can be realized. Depending on the shape of the alloy product that is desired, for example, reduction by rolling can be employed for sheet-form materials, for example.

[0042] Characterization of transition metal carbide amount required for manifesting superplasticity

Experiment 1

[0043] TiC powder with an average particle diameter of 0.7 μm (manufactured by Soekawa Chemical Co., Ltd.) was added to tungsten powder with an average particle diameter of 4 μm (Manufactured by A.L.M.T. Corp.) using the Fischer method. The material was introduced into a molybdenum boat in a hydrogen atmosphere and was then subjected to a degassing treatment by heating for 1.5 h at 950°C under high vacuum ($< 1 \times 10^{-4}$ Pa). Next, the material was subjected to a mechanical alloying (MA) treatment by mixing for 70 h at a vibration frequency of 360 cycles/min (6Hz) in a TZM (titanium, zirconium-containing molybdenum alloy) container (pot) using a tri-axial vibrating ball mill (TKMAC 1200, manufactured by Topology Systems). In order to characterize the appropriate TiC powder addition range, eight MA treatment sample runs were carried out with TiC powder contents of 0 to 6.0 mass%.

[0044] Next, the MA-treated powder was introduced into a molybdenum boat and was heated for 1.5 h at 950°C under high vacuum in order to degas the hydrogen that had admixed in the TiC powder and the tungsten during the MA treatment. This degassed powder was then sealed in an HIP capsule (mild steel), and the container (capsule) was vacuum-sealed before carrying out a HIP treatment for 3 h at 1350°C and 196 MPa in argon gas to obtain a sintered body. The resulting sintered body is referred to as "as-HIPed compact".

[0045] Pieces having dimensions of 0.4 mm $\times$ 4 mm $\times$ 16 mm were then wire-cut from the as-HIPed compact (parallel part length 5 mm; I-shaped flat sheet-form tensile test piece similar to the test piece shown in Fig. 1 of T. Kuwabara, H. Kurishita, M. Hasegawa, Development of an Ultra-Fine Grained V - 1.7 mass% Y alloy Dispersed with Yttrium Compounds Having Superior Ductility and High Strength, Mater. Sci. Eng. A 417 (2006) 16-23). The entire surface was mechanically polished with waterproof paper (to #1500), the four edges were then chamfered, and the piece was mounted on a tensile test fixture and subjected to high-temperature tensile testing. The tensile fixture was a test-piece shoulder-bearing" (R part) type whereby alignment is ensured by a system in which the compressive load on the fixture is converted to tensile load on the test piece, allowing one-touch mounting of the test piece on the fixture. Heating of the test piece was carried out by high-frequency induction heating using a graphite susceptor. The surface temperature of the test piece was continually observed and recorded using a two-color radiation thermometer (Chino, model 1R-AQ). The tensile test was carried out using an Instron model R1362 Electrically Actuated Tester at temperatures of 1500°C, 1600°C, and 1700°C, an initial strain rate of 5×10^{-4} /s (cross-head speed: 0.0025 mm/s), and an evacuation level of 5×10^{-4} Pa. Load and elongation (%) were measured during the tensile test. The oxygen and nitrogen concentrations in the sample were measured by infrared absorption on a LECO-TC600 device using a thermal conductivity method. With all of the samples, the oxygen concentration was 850 ppm or less, and the nitrogen concentration was 50 ppm or less. The results are shown in Table 1. In the table, >160 denotes that no break occurred, even at a deformation of 160%.

[Table 1]

Sample No.	TiC content Mass%	1500°C Elongation (%)	1600°C Elongation (%)	1700°C Elongation (%)
1	0	2	5	5
2	0.15	3	10	30
3	0.25	70	105	>160
4	0.5	>160	>160	>160
5	1.1	>160	>160	>160
6	1.5	>160	>160	>160
7	5	>70	>100	>160
8	6	10	30	60

Experiment 2

[0046] The same test as in Experiment 1 was carried out, with the exception that the hydrogen in Experiment 1 was changed to argon, and nine samples were used in which the TiC content was varied. The results are shown in Table 2

[Table 2]

Sample No.	TiC content Mass%	1500°C Elongation (%)	1600°C Elongation (%)	1700°C Elongation (%)
9	0	2	5	5
10	0.25	3	7	7
11	0.5	30	40	60
12	0.7	50	70	>160
13	0.8	70	110	>160
14	1.1	120	>160	>160
15	1.5	70	>160	>160
16	5	50	70	>160
17	6	10	30	60

[0047] Experiment 1 and Experiment 2 above show that the TiC amount required for manifestation of superplasticity at 1600 to 1700°C (elongation at break: 100% or greater) is 0.25 to 5 mass% with the as-HIPed compacts produced from powder that was MA-treated in hydrogen atmosphere, and 0.7 to 5 mass% with those produced using an argon atmosphere. If the TiC amount is below these ranges, then weak grain boundaries occur in great numbers among the grain boundaries of the tungsten phase, and there are few grains of a second phase that inhibit grain boundary movement. For this reason, grain growth is rapid in the tungsten phase, resulting in the production of large-size crystal grains. The TiC phase is essential for rotation and movement of crystal grains during grain boundary sliding and for maintaining fine equiaxed crystal grains that are required for superplastic deformation. For this reason, if the amount of TiC phase is small, then when grain boundary sliding non-uniform deformation arises in high-temperature tensile testing, grain boundary cracks will form and grow, and the elongation at break will be low.

[0048] Conversely, if the amount of TiC exceeds these ranges, then the contact frequency between TiC phases will increase, and the proportion of TiC/TiC interfaces will increase. In comparison to the tungsten matrix phase, the TiC phase has low plastic deformation capability, and it is thought that TiC/TiC interfaces also do not readily slide. Consequently, overloading of the harmony of the tungsten phase occurs in relation to continuous grain boundary sliding of the tungsten grains, and grain boundary (interfacial) cracking arises, thereby also decreasing the elongation at break.

Experiment 3

[0049] An experiment was carried out in the same manner as in Experiment 1, with the exception that the material was changed to titanium carbide of Experiment 1, and zirconium carbide, niobium carbide, tungsten carbide, or mixtures thereof were added while varying the content thereof. In addition, high-temperature tensile testing was carried out only at 1600°C. The results are shown in Table 3.

[Table 3]

Carbide content in tungsten	1600°C Elongation (%)
ZrC 0.3 mass%	120
ZrC 4.7 mass%	>160
NbC 0.32 mass%	130
NbC 4.5 mass%	>160
TaC 0.28 mass%	130
TaC 3.3 mass%	>160
TaC 5.0 mass%	>160
ZrC 0.3 mass% + TaC 2 mass%	>160
NbC 0.3 mass% + TiC 2 mass%	>160
TiC 1 mass% + TaC 2 mass%	>160

(continued)

Carbide content in tungsten	1600°C Elongation (%)
TaC 0.1 mass%	2
TiC 0.08 mass% + TaC 0.03 mass%	5
ZrC 6 mass%	Could not be performed

[0050] As is clear from Table 3, even when transition metal carbides other than TiC were added to the alloy at about 0.25 to 5 mass%, it was clear that there was an improvement in ductile characteristics.

Embodiment 1

[0051] An as-HIPed compact material was produced in the same manner as with sample no. 5 of Experiment 1, with the exception that the degassing conditions involved heating for 1.5 h at 1050°C under high vacuum (1×10^{-4} Pa). Next, the as-HIPed material that had been produced was wire-cut to produce a sintered body with a diameter of about 9 to 10 mm and a height of about 20 mm. In order to strengthen the weak random grain boundaries by superplastic deformation that can maximally utilize grain boundary sliding, a disk shape material was produced by compression deformation to a thickness of about 3.5 mm (diameter of about 21 to 23 mm) at a temperature of 1650°C and a strain rate of 0.5 to $2 \times 10^{-4} \text{ s}^{-1}$ (superplastic behavior tends to more readily occur with slower strain rates, and so a rate was selected at which experiments were most easily carried out, while considering response (increase in flow stress) exhibited by the material as a result of incremental increases in strain rates). Heating of the sintered body was carried out by high-frequency induction heating under evacuation using a graphite susceptor. An Instron model R1362 Electrically Actuated Tester was used for high-temperature compressive deformation. A piece with dimensions of $1 \text{ mm} \times 1 \text{ mm} \times 20 \text{ mm}$ was cut perpendicularly in the compressive direction from this disk shape material, and the surfaces and edges were polished with water-proof emery paper out to #1500, thereby producing a bending test piece. The oxygen concentration was 40 ppm and the nitrogen concentration was 30 ppm in the test piece, as measured by infrared absorption on a LECO-TC600 device using a thermal conductivity method. Next, the test piece was subjected to three-point bend testing at a temperature range of room temperature to 600°C with a cross-head speed of 0.001 mm/s in an atmosphere produced by a flow of high-purity Ar containing 4% H_2 . The three-point bend test was carried out using a Servopulser EHF-2 model fatigue testing machine, manufactured by Shimadzu Corporation (load capacity of 5 ton), connecting a span $\pm 2.5 \text{ mm}$ LVDT (Linear Variable Differential Transformer) to the actuator head and attaching a shear-type load sensor with a load capacity of 5 kN directly below a load cell with a capacity of 5 ton. Control of testing was carried out using a static test application program. An infrared heating furnace (ULVAC-RIKO, Inc.) was used for heating the test pieces, and measurement of the test piece temperature and atmosphere (at a location separated by a few millimeters from the test piece) was carried out in advance on a dummy test piece having a spot-welded thermocouple. In actual testing, the temperature of the atmosphere was controlled and measured. Flexural strength was measured at room temperature, and the minimum value of the measured averages of five bending test pieces was taken as the minimum flexural strength, whereas the maximum value was taken as the maximum flexural strength. The DBTT was determined by recording the variation of measurements on the plastic strain at respective temperatures while increasing the testing temperature by roughly 50 increments starting from room temperature. The temperature found by extrapolating to a plastic strain of zero using a linear approximation was taken as the DBTT. In determining a single DBTT, it is necessary to measure the plastic strain while varying the testing temperature, and measurements were carried out by preparing three to five bar shape test pieces having the same impurity concentrations and structures.

Embodiments 2 to 7

[0052] The degassing conditions involved heating for 1.5 h at 950°C in Embodiment 2, heating for 1 h at 950°C in Embodiment 3, heating for 1 h at 900°C in Embodiment 4, heating for 1.5 h at 850°C in Embodiment 5, heating for 1 h at 850°C in Embodiment 6, and heating for 1 h at 800°C in Embodiment 7. With the exception that the oxygen amount and nitrogen amount in the tungsten alloy were changed, test pieces were produced out using the same procedure as in Embodiment 1. The oxygen amount, nitrogen amount, minimum flexural strength and maximum flexural strength at room temperature, and DBTT were measured.

Comparative Example 1

[0053] Test pieces were prepared from as-HIPed compacts without carrying out a compressive deformation treatment

for GSMM, and measurements were performed using the same procedure as in Embodiment 2.

Comparative Example 2

[0054] With the exception that the TiC content was changed to 1.1 mass% and the degassing treatment was not carried out, test pieces were prepared by the same procedure as in Embodiment 1, and measurements were performed.

[0055] The results of measurements in Embodiments 1 to 7 and Comparative Examples 1 and 2 are shown in Table 4.

[Table 4]

		Oxygen amount (ppm)	Nitrogen amount (ppm)	TiC (%)	Minimum flexure strength (MPa)	Maximum flexure strength (MPa)	DBTT (K)
Embodiments	1	40	30	1.1	2800	3200	210
	2	160	30	1.1	2700	2800	230
	3	230	40	1.1	2690	2940	240
	4	610	40	1.1	1840	2380	310
	5	850	50	1.1	1450	1620	330
	6	870	140	1.1	1240	1500	420
	7	950	60	1.1	1340	1470	500
Comparative examples	1	160	30	1.1	1610	2160	850*
	2	2120	180	1.1	1000	1260	≥ 630

[0056] As is clear from Table 4, the tungsten alloy flexural strength increased as the concentrations of oxygen and nitrogen decreased when the material was subjected to a GSMM treatment. In addition, it was clear that the DBTT decreased dramatically when the as-HIPed material was subjected to the GSMM treatment, and ductility was obtained even at low temperatures.

Three-point bending testing

[0057] FIG. 5 shows the three-point bending behavior at a temperature of 400K for Experiment 4 (DBTT: 310 K) and Experiment 6 (DBTT: 420K). FIG. 6 shows the three-point bending behavior for Experiment 4 at 300K. As is clear from FIGS. 5 and 6, break (fracture) occurred without manifestation of ductility at lower temperatures than the DBTT temperatures of the resulting alloys, and thus it was clear that the amounts of oxygen and nitrogen must be decreased in addition to carrying out the GSMM treatment (by compression).

X-ray diffraction pattern measurement

[0058] FIG. 7 compares the X-ray diffraction patterns for Experiment 2 (GSMM treatment performed) and Comparative Example 1 (GSMM treatment not performed). From a comparison of the two, a large difference in intensity was seen with the TiC peak, indicating that TiC precipitation progressed during the GSMM treatment. This was confirmed by transmission electron microscopy.

Transmission Electron Micrographs

[0059] FIG. 8(1) is a transmission electron micrograph of Comparative Example 1, and FIG. 8(2) is a transmission electron micrograph of Embodiment 2. FIG. 8(3) is an enlarged view of the portion indicated by "←" in FIG. 8(2). As is clear from the micrographs, the tungsten alloy that had been subjected to the GSMM treatment was confirmed to have experienced TiC grain boundary precipitation in the alloy. It was simultaneously confirmed that the TiC constituent elements had undergone solid dissolution and segregated at the grain boundaries.

X-ray Diffraction Analyses

[0060] FIG. 9 compares the X-ray diffraction patterns of Embodiment 5 (GSMM treated) and the as-HIPed material

prior to GSMM treatment in Embodiment 5. It is clear that TiC precipitation similarly progressed as a result of GSMM treatment, but that the ductility-impeding (i.e., easily fractured) carbide W_2C , had formed, in contrast to FIG. 7. It is thought that this material is produced as a result of an increase in oxygen level, which provides oxygen distribution between the TiC and tungsten and results in a reaction between some of the carbon that has dissociated from the TiC with the surrounding tungsten.

Confirmation of equiaxed recrystallized grains

[0061] With the tungsten alloy of Embodiment 2, a thin film having a small perforation was formed at the center by electrolytic polishing (TenuPol) at a thickness of about 50 μm and a diameter of 3 mm, whereupon the material was observed with a transmission electron microscope (JEOL 2000) at an acceleration voltage of 200 kV. FIG. 10(1) shows the observation direction of the transmission electron microscope, and FIG. 10(2) shows a micrograph of the sample as observed from above (specifically, from a direction parallel to the compression direction). FIG. 10(3) is a micrograph of the sample as observed from the side (from a direction perpendicular to the compression direction). In all cases, clear images were obtained with an observational magnification of roughly 10,000 $\times$. As is clear from FIG. 10, the crystal grains were equiaxed grains, with crystal grain aspect ratios in the range of 1 to 2.

[0062] In addition, upon observing the thin film under diffraction conditions and at additionally high resolution, almost no dislocations were observed in the crystal grains, and the number of dislocations with the observed crystal grains was extremely low, at about 1 to 3, in many cases. From the results of observations described above, it is clear that the structure of the articles of the present invention is a recrystallized structure. Dislocations are present at 1000 or greater in the crystal grains of tungsten that has not been recrystallized, including work-deformed structure. In contrast, it was found that there are 50 or less dislocations in the crystal grains of recrystallized tungsten. It became clear that, if this condition is satisfied, then the characteristics of unstrained tungsten crystal grains are exhibited.

[0063] In addition, an unstrained condition was confirmed based on XRD measurements using a Rigaku RAD II-B device. From the results of XRD measurements, although the effect of fine crystal grains was obtained, the diffraction width of the diffraction peaks increased with increasing strain in the non-recrystallized state. For example, by investigating XRD results obtained by measurements on stress-relieved commercial tungsten material and tungsten alloy of Embodiment 2 under conditions of 40 kV and 30 mA using a Cu target and a 1° slit, it was clear that if the full width at half maximum exceeds 3° in (220) diffraction of tungsten with a lattice constant of 0.11188 nm, strain remains and the material does not have a recrystallized structure (commercially available pure tungsten subjected to stress relief treatment), whereas the material has a recrystallized structure without strain if the full width at half maximum is 3° or less.

Confirmation of grain diameter

[0064] The tungsten alloys produced in Embodiments 1 to 7 were used, thin films having a small perforation was formed at the center by electrolytic polishing (TenuPol) at a thickness of about 50 μm and a diameter of 3 mm, whereupon the materials were observed with a transmission electron microscope (JEOL 2000) at an acceleration voltage of 200 kV. In the transmission electron micrographs of all of the embodiments, the crystal grain diameters could be measured for 80% or more of the entire field of the micrographs, and it was confirmed that 80% or more of the crystal grains that were measured were in the grain diameter range of 0.05 to 10 μm .

Confirmation of carbide orientation and tungsten matrix orientation in tungsten alloy structure

[0065] In contrast that the case described in "Confirmation of grain diameter" above, bright-field images, dark-field images, and selected area diffraction patterns at magnifications of several hundred thousand were taken in numerous fields including a single carbide grain within a tungsten matrix phase. The orientation relationship between the carbide and the tungsten matrix phase were thus analyzed. As a result, in the transmission electron micrographs from all of the embodiments, it was confirmed that the carbide present in the tungsten alloy structure and the tungsten matrix satisfied the Kurdjumov-Sachs orientation relationship: $\{111\}W // \{110\}$ transition metal carbide $<110>W // <111>$ transition metal carbide.

Embodiment 8

[0066] After weighing and blending raw material powders at a vanadium:yttrium:tungsten:TiC mass ratio of 89.8:1.4:8.0:0.8, the material was placed in a Mo boat, and a degassing treatment was carried out for 1 h at 200°C. Next, a container and balls used for MA treatment (material: TZM (Mo-0.5 Ti-0.1 Zr)) was baked for 10 h at 150 to 200°C under high vacuum, whereupon the blended raw material powder was introduced into the container along with the balls, and an MA treatment was carried out using a tri-axial vibrating ball mill for 70 h in a purified hydrogen atmosphere. In

order to eliminate the hydrogen that had been admixed from the atmosphere during MA, a dehydrogenation treatment was carried out for 1 h at 600°C under a vacuum of 1×10^{-4} Pa or less. Subsequently, the MA-treated vanadium alloy powder was sealed in a hydrogen atmosphere in an HIP capsule (soft (mild) steel) that had been degassed by heating under vacuum at 900°C, and, while degassing under vacuum at room temperature, the HIP capsule was vacuum-sealed under a high vacuum (2×10^{-5} Pa). Consequently, the HIP capsule interior was in a highly evacuated tightly-sealed condition. This material was then subjected to an HIP treatment for 3 h at 196 MPa and 1000°C in argon gas to produce a sintered body with a relative density of 99.5% or more. Tensile test pieces were then cut out from the sintered body in the same manner as in Embodiment 1, and superplastic deformation allowing maximal utilization of grain boundary sliding was employed. In order to strengthen weak portions, such as interface boundaries between precipitates and vanadium matrix phase that generally work as crack initiation sites, a GSMM treatment was carried out at a temperature of 1300°C and a strain rate of 0.5 to 2×10^{-4} s⁻¹. The resulting test piece was subjected to tensile testing under conditions of room temperature and an initial strain rate of 1×10^{-3} /s using a Servopulser EHF-2 model device manufactured by Shimadzu Corporation. The yield strength (= 0.2% proof strength), tensile strength, uniform elongation and elongation at break (total elongation) were measured.

Comparative Example 3

[0067] Production of test pieces and measurements were carried out using the same procedure as in Embodiment 8, with the exception at a GSMM treatment was not carried out.

Embodiment 9

[0068] SUS316L (316L stainless steel alloy powder supplied by Höganäs AB) and TiC were used at a SUS316L:TiC mass ratio of 98:2 as alloy raw material powder. A degassing treatment was carried out for 1.5 h at 450°C. After an MA treatment, a dehydrogenation treatment was carried out for 1.5 h at 450°C. The heating temperature while sealed under vacuum in the HIP capsule was 750°C, and a HIP treatment was carried out for 3 h at 850 to 900°C. In addition, a GSM treatment was carried out at 950°C. With these exceptions test pieces were produced and measurements were carried out in the same manner as in Embodiment 8.

Comparative Example 4

[0069] Production of test pieces and measurements were carried out using the same procedure as in Embodiment 9, with the exception that a GSMM treatment was not used.

[0070] The results of measurement in Embodiments 8 to 9 and in Comparative Examples 3 and 4 are shown in Table 5.

[Table 5]

		0.2% Proof strength (GPa)	Tensile strength (GPa)	Uniform elongation (%)	Elongation at break (%)
Embodiment	8	0.66	0.7	14	20
	9	0.84	1.13	20	23
Comparative Example	3	0.71	0.72	5	9
	4	0.68	0.95	10	10

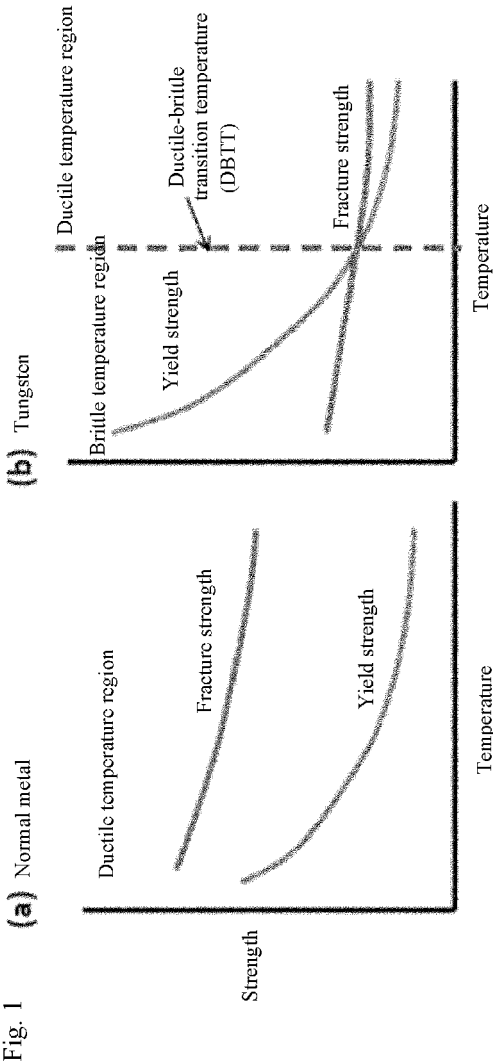
[0071] As is clear from Table 5, with vanadium alloys and stainless steel alloys that were subjected to the GSMM treatment, uniform elongation and elongation at break were at least doubled, and it was clear that the GSMM treatment can improve the ductility characteristics of various types of metals or alloys, including tungsten.

{INDUSTRIAL APPLICABILITY}

[0072] Because low-temperature embrittlement, recrystallization embrittlement, and irradiation embrittlement of alloys, particularly tungsten, can be dramatically remedied by subjecting the alloy to a GSMM treatment, new avenues for the utilization of alloys, particularly tungsten, are expected in regard to use in extreme environments involving exposure to severe thermal loads, such as with high-temperature structural materials, molybdenum substitute materials, plasma-facing materials for international thermonuclear experimental reactor (ITER), high-temperature test fixtures, and solid rotating targets for spallation neutron sources.

Claims

1. A method for manufacturing an alloy, **characterized by** having a step for mechanical alloying of a metal raw material and at least one selected from carbides of group IVA, VA, or VIA transition metals, a step for sintering the raw material powder obtained in said mechanical alloying step using hot isostatic pressing, and a step for subjecting the alloy obtained in said sintering step to grain boundary sliding based plastic deformation of 60% or greater at 500 to 2000°C and a strain rate of 10^{-5} s^{-1} to 10^{-2} s^{-1} .
2. The method for manufacturing an alloy according to claim 1, **characterized by** having a step in which said transition metal carbide and the metal raw material are degassed by heating prior to said mechanical alloying step.
3. A tungsten alloy comprising 0.25 to 5 mass% of at least one type selected from carbides of a group IVA, VA, or VIA transition metals, the tungsten alloy **characterized in that** the oxygen content is 950 ppm by mass or less, the nitrogen content is 60 ppm by mass or less, 80% or more of an observed cross sectional area in the tungsten phase is recrystallized equiaxed grains with grain diameters of 0.05 to 10 μm , the ductile-brittle transition temperature determined by three-point flexure is 500K or less, and plastic deformation due to grain boundary sliding is possible at or above this temperature.
4. The tungsten alloy according to claim 3, **characterized in that** 90% or greater of the azimuths of the carbide present in the tungsten alloy structure and the azimuths of the tungsten matrix are in the (Kurdjumov-Sachs) azimuth relationship: $\{111\} \text{ W} // \{110\} \text{ transition metal carbide}$ $<110> \text{ W} // <111> \text{ transition metal carbide}$.
5. The tungsten alloy according to claim 3 or 4, **characterized in that** the full width at half maximum for reflection of the (220) diffraction planes is 3° or less as determined by X-ray diffraction, or that there are 50 or fewer dislocations within crystal grains as determined by transmission electron microscopy.
6. The tungsten alloy according to any of claims 3 to 5, **characterized in that** the maximum bend strength determined by three-point flexure is 1470 MPa or greater.
7. The alloy that is manufactured by the manufacturing method according to claim 1 or 2.



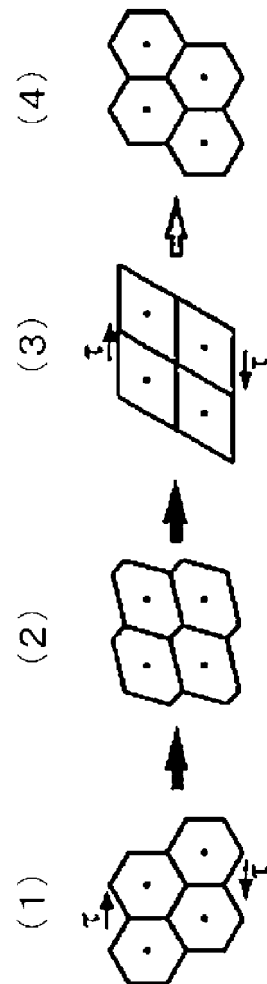
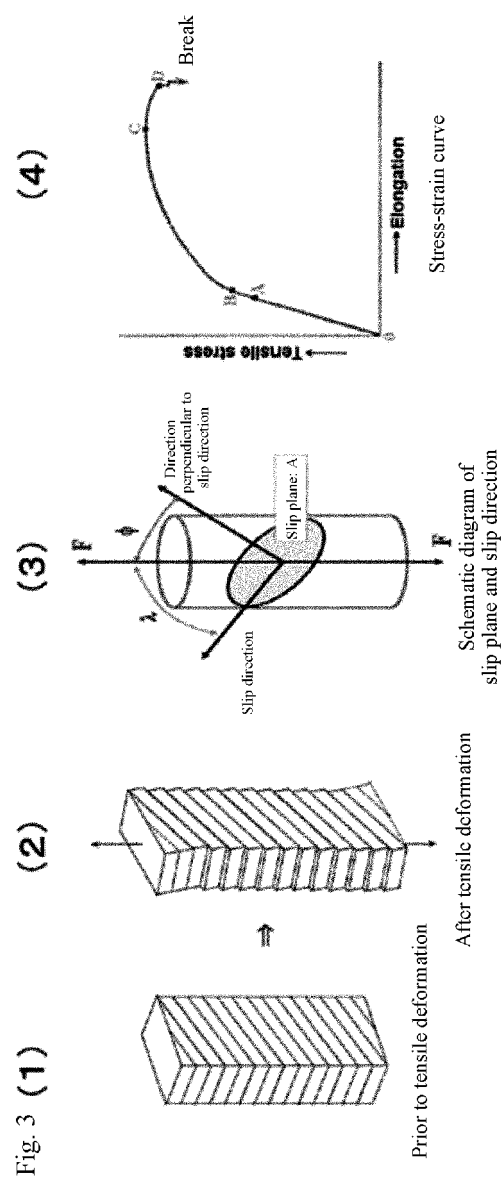


Fig. 2



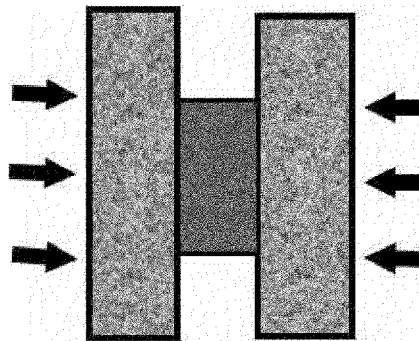


Fig. 4

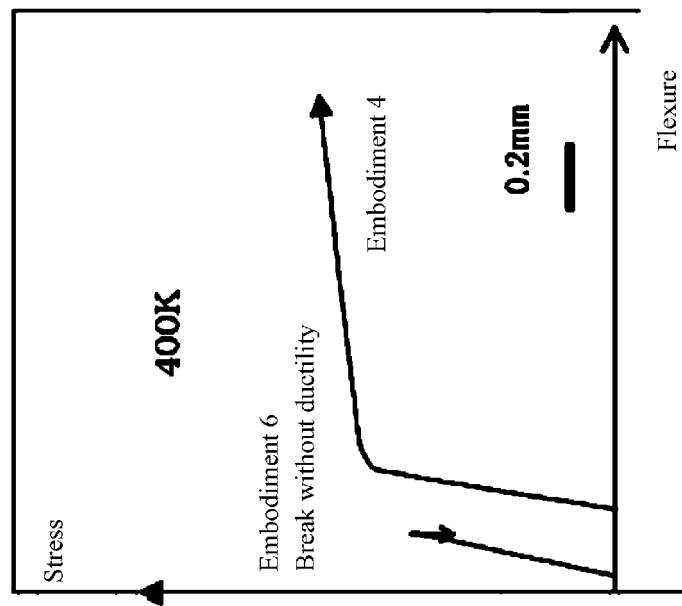
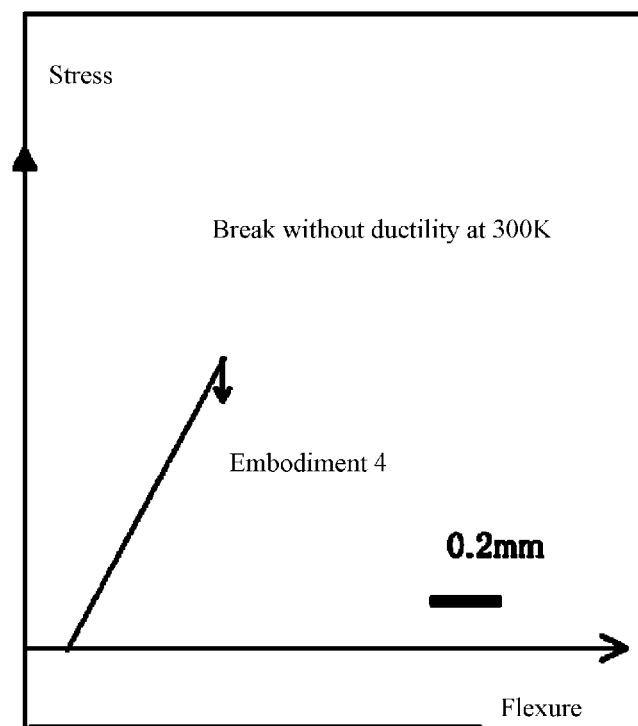


Fig. 5

Fig. 6



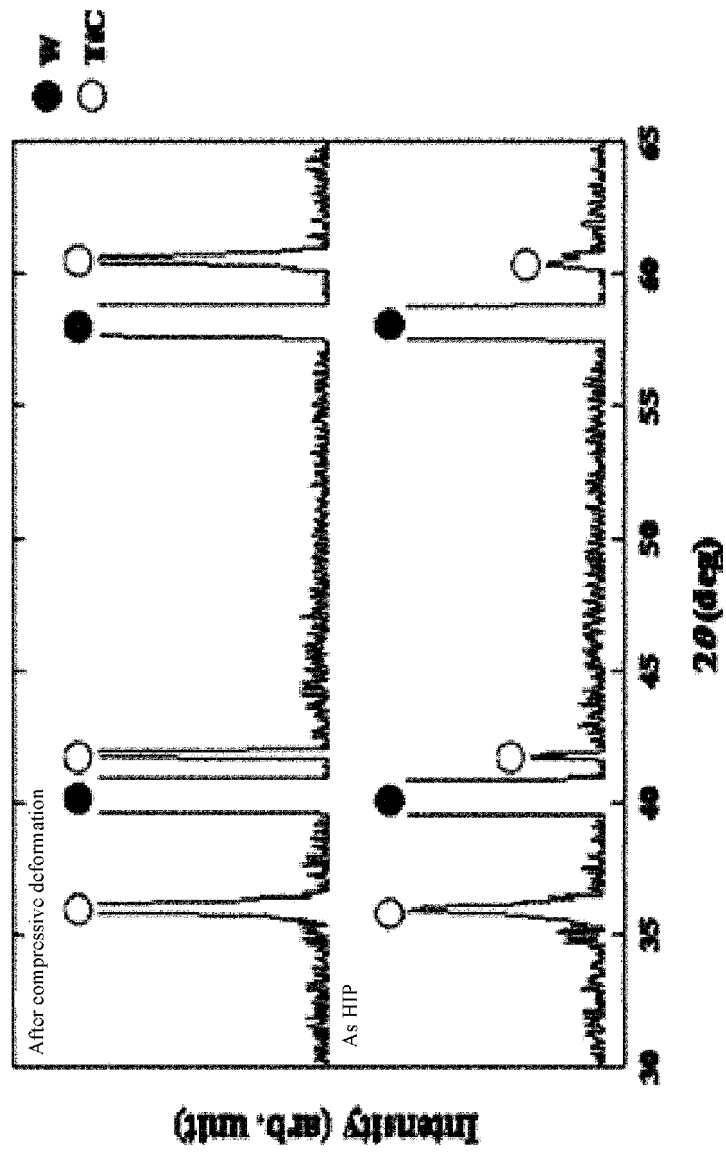
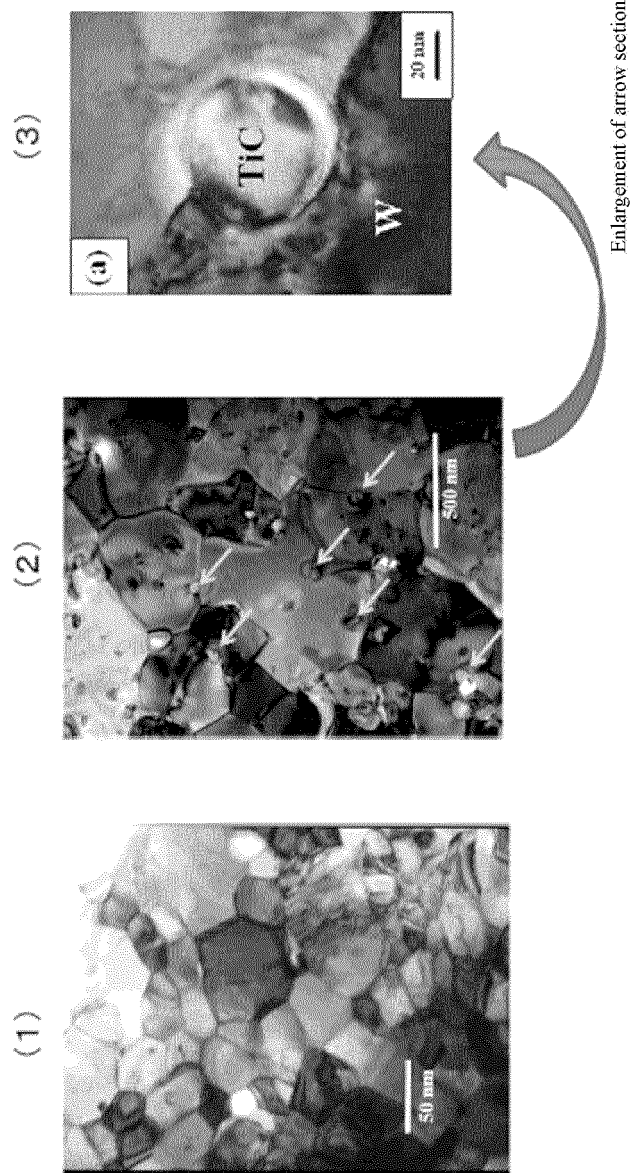


Fig. 7

Fig. 8



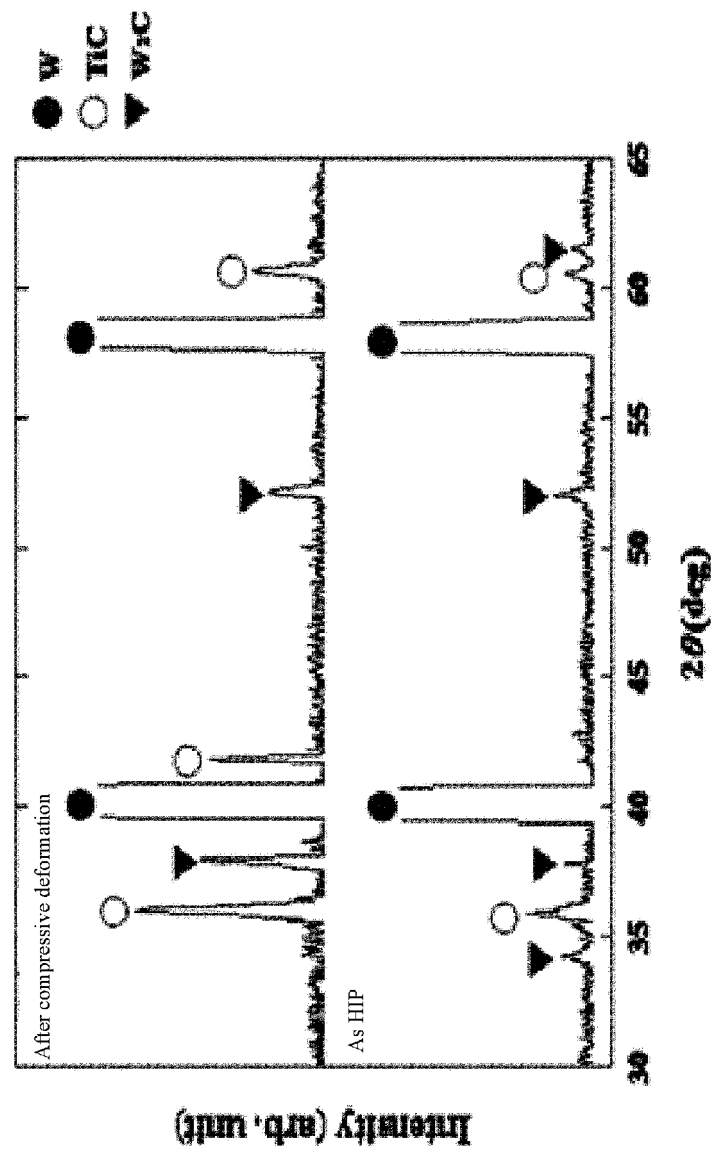
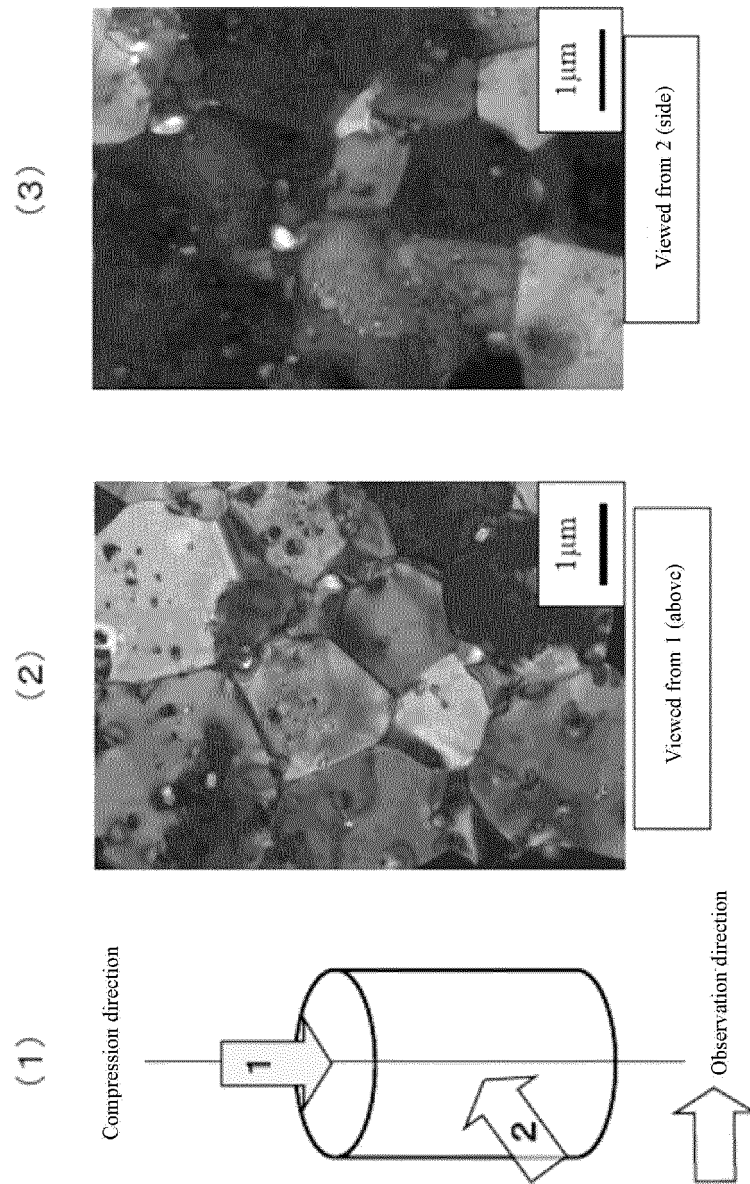


Fig. 9

Fig. 10



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/069190

A. CLASSIFICATION OF SUBJECT MATTER

B22F3/24(2006.01)i, B22F1/00(2006.01)i, B22F3/15(2006.01)i, C22C1/04
(2006.01)i, C22C27/04(2006.01)i, C22F1/18(2006.01)i, C22F1/00(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B22F3/24, B22F1/00, B22F3/15, C22C1/04, C22C27/04, C22F1/18, C22F1/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

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.
Y A	JP 08-085840 A (Hiroaki KURISHITA), 02 April 1996 (02.04.1996), claim 6 (Family: none)	1, 2, 7 3-6
Y A	JP 05-279705 A (Kobe Steel, Ltd.), 26 October 1993 (26.10.1993), claims (Family: none)	1, 2, 7 3-6
Y A	JP 05-163505 A (Kobe Steel, Ltd.), 29 June 1993 (29.06.1993), claims (Family: none)	1, 2, 7 3-6

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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Date of the actual completion of the international search
22 October, 2012 (22.10.12)

Date of mailing of the international search report
06 November, 2012 (06.11.12)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/069190

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 60-002603 A (Director General, Agency of Industrial Science and Technology), 08 January 1985 (08.01.1985), claims (Family: none)	1, 2, 7 3-6
Y A	JP 62-205202 A (Director General, Agency of Industrial Science and Technology), 09 September 1987 (09.09.1987), claims (Family: none)	1, 2, 7 3-6
A	JP 2004-279194 A (Allied Material Corp.), 07 October 2004 (07.10.2004), claims (Family: none)	1-7
A	JP 2001-226735 A (Allied Material Corp.), 21 August 2001 (21.08.2001), claims (Family: none)	1-7

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 1502680 A [0010]
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Non-patent literature cited in the description

- *Collected abstracts of the Japan Institute of Metals and Materials*, vol. 148, 235 [0011]
- *Collected abstracts of the Japan Institute of Metals and Materials*, vol. 143, 322 [0011]
- **T. KUWABARA ; H. KURISHITA ; M. HASEGAWA.** Development of an Ultra-Fine Grained V - 1.7 mass% Y alloy Dispersed with Yttrium Compounds Having Superior Ductility and High Strength. *Mater. Sci. Eng. A*, 2006, vol. 417, 16-23 [0045]