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

(11) EP 2 789 708 A1

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

(43) Date of publication:
15.10.2014 Bulletin 2014/42

(21) Application number: **12856450.7**

(22) Date of filing: **27.11.2012**

(51) Int Cl.:
C22C 27/04 *(2006.01)*
B22F 3/24 *(2006.01)*
C22C 1/04 *(2006.01)*
C22F 1/18 *(2006.01)*
C22F 1/00 *(2006.01)*

(86) International application number:
PCT/JP2012/080565

(87) International publication number:
WO 2013/084749 (13.06.2013 Gazette 2013/24)

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

(30) Priority: **07.12.2011 JP 2011267845**

(71) Applicant: **A.L.M.T. Corp.**
Minato-ku
Tokyo 105-0014 (JP)

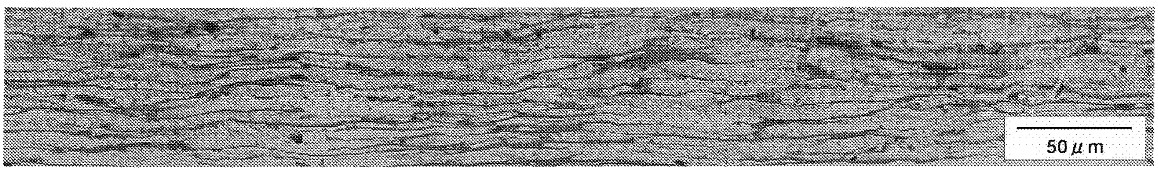
(72) Inventors:
- **TOYOSHIMA, Gouhei**
  Itami-shi
  Hyogo 664-0016 (JP)
- **UENISHI, Noboru**
  Itami-shi
  Hyogo 664-0016 (JP)
- **GOMA, Norihito**
  Itami-shi
  Hyogo 664-0016 (JP)
- **UMEMOTO, Satoshi**
  Itami-shi
  Hyogo 664-0016 (JP)
- **KADOKURA, Takanori**
  Toyama-shi
  Toyama 931-8543 (JP)
- **TAKIDA, Tomohiro**
  Toyama-shi
  Toyama 931-8543 (JP)
- **SAKAKIBARA, Kazunaga**
  Toyama-shi
  Toyama 931-8543 (JP)

(74) Representative: **Prüfer & Partner GbR**
European Patent Attorneys
Sohnckestrasse 12
81479 München (DE)

(54) SINTERED TUNGSTEN ALLOY

(57) There is provided a flat plate-like sintered tungsten alloy that can be molded into a complex shape by press working or forge processing. The flat plate-like sintered tungsten alloy contains 85% by mass or more and 98% by mass or less of W, 1.4% by mass or more and 11% by mass or less of Ni, and 0.6% by mass or more and 6% by mass or less of at least one substance selected from the group consisting of Fe, Cu and Co, wherein an elongation percentage of the flat plate-like sintered tungsten alloy in a planar direction is 20% or more.

FIG.6



EP 2 789 708 A1

Description

TECHNICAL FIELD

[0001] The present invention generally relates to a sintered tungsten alloy, and particularly to a sintered tungsten alloy used as a radiation shield material in radiation medical devices, nuclear reactor-related devices and the like.

BACKGROUND ART

[0002] It is conventionally known to use, as a radiation shield material, a tungsten-based alloy material containing tungsten as a main component.

[0003] Japanese Patent Laying-Open No. 9-71828 (hereinafter referred to as "PTD 1"), for example, discloses a tungsten-based alloy material for radiation shielding, which has a layered structure obtained by performing plastic working on a sintered body containing 85% by weight or more of tungsten as a main component, with the rest consisting of nickel and iron or copper, and flattening tungsten particles and a binder layer containing nickel, and layering these flattened layers. This tungsten-based alloy material is obtained by sintering a molded body at 1470°C to form a sintered body, and rolling the obtained sintered body at a heating temperature of 1300°C such that a processing rate in total becomes about 60%, and flattening the tungsten particles and the binder layer.

[0004] Japanese Patent Laying-Open No. 9-235641 discloses a tungsten heavy alloy plate containing tungsten at a weight ratio of 80 to 97%, nickel at a weight ratio of 2 to 15%, and one or two or more of iron, copper and cobalt at a weight ratio of 1 to 10% in total, having a thickness of 0.3 mm or smaller, and having such a dimension that both sides are more than 200 times as large as the thickness. This heavy alloy plate is obtained by mixing material powders, molding the mixture into a thin plate having a thickness of 0.35 mm or smaller by a powder rolling press, and then, sintering the molded body in the non-oxidizing atmosphere, hot-rolling and/or cold-rolling the sintered body as needed, and then, performing finish rolling for flattening and smoothing.

CITATION LIST

PATENT DOCUMENT

[0005]

PTD 1: Japanese Patent Laying-Open No. 9-71828
PTD 2: Japanese Patent Laying-Open No. 9-235641

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0006] As disclosed in PTD 1, the sintered tungsten alloy containing 85% by mass or more of tungsten has the radiation shielding effect, and thus, is used as a radiation shield material in radiation medical devices, nuclear reactor-related devices and the like. When the sintered tungsten alloy is used in such an application, it is necessary to fabricate a flat plate-like sintered tungsten alloy having a large area of a certain degree or more.

[0007] However, the conventional sintered tungsten alloy is not sufficient in elongation as a material property. Therefore, there is a problem that a flat plate-like radiation shield member having a complex shape cannot be molded by press working or forge processing.

[0008] Thus, an object of the present invention is to provide a flat plate-like sintered tungsten alloy that can be molded into a complex shape by press working or forge processing.

SOLUTION TO PROBLEM

[0009] A sintered tungsten alloy according to the present invention is a flat plate-like sintered tungsten alloy, containing 85% by mass or more and 98% by mass or less of tungsten, 1.4% by mass or more and 11% by mass or less of nickel, and 0.6% by mass or more and 6% by mass or less of at least one substance selected from the group consisting of iron, copper and cobalt. An elongation percentage of the flat plate-like sintered tungsten alloy in a planar direction is 20% or more.

[0010] Preferably, in the sintered tungsten alloy according to the present invention, a thickness of the flat plate-like sintered tungsten alloy is 1.5 mm or smaller.

[0011] Preferably, in the sintered tungsten alloy according to the present invention, an X-ray diffraction intensity ratio of a (111) plane of a Ni-(Fe, Cu, Co) phase in a flat plate surface of the flat plate-like sintered tungsten alloy (assuming that X-ray diffraction intensities of the (111) plane, a (100) plane, a (110) plane, and a (311) plane are I(111), I(100), I(110), and I(311), respectively, the X-ray diffraction intensity ratio of the (111) plane is a value of [I(111)/{I(111)+I(100)+I(110)+I(311)}]) is 0.68 or more and 0.9 or less.

ADVANTAGEOUS EFFECTS OF INVENTION

[0012] According to the present invention, there can be provided a flat plate-like sintered tungsten alloy that can be molded into a complex shape by press working or forge processing.

BRIEF DESCRIPTION OF DRAWINGS

[0013]

Fig. 1 is an optical microscope photograph showing a cross section of a flat plate-like sintered tungsten alloy after a sintering step is performed during fabrication in Example 1 of the present invention.
Fig. 2 is an optical microscope photograph showing a cross section of the flat plate-like sintered tungsten alloy after a distortion introducing step and a heat treatment step are performed during fabrication in Example 1 of the present invention.
Fig. 3 is an optical microscope photograph showing a cross section of the flat plate-like sintered tungsten alloy fabricated in Example 1 of the present invention.
Fig. 4 is an optical microscope photograph showing a cross section of a flat plate-like sintered tungsten alloy fabricated in Comparative Example 2 of the present invention.
Fig. 5 is a schematic perspective view showing two cross sections observed in the flat plate-like sintered tungsten alloy fabricated as an intermediate product in Examples and Comparative Examples of the present invention.
Fig. 6 is a scanning electron microscope (SEM) photograph showing a cross section portion observed in the flat plate-like sintered tungsten alloy fabricated as an intermediate product in Example 1 of the present invention.
Fig. 7 is a diagram schematically showing the measured thicknesses and lengths of tungsten crystal grains at the cross section portion observed in the flat plate-like sintered tungsten alloy fabricated as an intermediate product in Examples and Comparative Examples of the present invention.
Fig. 8(A) is a plan view and Fig. 8(B) is a side view showing the dimension of a tensile test piece fabricated from the flat plate-like sintered tungsten alloy as a final product fabricated in Examples and Comparative Examples of the present invention.

DESCRIPTION OF EMBODIMENTS

[0014] A flat plate-like sintered tungsten alloy of the present invention as an intermediate product contains 85% by mass or more and 98% by mass or less of tungsten (W), 1.4% by mass or more and 11% by mass or less of nickel (Ni), and 0.6% by mass or more and 6% by mass or less of at least one substance selected from the group consisting of iron (Fe), copper (Cu) and cobalt (Co). This sintered tungsten alloy has such a structure that a plurality of flattened tungsten crystal grains extending along the extending direction of a plane of the flat plate-like sintered tungsten alloy are stacked. A first cross section along the thickness direction orthogonal to the extending direction of the plane of the flat plate-like sintered tungsten alloy and a second cross section which is a cross section along the thickness direction orthogonal to the extending direction of the plane of the flat plate-like sintered tungsten alloy and which is orthogonal to the first cross section are observed to obtain a first cross section portion of a certain width and a certain thickness selected from the first cross section and a second cross section portion of a certain width and a certain thickness selected from the second cross section. A ratio of an average length to an average thickness of a plurality of tungsten crystal grains which are observed at the first cross section portion and the second cross section portion and which intersect with a center line passing through a center of the certain width and extending in the direction of the certain thickness is 9 or more and 125 or less.

[0015] Since the ratio of the average length to the average thickness of the tungsten crystal grains observed as described above is 9 or more and 125 or less in the flat plate-like sintered tungsten alloy as an intermediate product configured as described above, higher strength can be obtained at high temperature than that of the conventional sintered tungsten alloy. If the ratio of the average length to the average thickness of the tungsten crystal grains observed as described above is less than 9, there is a possibility that sufficiently high strength cannot be obtained at high temperature. If the ratio of the average length to the average thickness of the tungsten crystal grains observed as described above exceeds 125, fracture may occur.

[0016] In order to achieve the aforementioned ratio, the average thickness of the tungsten crystal grains observed as described above is preferably 2 μm or larger and 10 μm or smaller, and the average length of the tungsten crystal grains observed as described above is preferably 30 μm or longer and 250 μm or shorter. It is difficult to set the average thickness of the tungsten crystal grains to be smaller than 2 μm or to set the average length to exceed 250 μm.

[0017] If the average thickness of the tungsten crystal grains observed as described above is 2 μm or larger and 3 μm or smaller, the average length of the tungsten crystal grains observed as described above is preferably within a range of 30 μm to 250 μm, and the ratio of the average length to the average thickness is preferably 10 or more and 125 or less.

[0018] If the average thickness of the tungsten crystal grains observed as described above exceeds 3 μm and is 6 μm or smaller, the average length of the tungsten crystal grains observed as described above is preferably within a range of 54 μm to 250 μm, and the ratio of the average length to the average thickness is preferably 9 or more and 84 or less, in order to obtain sufficiently high strength at high temperature.

[0019] Furthermore, if the average thickness of the tungsten crystal grains observed as described above exceeds 6 μm and is 10 μm or smaller, the average length of the tungsten crystal grains observed as described above is preferably within a range of 90 μm to 250 μm, and the ratio of the average length to the average thickness is preferably 9 or more and 42 or less, in order to obtain sufficiently high strength at high temperature.

[0020] The tungsten crystal grain in the planar direction of the flat plate-like sintered tungsten alloy has various shapes such as a substantially circular shape, a substantially oval shape, a substantially square shape, a substantially rectangular shape, and an indefinite shape.

[0021] The flat plate-like sintered tungsten alloy of the present invention as an intermediate product is manufactured through (1) materials preparing step, (2) mixing step, (3) molding step, (4) sintering step, (5) distortion introducing step, (6) heat treatment step, and (7) hot-rolling step.

[0022] In short, a method for manufacturing the flat plate-like sintered tungsten alloy of the present invention as an intermediate product is a method for manufacturing a sintered tungsten alloy containing 85% by mass or more and 98% by mass or less of tungsten, 1.4% by mass or more and 11% by mass or less of nickel, and 0.6% by mass or more and 6% by mass or less of at least one substance selected from the group consisting of iron, copper and cobalt, characterized in that a distortion is introduced into a sintered body and heat treatment is performed on the sintered body having the distortion introduced therein, and then, the sintered body is hot-rolled at a rolling processing rate of 60% or more.

[0023] The flat plate-like sintered tungsten alloy thus manufactured can have such a structure that the ratio of the average length to the average thickness of the tungsten crystal grains observed as described above is 9 or more and 125 or less, and higher strength can be obtained at high temperature than that of the conventional sintered tungsten alloy.

[0024] In particular, a certain level of distortion is provided to a sintered tungsten alloy (sintered body) that has tungsten crystal grains with a grain size of 30 to 50 μm fabricated in accordance with a conventionally known manufacturing method (a mixing step, a molding step and a sintering step of material powders), and then, a certain level of heat treatment is performed. As a result, the grain size of the tungsten crystal grain in the sintered tungsten alloy can be decreased to a certain value or smaller (5 to 20 μm). Thereafter, the sintered body is hot-rolled at a rolling processing rate of 60% or more. As a result, the thickness of the tungsten crystal grain can be decreased to a certain value or smaller and the length of the tungsten crystal grain can be increased to a certain value or larger, and thus, there can be obtained a sintered tungsten alloy having such a structure that a plurality of flattened tungsten crystal grains extending in the planar direction of the flat plate-like sintered tungsten alloy are stacked. As a result, higher strength can be obtained at high temperature than that of the conventional sintered tungsten alloy.

[0025] The flat plate-like sintered tungsten alloy according to the present invention contains 85% by mass or more and 98% by mass or less of tungsten, 1.4% by mass or more and 11% by mass or less of nickel, and 0.6% by mass or more and 6% by mass or less of at least one substance selected from the group consisting of iron, copper and cobalt. An elongation percentage of the flat plate-like sintered tungsten alloy in the planar direction is 20% or more.

[0026] Since the elongation percentage of the flat plate-like sintered tungsten alloy in the planar direction is 20% or more in the flat plate-like sintered tungsten alloy configured as described above, the flat plate-like sintered tungsten alloy can be molded into a complex shape by press working or forge processing.

[0027] If the elongation percentage of the flat plate-like sintered tungsten alloy in the planar direction is less than 20%, there is no difference in elongation percentage from the conventional sintered tungsten alloy and there is a possibility that the flat plate-like sintered tungsten alloy cannot be molded into a complex shape by press working or forge processing. An upper limit value of the elongation percentage of the flat plate-like sintered tungsten alloy in the planar direction is 45%. It is difficult to obtain a flat plate-like sintered tungsten alloy in which the elongation percentage of the flat plate-like sintered tungsten alloy in the planar direction exceeds 45%.

[0028] The flat plate-like sintered tungsten alloy according to the present invention is manufactured through (1) materials preparing step, (2) mixing step, (3) molding step, (4) sintering step, (5) distortion introducing step, (6) heat treatment step, (7) hot-rolling step, and (8) heat treatment step.

[0029] In short, the method for manufacturing the flat plate-like sintered tungsten alloy according to the present invention is a method for manufacturing a sintered tungsten alloy containing 85% by mass or more and 98% by mass or less of tungsten, 1.4% by mass or more and 11% by mass or less of nickel, and 0.6% by mass or more and 6% by mass or less of at least one substance selected from the group consisting of iron, copper and cobalt, characterized in that a distortion is introduced into a sintered body and heat treatment is performed on the sintered body having the distortion introduced therein, and then, the sintered body is hot-rolled at a rolling processing rate of 60% or more and further heat treatment is performed on the hot-rolled sintered body.

[0030] In the flat plate-like sintered tungsten alloy thus manufactured, the elongation percentage of the flat plate-like sintered tungsten alloy in the planar direction can be 20% or more, and the flat plate-like sintered tungsten alloy can be molded into a complex shape by press working or forge processing.

[0031] In particular, the flat plate-like sintered tungsten alloy according to the present invention is obtained by performing further heat treatment on the flat plate-like sintered tungsten alloy of the present invention as an intermediate product. By this heat treatment, the flat plate-like sintered tungsten alloy does not have the structure of the sintered tungsten alloy of the present invention as an intermediate product, but has a structure very close to a structure of the conventional sintered tungsten alloy immediately after sintering. However, the sintered tungsten alloy according to the present invention is returned through the structure of the sintered tungsten alloy of the present invention as an intermediate product to the structure very close to the structure of the conventional sintered tungsten alloy. As a result, almost all defects present at an interface between the tungsten crystal grains and the binder (nickel, iron and the like) and in the binder, which are a cause of reduction in elongation in the conventional sintered tungsten alloy, disappear, and thus, it becomes easy for the tungsten crystal grains to slide in the binder component. Consequently, elongation of the sintered tungsten alloy according to the present invention is enhanced.

[0032] Preferably, the thickness of the flat plate-like sintered tungsten alloy according to the present invention is 1.5 mm or smaller.

[0033] Preferably, in the sintered tungsten alloy according to the present invention, an X-ray diffraction intensity ratio of a (111) plane of a Ni-(Fe, Cu, Co) phase in a flat plate surface of the flat plate-like sintered tungsten alloy (assuming that X-ray diffraction intensities of the (111) plane, a (100) plane, a (110) plane, and a (311) plane are I(111), I(100), I(110), and I(311), respectively, the X-ray diffraction intensity ratio of the (111) plane is a value of [I(111)/{I(111)+I(100)+I(110)+I(311)}]) is 0.68 or more and 0.9 or less.

[0034] A reason why the X-ray diffraction intensity ratio of the (111) plane of the Ni-(Fe, Cu, Co) phase in the flat plate surface of the flat plate-like sintered tungsten alloy of the present invention becomes high as described above, and the function and effect produced by this can be described as follows. When the flattened structure of the tungsten crystal grains having an extremely high aspect ratio is formed in (7) hot-rolling step described above, the Ni-(Fe, Cu, Co) phase serving as a binder phase is also stretched in the planar direction. As a result, in the Ni-(Fe, Cu, Co) phase serving as a binder phase, the (111) plane serving as a sliding plane of an FCC (face-centered cubic) structure is oriented in parallel to the planar direction. This has an influence even after (8) heat treatment step described above, and the orientation of the (111) plane remains in the flat plate-like sintered tungsten alloy as a final product. Since the sliding plane of the binder plane is oriented in parallel to the planar direction as described above, it can become easy for the tungsten crystal grains to slide in the binder component. By heat treatment, almost all defects present in the sintered tungsten alloy can be eliminated and elongation of the sintered tungsten alloy in the planar direction can be further enhanced.

[0035] In the conventional sintered tungsten alloy, warpage or distortion occurs, and thus, it is difficult to form a thin flat plate immediately after sintering. In addition, when rolling processing is performed on the conventional sintered tungsten alloy at a rolling processing rate of 60% or more, fracture and the like occur, and thus, it is necessary to finally perform grinding and polishing in order to obtain a thin flat plate. As a result, the manufacturing cost becomes high.

[0036] In contrast, in the method for manufacturing the sintered tungsten alloy according to the present invention, a distortion is introduced into the sintered body and heat treatment is performed on the sintered body having the distortion introduced therein, and then, hot-rolling processing is performed. Therefore, the sintered body can be hot-rolled at a rolling processing rate of 60% or more. As a result, the flat plate-like sintered tungsten alloy having a thickness of 1.5 mm or smaller can be formed. Therefore, the manufacturing method of the present invention is particularly advantageous to obtain a thin flat plate and the manufacturing cost can be reduced.

[0037] In particular, in the method for manufacturing the sintered tungsten alloy according to the present invention, further heat treatment is performed after hot-rolling processing, and thus, elongation can be enhanced. Therefore, the obtained flat plate-like sintered tungsten alloy can be further thinned by rolling processing and the like. A lower limit value of the thickness of the flat plate-like sintered tungsten alloy according to the present invention is 0.05 mm. It is difficult to set the thickness of the flat plate-like sintered tungsten alloy to be smaller than 0.05 mm.

[0038] The sintered tungsten alloy according to the present invention may contain elements other than nickel (Ni), iron (Fe), copper (Cu), and cobalt (Co), and may contain, for example, 0% by mass or more and 2% by mass or less of an element such as manganese (Mn), molybdenum (Mo), silicon (Si), rhenium (Re), chromium (Cr), titanium (Ti), vanadium (V), niobium (Nb), and tantalum (Ta), to such an extent that the function and effect of the present invention are not impaired.

[0039] The method for manufacturing the flat plate-like sintered tungsten alloy of the present invention will be described hereinafter.

(1) Materials Preparing Step

[0040] A tungsten powder, a nickel powder, and a metal powder of at least one substance selected from the group consisting of iron, copper and cobalt are prepared. The materials are prepared to contain the tungsten powder at a blending ratio of 85% by mass or more and 98% by mass or less, nickel at a blending ratio of 1.4% by mass or more and 11% by mass or less, and the metal powder of at least one substance selected from the group consisting of iron, copper and cobalt at a blending ratio of 0.6% by mass or more and 6% by mass or less.
[0041] If the blending ratio of the tungsten powder is less than 85% by mass, the strength of the obtained sintered tungsten alloy may be insufficient. If the blending ratio of the tungsten powder exceeds 98% by mass, the binder component may be insufficient and fracture may occur in the obtained sintered tungsten alloy during the rolling step.
[0042] If the blending ratio of the nickel powder is less than 1.4% by mass, fracture may occur in the obtained sintered tungsten alloy during the rolling step. If the blending ratio of the nickel powder exceeds 11% by mass, the strength of the obtained sintered tungsten alloy may be insufficient.
[0043] Iron, copper and cobalt serve as a sintering aid. If the blending ratio of the metal powder of at least one substance selected from the group consisting of iron, copper and cobalt is less than 0.6% by mass, the dense sintered body cannot be obtained, and thus, fracture may occur in the obtained sintered tungsten alloy during the rolling step. If the blending ratio of the aforementioned metal powder exceeds 6% by mass, the binder component is excessively cured, and thus, the toughness of the obtained sintered tungsten alloy itself may be reduced.
[0044] The average grain size of each of the tungsten powder, the nickel powder and the aforementioned metal powder is preferably 1 μm or larger and 10 μm or smaller. If the average grain size of each of these powders is smaller than 1 μm, the manufacturing cost may increase. If the average grain size of each of these powders exceeds 10 μm, a gap is likely to be formed in the obtained sintered tungsten alloy, and thus, fracture may occur in the sintered tungsten alloy during the rolling step.

(2) Mixing Step

[0045] The tungsten powder, the nickel powder, and the metal powder of at least one substance selected from the group consisting of iron, copper and cobalt, which were prepared as described above, are mixed to obtain a mixture. Mixing can be performed by using a Lodige mixer, an attritor, a ball mill or the like. At the time of mixing, a solvent and a binder may be added to the material powders. Camphor, Merball, stearic acid, paraffin or the like can be used as the binder. Ethanol, methanol, acetone or the like can be used as the solvent.

(3) Molding Step

[0046] Pressure is applied to the mixture obtained as described above and the mixture is molded to obtain a molded body. The pressure is applied to the mixture by using cold isotropic pressure press (CIP), dry CIP, mechanical press or the like. The pressure applied at the time of molding is preferably 49 MPa or higher and lower than 294 MPa. If the pressure is lower than 49 MPa, there is a possibility that the molded body cannot be obtained. Even if the molded body can be obtained, the molded body may be broken during handling and the subsequent steps. Even if the pressure is 294 MPa or higher, no problem arises, while the function for obtaining the molded body is not enhanced.

(4) Sintering Step

[0047] The molded body obtained as described above is sintered to obtain a sintered body. The atmosphere of a hydrogen gas, vacuum or an inert gas can be used as the atmosphere for sintering the molded body. A batch furnace, a continuous pressure furnace or the like can be used as a sintering furnace that houses the molded body.
[0048] The sintering temperature is preferably 1200°C or higher and 1550°C or lower. If the sintering temperature is lower than 1200°C, the dense sintered body cannot be obtained, and thus, fracture may occur in the obtained sintered tungsten alloy during the rolling step. If the sintering temperature exceeds 1550°C, the sintered body may melt.
[0049] The sintering time is preferably 10 minutes or longer and 300 minutes or shorter when the sintering temperature is maximum. If the sintering time is shorter than 10 minutes, the dense sintered body cannot be obtained, and thus, fracture may occur in the obtained sintered tungsten alloy during the rolling step. If the sintering time exceeds 300 minutes, the tungsten crystal grains become too coarse, and thus, there is a possibility that the tungsten crystal grains cannot become sufficiently fine grains during the subsequent steps.
[0050] The molding step and the sintering step may be simultaneously performed by using hot isotropic pressure press

(HIP). In this case, an inert gas such as a nitrogen gas and an argon gas can be used as the atmosphere.

[0051] The pressure is preferably 500 MPa or higher and 1500 MPa or lower. If the pressure is lower than 500 MPa, the dense sintered body cannot be obtained, and thus, fracture may occur in the obtained sintered tungsten alloy during the rolling step. Even if the pressure exceeds 1500 MPa, no problem arises, while the function for obtaining the sintered body is not enhanced.

[0052] The temperature is preferably 1200°C or higher and 1550°C or lower. If the temperature is lower than 1200°C, the dense sintered body cannot be obtained, and thus, fracture may occur in the obtained sintered tungsten alloy during the rolling step. If the temperature exceeds 1550°C, the sintered body may melt.

(5) Distortion Introducing Step

[0053] A distortion is introduced into the sintered body (sintered tungsten alloy) obtained as described above. The distortion is preferably introduced into the sintered body by, for example, deforming the flat plate-like sintered body in the thickness direction at a deformation rate of 20% or more and 50% or less. If the deformation rate is less than 20%, an amount of distortion introduced into the sintered body is insufficient, and thus, there is a possibility that fine crystal grains cannot be formed even if heat treatment is performed in the subsequent step. If the deformation rate exceeds 50%, fracture may occur in the sintered body.

[0054] The temperature of the sintered body at the time of introduction of the distortion is preferably 0°C or higher and 600°C or lower. If the temperature is lower than 0°C, the sintered body becomes hard, and thus, fracture may occur. If the temperature exceeds 600°C, the introduced distortion is released, and thus, there is a possibility that fine crystal grains cannot be formed even if heat treatment is performed in the subsequent step.

[0055] A method for introducing the distortion into the sintered body can include deforming the sintered body by forge processing, mechanical press working, cold-rolling processing or the like.

(6) Heat Treatment Step

[0056] Heat treatment is performed on the sintered body (sintered tungsten alloy) having the distortion introduced therein. By this heat treatment, the distortion introduced into the sintered body is recovered to an appropriate level and the tungsten crystal grains become fine grains.

[0057] The atmosphere of vacuum, a hydrogen gas, a nitrogen gas, an argon gas, or a carbon monoxide gas can be used as the atmosphere for performing heat treatment on the sintered body.

[0058] The heat treatment temperature is preferably 900°C or higher and 1400°C or lower. If the heat treatment temperature is lower than 900°C, recovery of the distortion is insufficient and the tungsten crystal grains do not become fine grains, and thus, fracture may occur in the sintered body during the subsequent hot-rolling step. If the heat treatment temperature exceeds 1400°C, the distortion is completely recovered and the tungsten crystal grains become coarse, and thus, fracture may occur in the sintered body during the subsequent hot-rolling step.

[0059] The heat treatment time is preferably 20 minutes or longer and 5 hours or shorter. If the heat treatment time is shorter than 20 minutes, recovery of the distortion is insufficient and the tungsten crystal grains do not become fine grains, and thus, fracture may occur in the sintered body during the subsequent hot-rolling step. If the heat treatment time exceeds 5 hours, the distortion is completely recovered and the tungsten crystal grains become coarse, and thus, fracture may occur in the sintered body during the subsequent hot-rolling step.

[0060] The average grain size of the tungsten crystal grains in the sintered tungsten alloy after heat treatment is preferably 5 μm or larger and 20 μm or smaller. It is difficult to set the average grain size of the tungsten crystal grains to be smaller than 5 μm. If the average grain size of the tungsten crystal grains exceeds 20 μm, fracture may occur in the sintered body during the subsequent hot-rolling step.

(7) Hot-rolling Step

[0061] Rolling processing is performed on the sintered body (sintered tungsten alloy) subjected to heat treatment as described above at a rolling processing rate of 60% or more, with the sintered body heated. The atmosphere of a hydrogen gas, a nitrogen gas, an argon gas or the like can be used as the atmosphere for heating the sintered body.

[0062] The rolling processing temperature is preferably 800°C or higher and 1400°C or lower. If the rolling processing temperature is lower than 800°C, a large load is applied to a rolling machine, and thus, rolling processing cannot be performed or fracture may occur in the sintered body. If the rolling processing temperature exceeds 1400°C, the tungsten crystal grains become coarse, and thus, fracture may occur in the sintered body when rolling processing is performed.

[0063] The rolling processing rate of one rolling is preferably 5% or more and 30% or less. If the rolling processing rate of one rolling is less than 5%, the number of rolling for achieving the rolling processing rate of 60% or more in total increases and the manufacturing cost increases. If the rolling processing rate of one rolling exceeds 30%, a large load is applied to the rolling machine, and thus, rolling processing cannot be performed or fracture may occur in the sintered body.

[0064] The rolling processing rate in total is preferably 60% or more and 95% or less. If the rolling processing rate in total is less than 60%, the tungsten crystal grains do not become flattened particles, and thus, there is a possibility that sufficiently high strength of the sintered tungsten alloy at high temperature is not obtained. If the rolling processing rate in total exceeds 95%, fracture may occur in the sintered body due to rolling processing.

[0065] Even when (5) distortion introducing step and (6) heat treatment step are not performed on the conventional sintered tungsten alloy and (7) hot-rolling step is performed on the sintered tungsten alloy immediately after sintering, rolling is performed at a rolling processing rate of approximately 60% at most. Even when the hot-rolling step is performed on the flat plate-like sintered tungsten alloy having, for example, a plane of approximately 100 mm×100 mm or larger, the sintered tungsten alloy having a thickness of approximately 2 mm is only obtained.

[0066] In contrast, in the present invention, (5) distortion introducing step and (6) heat treatment step are performed and then (7) hot-rolling step is performed on the sintered body (sintered tungsten alloy) obtained in (4) sintering step. As a result, rolling can be performed at a rolling processing rate of 60% or more and 95% or less and the flat plate-like sintered tungsten alloy as an intermediate product having a thickness of 1.5 mm or smaller can be manufactured. A lower limit value of the thickness of the sintered tungsten alloy of the present invention as an intermediate product is 0.5 mm. It is difficult to obtain the sintered tungsten alloy having a thickness of smaller than 0.5 mm, even when (5) distortion introducing step and (6) heat treatment step are performed and then (7) hot-rolling step is performed.

(8) Heat Treatment Step

[0067] Heat treatment is performed on the sintered body (sintered tungsten alloy) subjected to hot-rolling processing as described above. By this heat treatment, almost all defects present at the interface between the tungsten crystal grains and the binder and in the binder can be eliminated, and thus, it becomes easy for the tungsten crystal grains to slide in the binder component. Consequently, elongation of the sintered tungsten alloy is enhanced.

[0068] The atmosphere of vacuum, a hydrogen gas or an inert gas can be used as the atmosphere for performing heat treatment on the sintered body subjected to hot-rolling processing. A batch furnace or a continuous pressure furnace can be used as a furnace for performing heat treatment.

[0069] The heat treatment temperature is preferably 1300°C or higher and 1550°C or lower. If the heat treatment temperature is lower than 1300°C, the tungsten crystal grains become coarse insufficiently, and thus, there is a possibility that the processability in cold working is not enhanced. If the heat treatment temperature exceeds 1550°C, the sintered body may melt.

[0070] The heat treatment time is preferably 10 minutes or longer and 5 hours or shorter. If the heat treatment time is shorter than 10 minutes, the tungsten crystal grains become coarse insufficiently, and thus, there is a possibility that the processability in cold working is not enhanced. If the heat treatment time exceeds 5 hours, the tungsten crystal grains become coarse and the processability decreases, and thus, fracture may occur in the sintered body when the sintered body is processed into a complex shape.

[0071] The average grain size of the tungsten crystal grains in the sintered tungsten alloy after heat treatment is preferably 20 μm or larger and 60 μm or smaller. If the average grain size of the tungsten crystal grains is smaller than 20 μm, the effect of heat treatment is insufficient and high elongation percentage is not obtained, and thus, there is a possibility that the processability in cold working is not enhanced. If the average grain size of the tungsten crystal grains exceeds 60 μm, the tungsten crystal grains become coarse and the processability decreases, and thus, fracture may occur in the sintered body when the sintered body is processed into a complex shape.

Examples

[0072] Examples 1 to 29 and Comparative Examples 1 to 13 of the present invention in which the flat plate-like sintered tungsten alloy is fabricated to check the effects of the aforementioned embodiment will be described hereinafter.

(Example 1)

[0073] In this Example, the aforementioned flat plate-like sintered tungsten alloy of the present invention as an intermediate product was fabricated. Namely, the aforementioned steps (1) to (7) were performed to fabricate the flat plate-like sintered tungsten alloy.

[0074] First, preparation was made such that a tungsten powder having an average grain size of 3 μm was contained at a blending ratio of 95% by mass, a nickel powder having an average grain size of 4 μm was contained at a blending ratio of 3.5% by mass, and an iron powder having an average grain size of 3 μm was contained at a blending ratio of 1.5% by mass ((1) materials preparing step).

[0075] Next, the tungsten powder, the nickel powder and the iron powder prepared as described above were mixed by using the Lodige mixer, to obtain a mixture ((2) mixing step).

[0076] Then, by using cold isotropic pressure press (CIP), a pressure of 196 MPa was applied to the mixture obtained as described above and the mixture was molded to obtain a molded body ((3) molding step). The obtained molded body had a dimension of 176 mm×176 mmx8.2 mm.

[0077] Furthermore, the molded body obtained as described above was sintered in the hydrogen gas atmosphere furnace at a temperature of 1460°C for 80 minutes to obtain a sintered body ((4) sintering step). The obtained sintered body had a dimension of 150 mm×150 mmx7 mm.

[0078] Fig. 1 shows an optical microscope photograph obtained by observing a cross section of the flat plate-like sintered tungsten alloy obtained as described above.

[0079] Thereafter, by using a forging machine, the obtained flat plate-like sintered tungsten alloy was deformed in the thickness direction at a temperature of 25°C at a deformation rate of 30% to introduce a distortion into the sintered tungsten alloy ((5) distortion introducing step). The flat plate-like sintered tungsten alloy having the distortion introduced therein had a dimension of 177 mm×177 mm×5 mm.

[0080] Heat treatment was performed on the flat plate-like sintered tungsten alloy having the distortion introduced therein, in the vacuum furnace at a temperature of 1200°C for 3 hours ((6) heat treatment step).

[0081] Fig. 2 shows an optical microscope photograph obtained by observing a cross section of the flat plate-like sintered tungsten alloy obtained as described above. As shown in Fig. 2, it can be seen that the tungsten crystal grains have become fine grains and the average grain size is approximately 10 μm.

[0082] Finally, a sample of the flat plate-like sintered tungsten alloy subjected to heat treatment was heated in the hydrogen gas atmosphere furnace to a temperature of 1100°C, and then, the sample was taken out from the furnace and rolling processing was immediately performed at a rolling processing rate of approximately 10%, and the rolling processing was repeated until the rolling processing rate in total reached 80% ((7) hot-rolling step). The flat plate-like sintered tungsten alloy after hot-rolling processing had a dimension of 100 mm×1070 mm×1 mm.

[0083] The flat plate-like sintered tungsten alloy of the present invention as an intermediate product was thus fabricated.

[0084] Heat treatment was performed on the obtained flat plate-like sintered tungsten alloy as an intermediate product in the vacuum furnace at a temperature of 1450°C for 60 minutes ((8) heat treatment step).

[0085] Fig. 3 shows an optical microscope photograph obtained by observing a cross section of the flat plate-like sintered tungsten alloy as a final product obtained as described above. As shown in Fig. 3, it can be seen that the tungsten crystal grains have become coarse and the average grain size is approximately 35 μm.

(Example 2)

[0086] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that the heat treatment temperature was 1300°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using an optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 21 μm.

(Example 3)

[0087] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that the heat treatment temperature was 1550°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 43 μm.

(Example 4)

[0088] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that the heat treatment time was 10 minutes in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 25 μm.

(Example 5)

[0089] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1,

except that the heat treatment time was 3 hours in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 39 μm.

(Example 6)

[0090] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that the heat treatment time was 5 hours in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 57 μm.

(Example 7)

[0091] A flat plate-like sintered tungsten alloy having a thickness of 1.1 mm was fabricated similarly to Example 1, except that a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 20% in the distortion introducing step and the heat treatment temperature was 1500°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 19 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 39 μm.

(Example 8)

[0092] A flat plate-like sintered tungsten alloy having a thickness of 0.9 mm was fabricated similarly to Example 1, except that a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 40% in the distortion introducing step and the heat treatment temperature was 1500°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 10 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 38 μm.

(Example 9)

[0093] A flat plate-like sintered tungsten alloy having a thickness of 0.7 mm was fabricated similarly to Example 1, except that a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 50% in the distortion introducing step and the heat treatment temperature was 1500°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 5 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 39 μm.

(Example 10)

[0094] A flat plate-like sintered tungsten alloy having a thickness of 2.0 mm was fabricated similarly to Example 1, except that rolling processing was performed until the rolling processing rate in total reached 60% in the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 39 μm.

(Example 11)

[0095] A flat plate-like sintered tungsten alloy having a thickness of 1.5 mm was fabricated similarly to Example 1,

except that rolling processing was performed until the rolling processing rate in total reached 70% in the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 36 μm.

(Example 12)

[0096] A flat plate-like sintered tungsten alloy having a thickness of 0.7 mm was fabricated similarly to Example 1, except that rolling processing was performed until the rolling processing rate in total reached 85% in the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 37 μm.

(Example 13)

[0097] A flat plate-like sintered tungsten alloy having a thickness of 0.5 mm was fabricated similarly to Example 1, except that rolling processing was performed until the rolling processing rate in total reached 90% in the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 37 μm.

(Example 14)

[0098] A flat plate-like sintered tungsten alloy having a thickness of 0.5 mm was fabricated similarly to Example 1, except that the thickness of a sintered body obtained in the sintering step was 14 mm and rolling processing was performed until the rolling processing rate in total reached 95% in the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 39 μm.

(Example 15)

[0099] A flat plate-like sintered tungsten alloy having a thickness of 0.5 mm was fabricated similarly to Example 1, except that the thickness of a sintered body obtained in the sintering step was 20 mm, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 50% in the distortion introducing step, rolling processing was performed until the rolling processing rate in total reached 95% in the hot-rolling step, and the heat treatment temperature was 1300°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 5 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 23 μm.

(Example 16)

[0100] A flat plate-like sintered tungsten alloy having a thickness of 0.5 mm was fabricated similarly to Example 1, except that the thickness of a sintered body obtained in the sintering step was 20 mm, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 50% in the distortion introducing step, rolling processing was performed until the rolling processing rate in total reached 95% in the hot-rolling step, and the heat treatment temperature was 1450°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 5 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 37 μm.

(Example 17)

[0101] A flat plate-like sintered tungsten alloy having a thickness of 0.5 mm was fabricated similarly to Example 1,

except that the thickness of a sintered body obtained in the sintering step was 20 mm, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 50% in the distortion introducing step, rolling processing was performed until the rolling processing rate in total reached 95% in the hot-rolling step, and the heat treatment temperature was 1550°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 5 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 47 μm.

(Example 18)

[0102] A flat plate-like sintered tungsten alloy having a thickness of 2.2 mm was fabricated similarly to Example 1, except that a tungsten powder having an average grain size of 1 μm was used and a copper powder was used instead of the iron powder in the materials preparing step, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 20% in the distortion introducing step, rolling processing was performed until the rolling processing rate in total reached 60% in the hot-rolling step, and the heat treatment temperature was 1300°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 19 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 21 μm.

(Example 19)

[0103] A flat plate-like sintered tungsten alloy having a thickness of 1.7 mm was fabricated similarly to Example 1, except that a tungsten powder having an average grain size of 5 μm was used and a copper powder was used instead of the iron powder in the materials preparing step, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 20% in the distortion introducing step, rolling processing was performed until the rolling processing rate in total reached 70% in the hot-rolling step, and the heat treatment temperature was 1300°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 19 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 23 μm.

(Example 20)

[0104] A flat plate-like sintered tungsten alloy having a thickness of 0.7 mm was fabricated similarly to Example 1, except that a tungsten powder having an average grain size of 10 μm was used and a copper powder was used instead of the iron powder in the materials preparing step, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 20% in the distortion introducing step, rolling processing was performed until the rolling processing rate in total reached 90% in the hot-rolling step, and the heat treatment temperature was 1300°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 19 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 22 μm.

(Example 21)

[0105] A flat plate-like sintered tungsten alloy having a thickness of 0.5 mm was fabricated similarly to Example 1, except that preparation was made in the materials preparing step to contain a tungsten powder at a blending ratio of 85% by mass, a nickel powder at a blending ratio of 10.5% by mass, and an iron powder at a blending ratio of 4.5% by mass, rolling processing was performed until the rolling processing rate in total reached 90% in the hot-rolling step, and the heat treatment temperature was 1300°C and the heat treatment time was 3 hours in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 9 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 24 μm.

(Example 22)

[0106] A flat plate-like sintered tungsten alloy having a thickness of 0.5 mm was fabricated similarly to Example 1, except that preparation was made in the materials preparing step to contain a tungsten powder at a blending ratio of 90% by mass, a nickel powder at a blending ratio of 7% by mass, and an iron powder at a blending ratio of 3% by mass, rolling processing was performed until the rolling processing rate in total reached 90% in the hot-rolling step, and the heat treatment temperature was 1300°C and the heat treatment time was 3 hours in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 10 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 24 μm.

(Example 23)

[0107] A flat plate-like sintered tungsten alloy having a thickness of 0.5 mm was fabricated similarly to Example 1, except that preparation was made in the materials preparing step to contain a tungsten powder at a blending ratio of 98% by mass, a nickel powder at a blending ratio of 1.4% by mass, and an iron powder at a blending ratio of 0.6% by mass, rolling processing was performed until the rolling processing rate in total reached 90% in the hot-rolling step, and the heat treatment temperature was 1300°C and the heat treatment time was 3 hours in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 10 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 26 μm.

(Example 24)

[0108] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that a nickel powder having an average grain size of 1 μm was used and a cobalt powder was used instead of the iron powder in the materials preparing step, and the heat treatment temperature was 1300°C and the heat treatment time was 5 hours in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 11 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 28 μm.

(Example 25)

[0109] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that a nickel powder having an average grain size of 5 μm was used and a cobalt powder was used instead of the iron powder in the materials preparing step, and the heat treatment temperature was 1300°C and the heat treatment time was 5 hours in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 10 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 30 μm.

(Example 26)

[0110] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that a nickel powder having an average grain size of 10 μm was used and a cobalt powder was used instead of the iron powder in the materials preparing step, and the heat treatment temperature was 1300°C and the heat treatment time was 5 hours in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 10 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 27 μm.

(Example 27)

[0111] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that an iron powder having an average grain size of 1 μm was used in the materials preparing step, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 50% in the distortion introducing step, and rolling processing was performed until the rolling processing rate in total reached 60% in the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 5 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 32 μm.

(Example 28)

[0112] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that an iron powder having an average grain size of 5 μm was used in the materials preparing step, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 50% in the distortion introducing step, and rolling processing was performed until the rolling processing rate in total reached 60% in the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 5 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 35 μm.

(Example 29)

[0113] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that an iron powder having an average grain size of 10 μm was used in the materials preparing step, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 50% in the distortion introducing step, and rolling processing was performed until the rolling processing rate in total reached 60% in the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 5 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 33 μm.

(Comparative Example 1)

[0114] A conventional sintered tungsten alloy fabricated by performing the aforementioned steps (1) to (4) was processed to have a thickness of 1 mm by grinding and polishing.

(Comparative Example 2)

[0115] On a conventional sintered tungsten alloy fabricated by performing the aforementioned steps (1) to (4), the steps (5) and (6) were not performed and (7) hot-rolling step was performed until the rolling processing rate reached 60% (thickness became 2 mm) immediately after sintering. Thereafter, the sintered tungsten alloy subjected to rolling processing was processed to have a thickness of 1 mm by grinding and polishing.

[0116] Fig. 4 shows an optical microscope photograph obtained by observing a cross section of the flat plate-like sintered tungsten alloy obtained as described above.

(Comparative Example 3)

[0117] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that the heat treatment temperature was 1200°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 18 μm.

(Comparative Example 4)

[0118] An attempt was made to fabricate a flat plate-like sintered tungsten alloy having a thickness of 1.0 mm similarly to Example 1, except that the heat treatment temperature was 1600°C in the heat treatment step after the hot-rolling step. However, the flat plate-like sintered tungsten alloy melted.

(Comparative Example 5)

[0119] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that the heat treatment time was 6 minutes in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 17 μm.

(Comparative Example 6)

[0120] A flat plate-like sintered tungsten alloy having a thickness of 1.0 mm was fabricated similarly to Example 1, except that the heat treatment time was 6 hours in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 64 μm.

(Comparative Example 7)

[0121] An attempt was made to fabricate a flat plate-like sintered tungsten alloy similarly to Example 1, except that a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 17% in the distortion introducing step and the heat treatment temperature was 1500°C in the heat treatment step after the hot-rolling step. However, fracture occurred after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 24.3 μm.

(Comparative Example 8)

[0122] An attempt was made to fabricate a flat plate-like sintered tungsten alloy similarly to Example 1, except that a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 60% in the distortion introducing step and the heat treatment temperature was 1500°C in the heat treatment step after the hot-rolling step. However, fracture occurred in the distortion introducing step.

(Comparative Example 9)

[0123] A flat plate-like sintered tungsten alloy having a thickness of 2.5 mm was fabricated similarly to Example 1,

except that rolling processing was performed until the rolling processing rate in total reached 50% in the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 37 μm.

(Comparative Example 10)

[0124] An attempt was made to fabricate a flat plate-like sintered tungsten alloy similarly to Example 1, except that rolling processing was performed until the rolling processing rate in total reached 97% in the hot-rolling step. However, fracture occurred after the hot-rolling step.

(Comparative Example 11)

[0125] A flat plate-like sintered tungsten alloy having a thickness of 0.5 mm was fabricated similarly to Example 1, except that the thickness of a sintered body obtained in the sintering step was 20 mm, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 50% in the distortion introducing step, rolling processing was performed until the rolling processing rate in total reached 95% in the hot-rolling step, and the heat treatment temperature was 1200°C in the heat treatment step after the hot-rolling step. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 5 μm. In addition, similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy as a final product was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 17 μm.

(Comparative Example 12)

[0126] An attempt was made to fabricate a flat plate-like sintered tungsten alloy having a thickness of 0.5 mm similarly to Example 1, except that the thickness of a sintered body obtained in the sintering step was 20 mm, a distortion was introduced into the sintered tungsten alloy by deforming the sintered tungsten alloy in the thickness direction at a deformation rate of 50% in the distortion introducing step, rolling processing was performed until the rolling processing rate in total reached 95% in the hot-rolling step, and the heat treatment temperature was 1600°C in the heat treatment step after the hot-rolling step. However, the flat plate-like sintered tungsten alloy melted. Similarly to Example 1, a cross section of the flat plate-like sintered tungsten alloy after heat treatment after the distortion introducing step was observed by using the optical microscope. As a result of observation, the average grain size of the tungsten crystal grains was approximately 5 μm.

(Comparative Example 13)

[0127] When (7) hot-rolling step was performed on a conventional sintered tungsten alloy fabricated by performing the aforementioned steps (1) to (4) in Example 1, until the rolling processing rate reached 65% immediately after sintering, fracture occurred in the sintered tungsten alloy.

(Measurement of Average Thickness and Average Length of Tungsten Crystal Grains)

[0128] As shown in Fig. 5, by using a scanning electron microscope (SEM), observation was conducted of a first cross section 101 along the direction of a thickness To (1 mm) orthogonal to the extending direction of a plane 100 of a flat plate-like sintered tungsten alloy 1 obtained as an intermediate product in each of Examples 1 to 29 and Comparative Examples 1 to 6, 9, 11 and 12, and a second cross section 102 which is a cross section along the direction of thickness To orthogonal to the extending direction of plane 100 of flat plate-like sintered tungsten alloy 1 and which is orthogonal to the first cross section.

[0129] Specifically, in each of first cross section 101 and second cross section 102, a photograph of an arbitrary site (field of view) was taken at a magnification of 1000x, and a photograph of a site (field of view) displaced in this cross section from the arbitrary site along the extending direction of plane 100 was taken. 7 photographs of fields of view obtained by sequential displacement were connected in the extending direction of plane 100 to obtain a photograph of a cross section portion having a thickness T of 70 μm and a width W of 500 μm. There were thus obtained photographs of a first cross section portion of certain width W (500 μm) and certain thickness T (70 μm) selected from first cross section 101 and a second cross section portion of certain width W (500 μm) and certain thickness T (70 μm) selected from second cross section 102. Fig. 6 shows one example (Example 1) of the scanning electron microscope (SEM) photograph of the cross section portion.

[0130] Fig. 7 schematically shows the aforementioned cross section portion. As shown in Fig. 7, in the photograph of each of first cross section portion 101a and second cross section portion 102a obtained as described above, measurement was conducted of thicknesses t and lengths s of a plurality of tungsten crystal grains G1 to G4 which intersect with a center line 200 passing through a center of certain width W (500μm) and extending in the direction of certain thickness T (70 μm). Average values of these measurement values were obtained and defined as the average thickness and the average length of the tungsten crystal grains. A ratio of the average length to the average thickness of the tungsten crystal grains was also calculated.

[0131] Table 1 shows the average thickness and the average length as well as the ratio of the average length to the average thickness of the tungsten crystal grains calculated as described above.

(Measurement of Elongation Percentage of Sintered Tungsten Alloy)

[0132] As shown in Fig. 8, a tensile test piece 10 having thickness T was fabricated from the flat plate-like sintered tungsten alloy obtained as a final product in each of Examples 1 to 29 and Comparative Examples 1 to 3, 5, 6, 9, 11 and 12. The gauge length was set at 8 mm with center line 20 centered.

[0133] Tensile test piece 10 thus fabricated was placed in a tensile test machine of model No. 5867 manufactured by Instron Co., Ltd. and a tensile test was conducted in the ambient atmosphere at a test temperature of 20°C at a tensile speed of 300 mm/min. until rupture occurred. A rate of increase in gauge length of the test piece until rupture occurred was defined as the elongation percentage. As to the flat plate-like sintered tungsten alloy obtained as an intermediate product in Example 1 as well, the elongation percentage was measured similarly to the above.

[0134] Table 1 shows the measurement result of the elongation percentage obtained as described above. A parenthesized numerical value in "Example 1" in Table 1 represents the elongation percentage of the flat plate-like sintered tungsten alloy obtained as an intermediate product in Example 1.

(Measurement of X-ray Diffraction Intensity Ratio of (111) Plane of Ni-(Fe, Cu, Co) Phase)

[0135] A test piece having a thickness of 0.5 mm and having a plane of 8 mmx8 mm was fabricated from the flat plate-like sintered tungsten alloy obtained as a final product in each of Examples 1 to 29 and Comparative Examples 1 to 3, 5, 6, 9, 11 and 12.

[0136] The plane of 8 mmx8 mm of the fabricated test piece was irradiated with X rays by using an X-ray diffraction device of model No. SmartLab-2D-PILATUS manufactured by Rigaku Corporation, to measure X-ray diffraction intensities of a (111) plane, a (100) plane, a (110) plane, and a (311) plane of a Ni-(Fe, Cu, Co) phase in the flat plate surface. The X-ray diffraction conditions were such that the used X rays were Cu-Kα, excitation conditions were 45 kV and 200 mA, a collimator of ϕ0.8mm was used, and a measurement method was a θ-2θ method. The plane of 8 mmx8 mm serving as the measurement plane was subjected to mechanical polishing and then alkaline electrolytic polishing.

[0137] Based on the obtained values of the X-ray diffraction intensities of the respective planes, an X-ray diffraction intensity ratio of the (111) plane (assuming that the X-ray diffraction intensities of the (111) plane, the (100) plane, the (110) plane, and the (311) plane are I(111), I(100), I(110), and I(311), respectively, the X-ray diffraction intensity ratio of the (111) plane is a value of [I(111)/{I(111)+I(100)+I(110)+I(311)}]) was calculated.

[0138] Table 1 shows the measurement result of the X-ray diffraction intensity ratio of the (111) plane of the Ni-(Fe, Cu, Co) phase obtained as described above.

[Table 1]

Sample No.	Tungsten crystal grains (intermediate product)			Elongation percentage [%]	X-ray diffraction intensity ratio of (111) plane
	Average thickness [μm]	Average length [μm]	Ratio (average length/average thickness)		
Example 1	5.38	97.42	18.11	27.7(1.0)	0.75
Example 2	5.38	97.42	18.11	21.1	0.73
Example 3	5.38	97.42	18.11	29.7	0.69
Example 4	5.38	97.42	18.11	22.9	0.77
Example 5	5.38	97.42	18.11	27.5	0.74
Example 6	5.38	97.42	18.11	23.6	0.71

(continued)

Sample No.	Tungsten crystal grains (intermediate product)			Elongation percentage [%]	X-ray diffraction intensity ratio of (111) plane
	Average thickness [μm]	Average length [μm]	Ratio (average length/average thickness)		
Example 7	5.81	108.97	18.76	28.6	0.76
Example 8	4.23	94.63	22.37	29.2	0.79
Example 9	3.77	85.71	22.73	29.1	0.79
Example 10	5.88	54.78	9.32	22.3	0.70
Example 11	5.49	68.23	12.43	26.4	0.72
Example 12	4.02	97.46	24.24	32.7	0.75
Example 13	2.85	183.78	64.48	38.7	0.78
Example 14	2.33	227.85	97.79	41.5	0.84
Example 15	2.02	249.24	123.39	22.7	0.89
Example 16	2.02	249.24	123.39	44.3	0.88
Example 17	2.02	249.24	123.39	32.1	0.76
Example 18	9.69	90.50	9.34	20.5	0.68
Example 19	6.34	98.45	15.53	26.6	0.71
Example 20	3.01	185.47	61.62	32.4	0.76
Example 21	4.72	99.72	21.13	23.9	0.78
Example 22	4.98	102.89	20.66	24.5	0.78
Example 23	5.37	93.58	17.43	23.7	0.73
Example 24	5.42	98.25	18.13	24.5	0.76
Example 25	5.32	99.62	18.73	25.1	0.78
Example 26	5.47	96.31	17.61	24.1	0.74
Example 27	2.89	30.87	10.68	23.9	0.68
Example 28	2.94	31.78	10.81	22.7	0.71
Comparative Example 29	2.93	30.94	10.56	23.7	0.70
Comparative Example 1	-	-	-	18.4	0.57
Comparative Example 2	14.00	62.00	4.43	0.9	0.60
Comparative Example 3	5.38	97.42	18.11	14.5	0.71
Comparative Example 4	5.38	97.42	18.11	-	-
Comparative Example 5	5.38	97.42	18.11	7.7	0.81
Comparative Example 6	5.38	97.42	18.11	17.2	0.63
Comparative Example 9	6.22	25.71	4.13	18.7	0.63

(continued)

Sample No.	Tungsten crystal grains (intermediate product)			Elongation percentage [%]	X-ray diffraction intensity ratio of (111) plane
	Average thickness [μm]	Average length [μm]	Ratio (average length/average thickness)		
Comparative Example 11	2.02	249.24	123.39	13.7	0.91
Comparative Example 12	2.02	249.24	123.39	-	-

[0139] From Table 1, it can be seen that the sample in each Example of the present invention exhibits a high elongation percentage.

[0140] It can also be seen that a value of the X-ray diffraction intensity ratio of the (111) plane of the Ni-(Fe, Cu, Co) phase is 0.68 or more and 0.9 or less in the sample in each Example of the present invention.

[0141] It should be understood that the embodiments and the examples disclosed herein are illustrative and not limitative in any respect. The scope of the present invention is defined by the terms of the claims, rather than the embodiments and the examples above, and is intended to include any changes and modifications within the scope and meaning equivalent to the terms of the claims.

INDUSTRIAL APPLICABILITY

[0142] The sintered tungsten alloy of the present invention is used as a radiation shield material in radiation medical devices, nuclear reactor-related devices and the like.

REFERENCE SIGNS LIST

[0143] 1 sintered tungsten alloy; 100 plane; 101 first cross section; 101 a first cross section portion; 102 second cross section; 102a second cross section portion; 200 center line; G1 to G4 tungsten crystal grain; T, To thickness; W width; t thickness; s length.

Claims

1. A flat plate-like sintered tungsten alloy, containing 85% by mass or more and 98% by mass or less of tungsten, 1.4% by mass or more and 11% by mass or less of nickel, and 0.6% by mass or more and 6% by mass or less of at least one substance selected from the group consisting of iron, copper and cobalt, wherein
an elongation percentage of the flat plate-like sintered tungsten alloy in a planar direction is 20% or more.

2. The sintered tungsten alloy according to claim 1, wherein
a thickness of the flat plate-like sintered tungsten alloy is 1.5 mm or smaller.

3. The sintered tungsten alloy according to claim 1, wherein
an X-ray diffraction intensity ratio of a (111) plane of a Ni-(Fe, Cu, Co) phase in a flat plate surface of the flat plate-like sintered tungsten alloy (assuming that X-ray diffraction intensities of the (111) plane, a (100) plane, a (110) plane, and a (311) plane are I(111), I(100), I(110), and 1(311), respectively, the X-ray diffraction intensity ratio of the (111) plane is a value of [I(111)/{I(111)+I(100)+I(110)+I(311)}]) is 0.68 or more and 0.9 or less.

FIG.1

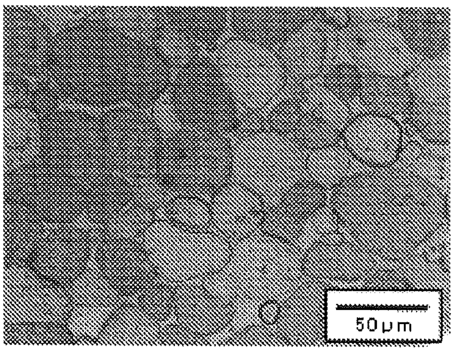


FIG.2

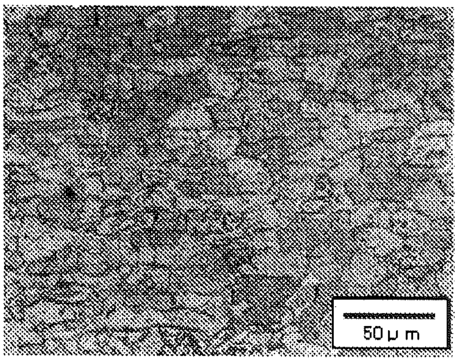


FIG.3

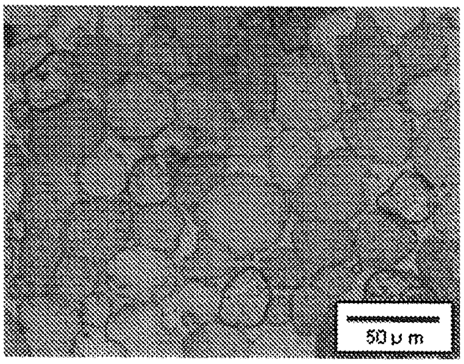


FIG.4

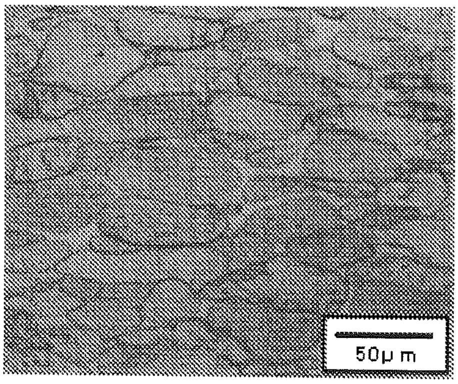
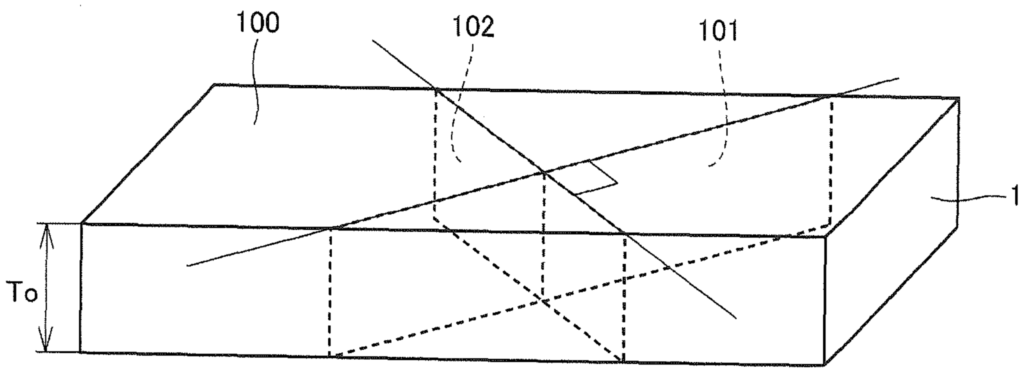


FIG.5



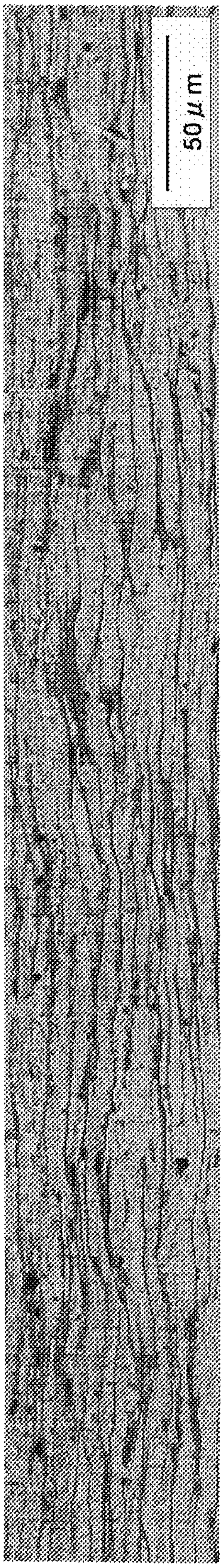


FIG.6

FIG.7

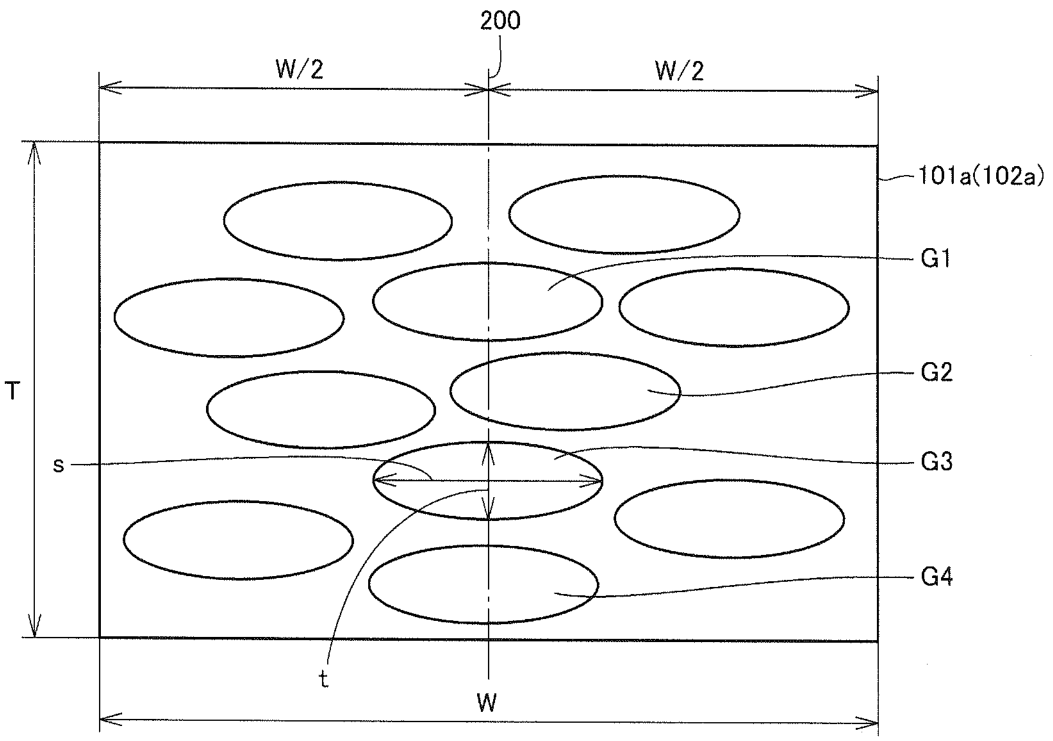
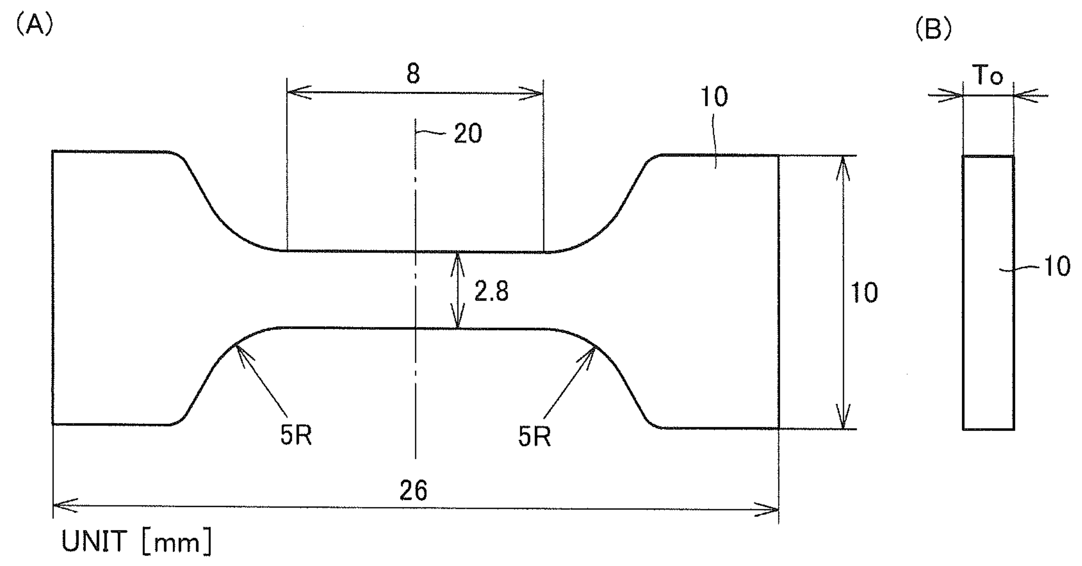

200
W/2
W/2
101a(102a)
G1
G2
G3
G4
T
s
t
W

FIG.8


(A)
(B)
8
To
10
20
10
2.8
10
5R
5R
26
UNIT [mm]

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2012/080565

A. CLASSIFICATION OF SUBJECT MATTER

C22C27/04(2006.01)i, *B22F3/24*(2006.01)i, *C22C1/04*(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)

C22C27/04, B22F3/24, C22C1/04, 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	1996-2013
Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 52-37503 A (The United States of America), 23 March 1977 (23.03.1977), claims; page 3, upper left column, lines 1 to 2; page 4, upper left column, line 2 to lower left column, line 17; page 4, lower right column, line 12 to page 6, lower left column, line 5; table 2 & US 3979234 A & GB 1529899 A & DE 2641997 A & FR 2324748 A & CA 1065653 A	1-3
X	JP 10-219414 A (The Japan Steel Works, Ltd.), 18 August 1998 (18.08.1998), claims 1 to 3; paragraphs [0002], [0007], [0008], [0013]; table 1, No.1 to 3, 5, 7, 8 (Family: none)	1-3

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

* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 08 January, 2013 (08.01.13)	Date of mailing of the international search report 15 January, 2013 (15.01.13)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/080565

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 01-142048 A (Cime Bocuze), 02 June 1989 (02.06.1989), claims; page 2, upper left column, line 10 to lower right column, line 3; page 3, upper left column, lines 3 to 16; page 4, lower left column; tables, cycles 2 to 4 & US 4938799 A & US 4960563 A & EP 313484 A1 & FR 2622209 A & BR 8805467 A & IN 171726 A & KR 10-1995-0008693 B & CN 1033651 A & DK 587288 A0	1-3
X	JP 03-226541 A (Mitsubishi Materials Corp.), 07 October 1991 (07.10.1991), claims; page 3, upper right column, line 13 to page 4, right column, line 13; table 1, kind types 6 to 9 (Family: none)	1-3
X	JP 06-316706 A (The Japan Steel Works, Ltd.), 15 November 1994 (15.11.1994), claims 1, 2; paragraphs [0002], [0009] to [0013]; table 1 (Family: none)	1-3
X	JP 06-192804 A (Poongsan Corp.), 12 July 1994 (12.07.1994), claims 1 to 7; paragraph [0004]; tables 1 to 4 & US 5294269 A & KR 10-1995-0005290 B1	1-3
X	JP 04-36428 A (Nippon Yakin Kogyo Co., Ltd.), 06 February 1992 (06.02.1992), claims; table 1 (Family: none)	1-3
X	JP 04-36436 A (Nippon Yakin Kogyo Co., Ltd.), 06 February 1992 (06.02.1992), claims; table 1 (Family: none)	1-3
X	JP 04-36437 A (Nippon Yakin Kogyo Co., Ltd.), 06 February 1992 (06.02.1992), claims; table 1 (Family: none)	1-3
X	JP 04-2736 A (The Japan Steel Works, Ltd.), 07 January 1992 (07.01.1992), claims; fig. 2, 4 (Family: none)	1-3
X	JP 03-173738 A (Nippon Yakin Kogyo Co., Ltd.), 29 July 1991 (29.07.1991), claims; table 1 (Family: none)	1-3

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2012/080565

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 03-173727 A (Nippon Yakin Kogyo Co., Ltd.), 29 July 1991 (29.07.1991), claims; table 1 (Family: none)	1-3
X	JP 02-122026 A (Nippon Yakin Kogyo Co., Ltd.), 09 May 1990 (09.05.1990), claims; table 1; fig. 2 (Family: none)	1-3
X	JP 02-122048 A (Nippon Yakin Kogyo Co., Ltd.), 09 May 1990 (09.05.1990), claims; table 1 (Family: none)	1-3
X	JP 05-263163 A (The Japan Steel Works, Ltd.), 12 October 1993 (12.10.1993), claims 1 to 3; paragraph [0008]; table 1 (Family: none)	1-3
A	JP 2002-30372 A (Allied Material Corp.), 31 January 2002 (31.01.2002), claims 1 to 5; paragraphs [0002] to [0007], [0029], [0030]; table 1 (Family: none)	1-3
A	JP 2005-163112 A (Nippon Paint Co., Ltd.), 23 June 2005 (23.06.2005), claims 1 to 9; paragraphs [0003] to [0005] (Family: none)	1-3

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 9071828 A **[0003] [0005]**
- JP 9235641 A **[0004] [0005]**