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(54) MOLYBDENUM MATERIAL

(57) Provided is an industrially advantageous molybdenum material which is capable of causing secondary recrystallization to occur at a temperature lower than conventional and which, after the secondary recrystallization, can have a structure that comprises giant crystal grains with less grain boundaries and thus is excellent in creep resistance. The molybdenum material has, in at least a part thereof, a portion having a region where the peak intensities of the (110) and (220) diffraction planes are each less than the peak intensity of the (211) diffraction plane, as measured by X-ray diffraction, in a region at a depth of one-fifth of the entire thickness in a plate thickness direction from a surface.

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Description

Technical Field

[0001] This invention relates to a molybdenum material.

Background Art

[0002] There are cases where a molybdenum material is used at a portion which becomes high in temperature and thus requires a heat-resistant material such as a high-temperature structural or component material. However, in the case of a pure molybdenum material in which a specific element is not intentionally added to the material, if it is used at about 1000°C or more, it is recrystallized into an equiaxed grain structure. If the equiaxed grain structure is formed, grain boundary sliding tends to occur so that creep resistance decreases. As a result, deformation tends to occur.

[0003] Therefore, when the molybdenum material is used at a high temperature of 1000°C or more, it is necessary to improve the creep resistance at high temperature.

[0004] As a method for improving the creep resistance of the molybdenum material at high temperature, there is known either a method for raising the recrystallization temperature above the use temperature or a method for achieving a structure which is excellent in creep resistance even after recrystallization.

[0005] Of these, as the method for raising the recrystallization temperature, there is known, as described in Non-Patent Document 1, a method for raising the primary recrystallization temperature by the use of a TZM alloy (molybdenum alloy containing titanium, zirconium, and carbon) (Non-Patent Document 1). However, while the recrystallization temperature of the TZM alloy is about 1400°C and thus is higher than that of the pure molybdenum material, the TZM alloy forms an equiaxed grain structure after recrystallization and thus is easily deformed like the pure molybdenum material at the recrystallization temperature or higher.

[0006] As the method for achieving a material which is excellent in creep resistance even after recrystallization, there is known a combination of Al, Si, and K as described in Non-Patent Document 2 or, as described in Non-Patent Document 3, a method of applying high-rate plastic working to a molybdenum sintered body added with a rare earth oxide such as La_2O_3 so that the structure after recrystallization becomes a laminated structure of elongated coarse grains which are elongated in a working direction (Non-Patent Documents 2 and 3). However, the additive and the structure control for the property improvement may cause the occurrence of cracks in the plastic working, such as forging or rolling, of the molybdenum material to adversely affect the product yield and may further cause anisotropy in bending properties or the like due to structural anisotropy, and therefore, the size of the molybdenum material should be limited. Further, if, as in the case of a firing floor plate, the molybdenum material is used in contact with a firing workpiece or the like made of other elements, the firing workpiece or the like in contact with the molybdenum material and the additive in the molybdenum material may react with each other and therefore there is a possibility that the kind of firing workpiece may be limited.

[0007] On the other hand, as a method for improving the creep resistance using a pure molybdenum material excellent in plastic workability, there is a method of using enlargement of crystal grains due to secondary recrystallization. This is because if the crystal grains are enlarged, grain boundaries are reduced in number so that grain boundary sliding is difficult to occur. As a striking example, a single crystal material can be given.

[0008] Herein, the secondary recrystallization will be explained. For example, in the case of a molybdenum material, a phenomenon that a fibrous structure formed by plastic working such as rolling is newly changed into a crystal grain of about 20 to 30μm by a heat treatment at 1000°C to 1100°C using as a nucleus a strain generated by the plastic working is called primary recrystallization or simply recrystallization while a phenomenon that a material comprising primary recrystallized grains is heat-treated at a higher temperature so that the adjacent primary recrystallized grains repeat combination and growth to be changed into a giant crystal grain is called secondary recrystallization (Non-Patent Document 4).

[0009] More specifically, primary recrystallized grains of about several ten μm are gradually enlarged to several ten μm to several hundred μm while being supplied with thermal energy and, when, for example, they reach a certain temperature or they are heated at a certain temperature for a long time, they rapidly grow into a crystal grain on the order of mm or more. This rapid grain enlargement phenomenon is called secondary recrystallization.

[0010] In view of this, in Patent Document 1, a molybdenum plate member with a purity of 99.9% or more containing substantially no additives is subjected to a grain control treatment for 0.5 to 5 hours in a hydrogen flow at 2250°C, thereby forming giant disk-shaped crystal grains each having a diameter of 15 to 150mm, so that the plate member can be excellent in creep resistance at 1800°C (Patent Document 1).

Prior Art Document

Patent Document

[0011]

Patent Document 1: JP-A-S61-143548

Non-Patent Document

[0012]

Non-Patent Document 1: T. Mrotzek et.al., "Hardening mechanisms and recrystallization behaviour of several molybdenum alloys" International Journal of Refractory Metals & Hard Materials, 2006, (24), p298-305.
Non-Patent Document 2: Y. Fukasawa et.al., "Very High Temperature Creep Behavior Of P/M Molybdenum Alloys", Proceedings of the 11th International Plansee Seminar, vol.1 1985, p295-308.
Non-Patent Document 3: R. Bianco et.al., "Mechanical Properties of Oxide Dispersion Strengthened (ODS) Molybdenum", Molybdenum and Molybdenum Alloys Edited by A. Crowson, E.S. Chen, J.A. Shields, and P.R. Subramanian, 1998, p125-142.
Non-Patent Document 4: "Powder and Powder Metallurgy Glossary" edited by The Japan Society of Powder and Powder Metallurgy, The Nikkan Kogyo Shimbun, Ltd., 2001, p558-559.

Summary of the Invention

Problem to be Solved by the Invention

[0013] The technique described in Patent Document 1 uses no additives and thus is free of the problem of the occurrence of cracks in the plastic working to cause the reduction in product yield and the problem of the reaction with the firing workpiece and, further, the technique does not require the high-rate plastic working and thus is free of the structural anisotropy and the anisotropy in properties. Therefore, this technique can be said to be an excellent technique.

[0014] However, in Patent Document 1, the heat treatment temperature required for causing the secondary recrystallization of the molybdenum plate member is 2250°C which is quite high in consideration of the primary recrystallization start temperature being 1000°C. Therefore, in terms of the productivity and the energy cost, it is desirable to lower the heat treatment temperature required for causing the secondary recrystallization.

[0015] This invention has been made in view of the above-mentioned problem and it is an object of this invention to provide an industrially advantageous molybdenum material which is capable of causing secondary recrystallization to occur at a temperature lower than conventional and which, after the secondary recrystallization, can have a structure that comprises giant crystal grains with less grain boundaries and thus is excellent in creep resistance.

Means for Solving the Problem

[0016] In order to solve the above-mentioned problem, the present inventors have paid attention to the relationship between the intensities of crystal diffraction planes by X-ray diffraction of a molybdenum material and the secondary recrystallization behavior of the molybdenum material and, as a result of intensive studies, have found that there is a significant relationship between the peak intensities of specific crystal diffraction planes in a certain region in a thickness direction of the molybdenum material and the secondary recrystallization temperature of the molybdenum material.

[0017] Further, the present inventors have found that enlargement of crystal grains due to secondary recrystallization can be achieved at a temperature lower than that of the prior art by controlling those peak intensities, and have completed this invention.

[0018] According to a first aspect of the present invention, there is provided a molybdenum material characterized by having, in at least a part thereof, a portion having a region where peak intensities of (110) and (220) diffraction planes are each less than a peak intensity of a (211) diffraction plane, as measured by X-ray diffraction, in a region at a depth of one-fifth of an entire thickness in a thickness direction from a surface.

[0019] According to a second aspect of the present invention, there is provided a molybdenum material characterized by being obtained by heat-treating the molybdenum material according to the first aspect at 1700°C or more, wherein the average grain size of crystal grains in a cross-section of the plate member by a linear analysis method is 15mm or more.

[0020] According to a third aspect of the present invention, there is provided a heating furnace structural member characterized by comprising the molybdenum material according to the first or second aspect.

[0021] According to a fourth aspect of the present invention, there is provided a firing floor plate characterized by comprising the molybdenum material according to the first or second aspect.

Effect of the Invention

[0022] According to this invention, it is possible to provide an industrially advantageous molybdenum material which is capable of causing secondary recrystallization to occur at a temperature lower than conventional and which, after the secondary recrystallization, can have a structure that comprises giant crystal grains with less grain boundaries and thus is excellent in creep resistance.

Brief Description of the Drawings

[0023]

Fig. 1 is a perspective view showing surfaces of a molybdenum plate member of this invention and a rolling direction.
Fig. 2 is a partial perspective view of the molybdenum plate member of this invention.
Fig. 3 is a diagram for explaining the principle of a linear analysis method.
Fig. 4A is an exemplary diagram showing the structural shape and size of the molybdenum plate member of this invention, wherein the structural shape and size after rolling are shown.
Fig. 4B is an exemplary diagram showing the structural shape and size of the molybdenum plate member of this invention, wherein the structural shape and size after primary recrystallization are shown.
Fig. 4C is an exemplary diagram showing the structural shape and size of the molybdenum plate member of this invention, wherein the structural shape and size after secondary recrystallization are shown.
Fig. 5 is a diagram showing the X-ray diffraction results of a molybdenum plate member according to an Example of this invention.
Fig. 6 is a diagram showing the X-ray diffraction results of a molybdenum plate member according to a Comparative Example.
Fig. 7 is a table showing the relationships between the heating temperature and the crystal grain size of molybdenum plate members according to the Example and the Comparative Example.
Fig. 8 is a schematic diagram of a load test for evaluating the creep resistance of the molybdenum plate members according to the Example and the Comparative Example.
Fig. 9 is a table showing the results of the load test of the molybdenum plate members according to the Example and the Comparative Example.

Mode for Carrying Out the Invention

[0024] Hereinbelow, a preferred embodiment of this invention will be described in detail with reference to the drawings.

[0025] As described before, a molybdenum material according to this invention is such that the peak intensities of specific diffraction planes in a certain region in a thickness direction are controlled. Hereinbelow, the conditions of the molybdenum material of this invention will be described in detail by using a plate member as an example.

<Composition>

[0026] The composition of a molybdenum plate member of this invention is sufficient if it is mainly composed of molybdenum.

[0027] Specifically, in consideration of contamination to a material which is brought into contact with the plate member of this invention when used at high temperature, such as a firing workpiece which is heated on the molybdenum plate member of this invention, the plate member of this invention preferably contains 99.9mass% or more molybdenum, but not limited thereto. For example, even in the case of a material in which molybdenum is a main component (98mass% or more), more specifically, for example, even in the case of a plate member containing molybdenum and 0.1 to 2.0mass% lanthanum oxide (La_2O_3) or a plate member containing molybdenum, 0.3 to 1.0mass% titanium, 0.01 to 0.10mass% zirconium, and 0.01 to 0.1mass% carbon, it is also possible to obtain an effect such that secondary recrystallization occurs at a temperature lower than conventional. That is, even if a molybdenum plate member with an additive is in the form of an alloy, the same effect is obtained.

<Manufacturing Method>

[0028] The molybdenum plate member of this invention is obtained by pressing a molybdenum powder and sintering and then applying thereto plastic working such as rolling or forging. Hereinbelow, a method for obtaining the molybdenum plate member by rolling will be described. However, if the peak intensities by X-ray diffraction are controlled according to this invention, the manufacturing method is not limited thereto.

[0029] The molybdenum powder for use in obtaining the molybdenum plate member of this invention preferably has a purity of 99.9mass% or more. The powder properties such as the particle size and bulk density of the material powder and the methods and conditions of a pressing process and a sintering process for obtaining a sintered body are satisfactory if it is possible to obtain a sintered body having a relative density of 90% or more which is a density large enough for plastic working.

[0030] If the relative density of the sintered body is less than 90%, this causes the occurrence of cracks or the like due to voids in the sintered body when plastic working is applied to the sintered body to form a plate member, which is thus not preferable.

[0031] As a molybdenum powder pressing method, for example, using a molybdenum powder having a particle size of 1.0 to 10μm as measured by the Fsss method (Fischer method, Fischer Sub-Sieve Sizer), a pressed body may be formed by the molybdenum powder with use of a known single-shaft press machine, a known cold isostatic press machine (CIP), or the like. As a pressed body sintering method, the above-mentioned pressed body may be sintered by a heat treatment at 1700 to 2000°C in a non-oxidizing atmosphere such as hydrogen, argon, or vacuum.

[0032] When an additive is present in addition to molybdenum as the main component, the powder properties such as the purity and particle size of the additive may be properly set so that the additive is uniformly dispersed in the sintered body and that the yield is not degraded in plastic working after the sintering.

[0033] When rolling the sintered body, the roll-to-roll distance, i.e. the rolling rate (= ((thickness before rolling) - (thickness after rolling)) x 100 / (thickness before rolling), the unit is %), per pass is controlled so that the intensities of specific crystal planes in X-ray diffraction are controlled in a region at a depth of one-fifth of the plate thickness in a plate thickness direction from an arbitrary portion of at least one of upper and lower surfaces, facing each other, of a plate member. A product of this invention is such that, by setting the rolling rate per rolling pass to less than 20% (not including 0), the peak intensities of the (110) and (220) diffraction planes can each be controlled to less than the peak intensity of the (211) diffraction plane, as measured by X-ray diffraction, in a region at a depth of one-fifth of the plate thickness in a plate thickness direction from an arbitrary portion of at least one of upper and lower surfaces, facing each other, of a plate member.

[0034] Herein, the reason for setting the rolling rate to less than 20% per rolling pass is that this condition can surely control the intensities of the specific diffraction planes according to this invention, while if the rolling rate is set to 20% or more, it is difficult to control the intensities of the crystal diffraction planes and further the product yield is reduced due to rolling cracks or the like. The lower limit of the rolling rate per pass is preferably 5% or more and more preferably 15% or more. This is because if it is less than 5%, the number of rolling passes increases to raise the manufacturing cost.

[0035] There is no particular limitation to the thickness of the sintered body for obtaining the molybdenum plate member of this invention. Therefore, for example, the thickness of the sintered body for obtaining the plate member of 20mm thick may be 50mm or 150mm.

[0036] Herein, unless the total rolling rate (= ((thickness of sintered body) - (final thickness of plate member after rolling)) x 100 / (thickness of sintered body), the unit is %) is at least 50% or more, it is difficult to obtain the X-ray diffraction peak intensities of this invention. More preferably, it is 85% or more.

[0037] In order to satisfy the rolling rate per pass and the total rolling rate described above, several tens of times, for example, 20 times, of rolling (number of rolling passes) are required. A surface and inner X-ray diffraction pattern of a molybdenum plate member which is obtained by limiting the rolling rate per pass to 20% largely changes due to many times of rolling (number of rolling passes).

[0038] Fig. 4A shows an exemplary diagram of the structure of an obtained molybdenum plate member, wherein a fibrous structure is exhibited due to the rolling.

<X-ray Diffraction Intensity>

[0039] Next, the X-ray diffraction intensities of crystal planes of a plate member of this invention will be described. Fig. 1 shows a schematic diagram of the plate member. ND plane of the plate member are surfaces to be rolled, i.e. surfaces to be brought into contact with rolling rolls, and correspond to upper and lower surfaces of the plate member as defined in this embodiment.

[0040] The molybdenum plate member of this invention has, in at least a part thereof, a portion having a region where the peak intensities of the (110) and (220) diffraction planes are each less than the peak intensity of the (211) diffraction plane, as measured by X-ray diffraction, in a region at a depth of one-fifth of the plate thickness in a plate thickness direction from at least one of upper and lower surfaces, facing each other, of the plate member.

[0041] That is, an important portion, which significantly affects secondary recrystallization, of the plate member in this invention, i.e. a region in which the X-ray diffraction intensities of the molybdenum plate member are controlled, is, as shown in Fig. 2, set to a region at one-fifth of the plate thickness in a plate thickness direction from an arbitrary portion of at least one of upper and lower surfaces, facing each other, of the plate member.

[0042] Herein, "a region at one-fifth of the plate thickness" represents a range of ±50μm of a depth corresponding to one-fifth from a substantial surface of the plate member, wherein the substantial surface is a surface after removing an oxide which is inevitably produced at a surface of a plastically worked material. The oxide removal is carried out after the rolling and removes an oxide layer of the surface produced during the rolling by a heat-reduction treatment in a hydrogen atmosphere, a chemical treatment using aqua regia, a mixture of hydrofluoric acid and nitric acid, or the like, mechanical removal by cutting, grinding, or the like, or a combination thereof.

[0043] The reason why the control of the intensities of the diffraction planes is carried out for at least one of the upper and lower surfaces, facing each other, of the plate member, i.e. the ND plane in Fig. 1, is that if either one of the upper and lower surfaces is controlled, secondary recrystallization occurs in the entire molybdenum plate member by a heat treatment at 1700°C or more so that the average size of crystal grains in plate cross-sections, i.e. on TD and RD plane in Fig. 1, becomes 15mm or more. Further, the reason for limiting the distance from the plate surface is that it has been found that the X-ray diffraction intensities in the region at one-fifth of the plate thickness from the plate surface significantly affect the secondary recrystallization temperature.

[0044] Details are unclear about the mechanism in which the secondary recrystallization occurs at the temperature lower than conventional by setting the peak intensities of the diffraction planes to the above-mentioned conditions. As recrystallization phenomena, there are primary recrystallization and secondary recrystallization. In the primary recrystallization, strains generated by applying working such as rolling or forging to crystal grains of a molybdenum plate member are released by a heat treatment and crystal grains are newly formed using as nuclei the strains generated by the working. The secondary recrystallization is a phenomenon in which enlargement and combination of the primary recrystallized grains occur. In the case of the molybdenum plate member according to this invention, the factor that largely affects the secondary recrystallization phenomenon is considered to be a state of the molybdenum plate member before the primary recrystallization such that portions to be nuclei for the recrystallization are present in the region where the peak intensities of the crystal diffraction planes satisfy the above-mentioned conditions.

[0045] Herein, while there are cases where only one of the ND plane in Fig. 1 exhibits the X-ray diffraction intensities of this invention as described above, this depends on the plastic working conditions, for example, in the case of rolling of the molybdenum plate member, this depends on conditions for reversal of the upper and lower surfaces and so on when rolling the plate member. On the other hand, when the upper and lower surfaces are uniformly rolled, both ND plane tend to exhibit the X-ray diffraction intensities of this invention.

[0046] The X-ray diffraction intensities in the region at one-fifth of the plate thickness do not necessarily satisfy the above-mentioned conditions over the entire surface of the plate member. If a portion satisfying the above-mentioned conditions is present in at least a part of the surface of the plate member, secondary recrystallization occurs starting from that portion.

<Primary Recrystallization Temperature>

[0047] The primary recrystallization temperature is generally about 1000°C to 1100°C although there is some difference depending on the processing conditions. Also in the case of the plate member of this invention, it is about 1000°C to 1100°C as the conventional one.

[0048] For reference, Fig. 4B shows an exemplary diagram of a primary recrystallized structure. An atmosphere for causing primary recrystallization is not particularly limited as long as it is a non-oxidizing atmosphere. For example, a hydrogen atmosphere, an argon atmosphere, a vacuum atmosphere, or the like can be given and it may alternatively be an atmosphere in a combination thereof.

<Secondary Recrystallization Temperature>

[0049] Next, in order to cause secondary recrystallization of the molybdenum plate member in this invention, it is necessary to carry out a heat treatment at 1700°C or more. This is because, with the current technique, it is difficult to cause secondary recrystallization to occur at less than that temperature, for example, by a heat treatment at 1600°C for 10 hours. The heating time is required to be about 10 hours at 1700°C while, at a temperature above it, secondary recrystallization occurs in a shorter time. An atmosphere for the heat treatment is the same as in the case of the primary recrystallization.

<Grain size after secondary recrystallization>

[0050] After the molybdenum plate member of this invention is heat-treated at 1700°C, the average size of crystal grains in a plate cross-section is preferably 15mm or more. This is because it is the grain size necessary for obtaining excellent creep resistance. In Patent Document 1, the maximum grain size is set to 150mm in terms of economic load for the treatment temperature and time. On the other hand, if the product of this invention is used, grains can be enlarged at a relatively low temperature in a relatively short time and, depending on the conditions, can be formed into a single crystal. Even if the size of the plate member increases, if a heating furnace having a size capable of heat-treating it is prepared, the grain size after secondary recrystallization can be increased according to the size of the plate member and therefore the maximum crystal grain size is not limited.

[0051] The average grain size referred to herein represents a value obtained by drawing three arbitrary lines parallel to plate member upper and lower surfaces of a single test piece as shown in Fig. 3, calculating grain sizes along the respective lines, and averaging them.

[0052] There is basically no limitation to the size of a molybdenum material of this invention. The size of the molybdenum material is determined by manufacturing facilities such as a heating furnace and a plastic working machine such as a rolling, forging, or wire drawing machine. In an experiment by the present inventors, it was possible to obtain a molybdenum material of this invention in the form of a large-size plate member with a length of 1500mm, a width of 1000mm, and a thickness of 20mm as one example.

Examples

[0053] Hereinbelow, this invention will be described in further detail with reference to an Example.

(Example 1 and Comparative Example 1)

[0054] Molybdenum plate members were prepared under various processing conditions and the relationship between the peak intensities in a plate thickness direction and the secondary recrystallization temperature, the creep resistance after secondary recrystallization, and so on were evaluated. Specific sequences were as follows.

<Preparation of Samples of Example 1>

[0055] A molybdenum powder having a purity of 99.9mass% and a particle size of 4μm as measured by the Fsss method was used as a starting material. The molybdenum powder was filled into rubber molds, pressed at a pressure of 2 ton/cm^2 by CIP (Cold Isostatic Pressing), and sintered in a hydrogen atmosphere at 1800°C for 10 hours, thereby obtaining two sintered bodies having a width of 300mm, a length of 400mm, and thicknesses of 20mm and 150mm. The relative densities of the obtained sintered bodies were respectively 94.2% and 94.4%.

[0056] These sintered bodies were heated at 1500°C for 20 minutes and then rolling in two to three passes and reheating at 1200°C were repeated, thereby finally obtaining molybdenum plate members having plate thicknesses of 1.0, 1.5, 2.0, 3.0, 10, and 20mm. In Example 1 of this invention, the plate members having the plate thicknesses of 1.0 to 3.0mm were prepared by rolling the sintered body having the thickness of 20mm while the plate members having the plate thicknesses of 10 and 20mm were prepared by rolling the sintered body having the thickness of 150mm.

[0057] Herein, for each sample of Example 1, the rolling rate (= ((thickness before rolling) - (thickness after rolling)) x 100 / (thickness before rolling), the unit is %) per pass was set to less than 20%, specifically 10 to 19.8%.

[0058] Finally, a surface oxide was removed by aqua regia after a reducing treatment in a hydrogen atmosphere at 800°C and, thereafter, washing with pure water was carried out, thereby obtaining samples of Example 1.

<X-ray Diffraction>

[0059] Then, X-ray diffraction was applied to the obtained samples in the following sequences, thereby measuring the peak intensities in a plate thickness direction.

[0060] First, an ND plane (rolling surface) of each sample was wet-polished using a waterproof abrasive paper sheet (#100 to #1000) and the polished sample was immersed in an electrolyte solution (perchloric acid:ethanol = 1:9) and subjected to electrolytic polishing with a current of 1A for 150 seconds, thereby polishing the sample to a plate thickness direction depth where X-ray diffraction was to be carried out.

[0061] Then, with an X-ray diffraction apparatus (RAD-2X) manufactured by Rigaku Corporation, X-ray diffraction of each sample was carried out using a Cu tube with a tube current of 30mA and a tube voltage of 40kV under the conditions such that scan speed: 1 deg/min, divergence slit: 1 degree, scattering slit: 1 degree, receiving slit: 0.15mm, and measurement angle 2θ = 30 to 120 degrees. Then, the magnitudes of the intensities of the (110), (220), and (211) planes as the output measurement results were compared. The data herein were obtained by automatically performing background processing, smoothing processing, and Kα2 removal of measured raw data using device software.

[0062] Then, again, the above-mentioned polishing was carried out to polish each sample to a plate thickness direction depth where X-ray diffraction was to be carried out and X-ray diffraction was carried out at that depth. This operation was repeated a plurality of times until a predetermined depth was reached, thereby measuring changes in peak density in the plate thickness direction of the ND plane in X-ray diffraction.

[0063] Table 1 shows one example (plate member thickness 1.5mm) of changes in peak density in the plate thickness direction of the ND plane in X-ray diffraction of the obtained molybdenum plate member. Fig. 5 shows a graph representing Table 1.

[Table 1]

	Intensity [cps]		
Plate Thickness Direction Depth from Surface [μm]	(110)	(211)	(220)
97	7347	16019	669
308	1018	21218	79
492	317	13767	22
740	223	9237	15
997	539	16173	36
1200	5338	20851	417
1394	4293	8970	3672

[0064] As is clear from Table 1 and Fig. 5, it is seen that, at the middle in the plate thickness direction, the intensity ratio of (211) is high compared to (110) and (220) and the intensities of (110) and (220) are values close to 0. In a region at 300μm from the surface which corresponds to one-fifth of the plate thickness, the intensities of (110) and (220) are less than the intensity of (211). In the other samples of Example 1, distributions of the crystal planes all showed the same tendency.

[0065] The crystal structure was in a state typified by the exemplary diagram of Fig. 4A.

<Composition Measurement Results>

[0066] Then, the compositions of the obtained samples were measured.

[0067] Specifically, metal components were measured using a plasma emission spectrometer ICPS-8100 manufactured by Shimadzu Corporation. As gas impurities, O and C were measured such that O was measured using TC-600 manufactured by LECO Corporation while C was measured using WC-230 manufactured by LECO Corporation.

[0068] As a result, the composition of each sample was composed of 98.0mass% or more molybdenum and the balance inevitable impurities. Herein, the inevitable impurities were metal impurities of Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni,) Pb, Si, Sn, Ti, Zr, and Zn and gas impurities of O and C. The purity excluding these impurities was defined as a molybdenum purity.

<Preparation of Samples of Comparative Example 1 and X-ray Diffraction>

[0069] In the same manner as in Example 1, two sintered bodies having a width of 300mm, a length of 400mm, and thicknesses of 20mm and 150mm were obtained, then these sintered bodies were heated at 1500°C for 20 minutes, and then rolling in two to three passes and reheating at 1200°C were repeated, thereby finally obtaining molybdenum plate members having plate thicknesses of 1.0, 1.5, 2.0, 3.0, 10, and 20mm. Herein, the rolling rate per pass was set to 20 to 23%. In the same manner as in Example 1, the plate members having the plate thicknesses of 1.0 to 3.0mm were prepared by rolling the sintered body having the thickness of 20mm while the plate members having the plate thicknesses of 10 and 20mm were prepared by rolling the sintered body having the thickness of 150mm, thereby obtaining samples of Comparative Example 1.

[0070] Using the sample having the plate thickness of 1.5mm among the samples of Comparative Example 1, changes in X-ray peak intensity in a plate thickness direction were measured in the same manner as in Example 1, thereby obtaining the results shown in Table 2 and Fig. 6.

[Table 2]

	Intensity [cps]		
Plate Thickness Direction Depth from Surface [μm]	(110)	(211)	(220)
102	25820	5279	7174
285	18506	11157	2099
521	915	10842	78
694	1388	7523	101
903	748	10244	111
1044	7208	12460	689
1311	28830	5000	7096

[0071] As shown in Table 2 and Fig. 6, the sample of Comparative Example 1 was the plate member in which the peak intensities of the (110) and (220) diffraction planes were respectively not less than the peak intensity of the (211) diffraction plane in a region at one-fifth in the plate thickness direction from a surface of the plate member.

<Secondary Recrystallization Temperature Measurement>

[0072] Then, the samples obtained in Example 1 and Comparative Example 1 were heat-treated in a hydrogen atmosphere at 1600 to 2200°C for 1 hour to 10 hours at maximum. Then, the structure of a TD plane (see Fig. 1) of each plate member after the heat treatment was observed to calculate an average grain size using the above-mentioned linear analysis method, thereby evaluating the secondary recrystallization temperature.

[0073] In the samples obtained in Example 1 and Comparative Example 1, primary recrystallization occurred before the above-mentioned temperature was reached, specifically, at 1000°C to 1100°C.

[0074] In the average grain size measurement, the structural observation of the TD plane in Fig. 1 was carried out to calculate the grain size. Each plate member was cut into a test piece having a length of 30mm. The test piece was adjusted by polishing and etching to enable observation of grain sizes and then the grain size was calculated by the linear analysis method. More specifically, three arbitrary lines parallel to plate member upper and lower surfaces of a single test piece were drawn as shown in Fig. 3, then grain sizes were calculated along the respective lines, and the average value thereof was defined as an average grain size of the sample.

[0075] However, crystal grain sizes after secondary recrystallization become 1 mm or more and the structure is as shown in an exemplary diagram of Fig. 4C so that there are cases where it is difficult to specify grain sizes. Therefore, grain sizes of 15mm or more were all indicated as "15mm or more". The results are shown in Fig. 7.

[0076] As is clear from Fig. 7, the grain size becomes 15mm or more by heating at 1700°C or more and for at least 10 hours in the entire region of the TD plane in each sample of Example 1, while, in Comparative Example 1, grains were enlarged to 15mm or more by a heat treatment at 2000°C only in the case of the sample having the plate thickness of 1.0mm and grains of 15mm or more were not obtained unless heating at 2200°C was carried out in the case of the other samples of Comparative Example 1. On the other hand, at 1600°C, the crystal grain sizes were 100μm or less and thus secondary recrystallization did not occur in Example 1 and Comparative Example 1. There was no significant difference among the three arbitrary lines used for measuring the average grain size. The structure having been subjected to the secondary recrystallization was similar to that shown in the exemplary diagram of Fig. 4C.

[0077] For each sample of Example 1, the measurement of the grain size in the molybdenum plate member cross-section was carried out by observing the TD plane. However, the same structure was obtained also on an RD plane.

[0078] In Patent Document 1, there is no description about the rolling conditions, crystal planes, or the like of the molybdenum plate member. However, on checking up with the results this time, it is considered that all the samples of Comparative Example 1 in which the grains were enlarged by heating at 2200°C regardless of the heating time are the plate members substantially corresponding to that of Patent Document 1. That is, it is seen that, in each sample of Example 1, the enlargement of grains occurred at a low temperature compared to the products similar to that of Patent Document 1.

<Creep Resistance Evaluation>

[0079] Then, the creep resistance of the samples of Example 1 and Comparative Example 1 was evaluated based on the deformation amount in a load test at 1800°C.

[0080] Specifically, test pieces of Example 1 were heated in a hydrogen atmosphere at 1800°C for 5 hours to cause secondary recrystallization and were processed to a size of width 20mm x length 150mm. The plate thicknesses were 1.0, 1.5, 2.0, 3.0, 10, and 20mm. Test pieces of Comparative Example 1 were also heat-treated and processed into the predetermined size in the same manner. Secondary recrystallization did not occur in any of the samples of Comparative Example 1.

[0081] Then, as shown in Fig. 8, a test piece 1 was set on tungsten jigs 2 and 2'. The distance between the jigs 2 and 2' was set to 100mm and a load 3 was applied to a middle portion of the test piece on the jigs 2 and 2'. In a test, the load was set to 125g for the thickness 1 mm, 280g for the thickness 1.5mm, 500g for the thickness 2mm, and 1.1 kg for the thickness 3mm. Taking into account the safety of the test, the load was set to 12.5kg for the thicknesses 10mm and 20mm.

[0082] Then, in the state where the load was applied to the test piece, the test piece was heated in a hydrogen atmosphere at 1800°C for 100 hours at maximum and the deformation amount of the sample was measured. The deformation amount is, as shown in Fig. 8, given by a difference between positions of upper surfaces of the test piece 1 before the test and a test piece 1' after the test and was measured using a micro-gauge. Taking into account the safety of the test, the test was stopped when the test piece was deformed by 20mm so that the test under the longer heating time conditions was not performed.

[0083] Fig. 9 shows measured deformation amounts. In the figure, "stop" means that the test was stopped due to the deformation amount having reached 20mm.

[0084] As shown in Fig. 9, the samples of Comparative Example 1 were deformed by 20mm after a lapse of 20 hours regardless of the plate thickness while the samples of Example 1 were hardly deformed even after a lapse of 100 hours and exhibited excellent creep resistance. In Patent Document 1 as prior art, data for the plate thickness 2mm obtained by the same test method is described. However, with the product of this invention, there were obtained excellent results equal to or better than those test results.

(Comparative Example 2)

[0085] With respect to the plate member having the thickness of 1.5mm among the plate members of Example 1, regions at a depth of one-fifth + 50μm from both surfaces were removed by polishing. Then, the plate member was heat-treated in a hydrogen atmosphere at 1600 to 2200°C for 1 hour to 10 hours at maximum. Then, the structure of a TD surface (see Fig. 1) of the sample after the heat treatment was observed to calculate an average grain size using the above-mentioned linear analysis method, thereby evaluating the secondary recrystallization temperature.

[0086] As a result, this plate member, like the samples of Comparative Example 1, did not cause enlargement of grains due to secondary recrystallization unless heated to 2200°C.

[0087] This is considered to be because nuclei serving to cause secondary recrystallization to occur at a temperature lower than conventional were formed in regions at a depth of one-fifth from both surfaces of the sample of Example 1.

[0088] From the results described above, it is seen that, by controlling the peak intensities of diffraction planes at a plane parallel to a rolling direction in a region at a depth of one-fifth of the plate thickness in a plate thickness direction from an arbitrary portion of at least one of upper and lower surfaces, facing each other, of a molybdenum plate member, it is possible to obtain an industrially advantageous molybdenum plate member which is capable of causing secondary recrystallization to occur at a temperature lower than that of the prior art (Patent Document 1) and which is excellent in creep resistance.

Industrial Applicability

[0089] While this invention has been described with reference to the embodiment and the Example, this invention is not limited thereto.

[0090] It is apparent that those skilled in the art can think of various changes and improvements in the scope of this invention and it is understood that those are also included in the scope of this invention.

[0091] For example, while the molybdenum plate member is manufactured by rolling in the above-mentioned embodiment and Example, even a molybdenum plate member by forging or the like can similarly cause secondary recrystallization as long as the peak control of X-ray diffraction planes described in the embodiment and the Example is carried out.

[0092] In the above-mentioned embodiment and Example, the shape of molybdenum is the plate shape. However, even in the case of a shape other than the plate shape, for example, a wire or rod shape, since the recrystallization phenomenon is basically the same, it is considered to be possible to cause secondary recrystallization to occur at a low temperature similarly as long as the peak control of X-ray diffraction planes described above is carried out. In this case, it is satisfactory if the peak intensities of X-ray diffraction planes in a region at a depth of one-fifth of the diameter of a linear rod toward the central axis from a surface of the linear rod satisfy the above-mentioned conditions.

[0093] This invention is applicable to high-temperature structural and component materials, in particular, a wall surface forming a high temperature furnace and other components supporting constituent materials, more specifically, materials forming a high temperature furnace body, such as a base plate, a heater, a reflector, and fasteners such as bolts, and firing floor plates for use in the manufacture of sintered products such as ceramics, MIM (metal injection molding) products , and rare earth magnets.

[0094] Further, this invention is also applicable to members of a single crystal growth furnace, specifically, for example, members forming a single crystal growth furnace for manufacturing a sapphire single crystal by melting alumina and members for use in lifting a sapphire single crystal because of less deformation after secondary recrystallization.

Description of Symbols

[0095]

1	test piece before creep test
1’	test piece after creep test
2, 2’	creep test jigs
3	creep test load

Claims

1. A molybdenum material **characterized by** having, in at least a part thereof, a portion having a region where peak intensities of (110) and (220) diffraction planes are each less than a peak intensity of a (211) diffraction plane, as measured by X-ray diffraction, in a region at a depth of one-fifth of an entire thickness in a thickness direction from a surface.

2. The molybdenum material according to claim 1, **characterized in that** the molybdenum content is 98.0mass% or more.

3. The molybdenum material according to claim 1 or 2, **characterized by** having a shape of a plate member and having, in at least a part thereof, a portion having a region where peak intensities of (110) and (220) diffraction planes are each less than a peak intensity of a (211) diffraction plane, as measured by X-ray diffraction, in a region at a depth of one-fifth of a plate thickness in a plate thickness direction from at least one of upper and lower surfaces, facing each other, of the plate member.

4. The molybdenum material according to claim 1 or 2, **characterized by** having a shape of a linear rod and having, in at least a part thereof, a portion having a region where peak intensities of (110) and (220) diffraction planes are each less than a peak intensity of a (211) diffraction plane, as measured by X-ray diffraction, in a region at a depth of one-fifth of a diameter toward a central axis from a surface.

5. The molybdenum material according to any one of claims 1 to 4, **characterized in that** an average grain size in a cross-section by a linear analysis method becomes 15mm or more when heat-treated at 1700°C or more.

6. A molybdenum material **characterized by** being obtained by heat-treating the molybdenum material according to any one of claims 1 to 5 at 1700°C or more, wherein the average grain size in a cross-section by a linear analysis method is 15mm or more.

7. A heating furnace structural member **characterized by** comprising the molybdenum material according to any one of claims 1 to 6.

8. A firing floor plate **characterized by** comprising the molybdenum material according to claim 3.

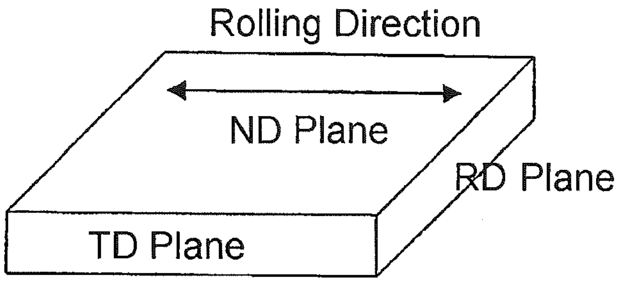

FIG. 1

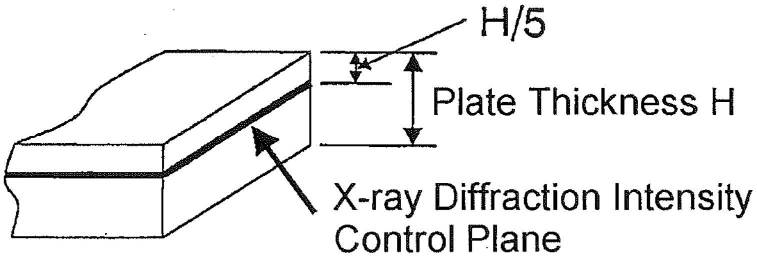

FIG. 2

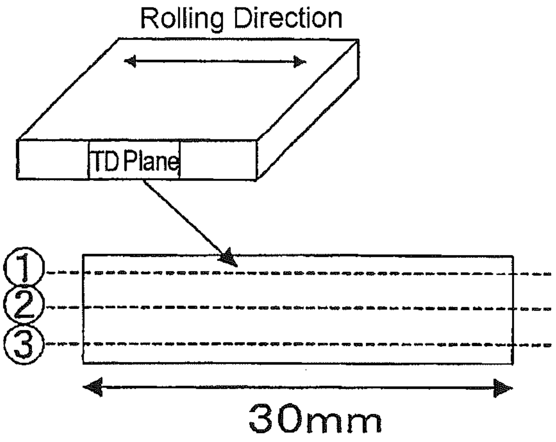

FIG. 3

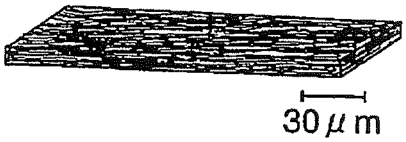

FIG. 4A

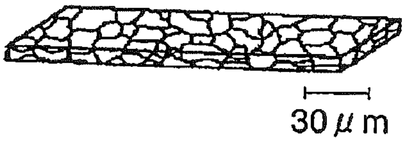

FIG. 4B

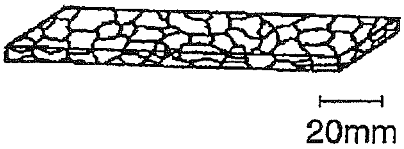

FIG. 4C

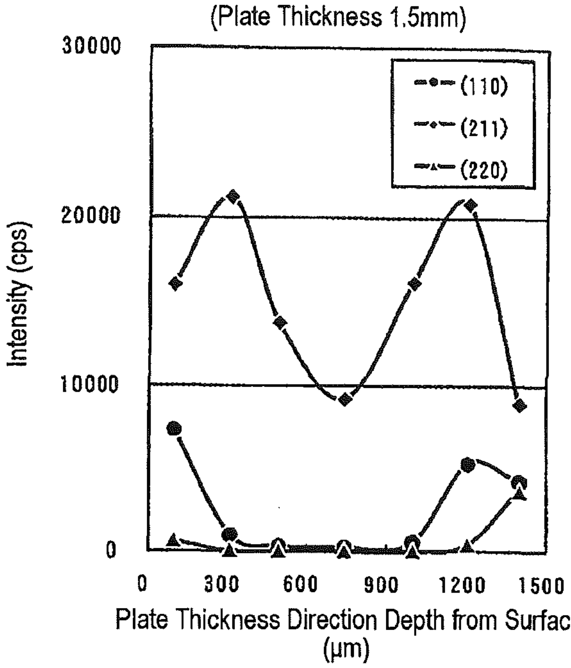
(Plate Thickness 1.5mm)
30000
20000
10000
0
Intensity (cps)
(110)
(211)
(220)
0
300
600
900
1200
1500
Plate Thickness Direction Depth from Surface (μm)

FIG. 5

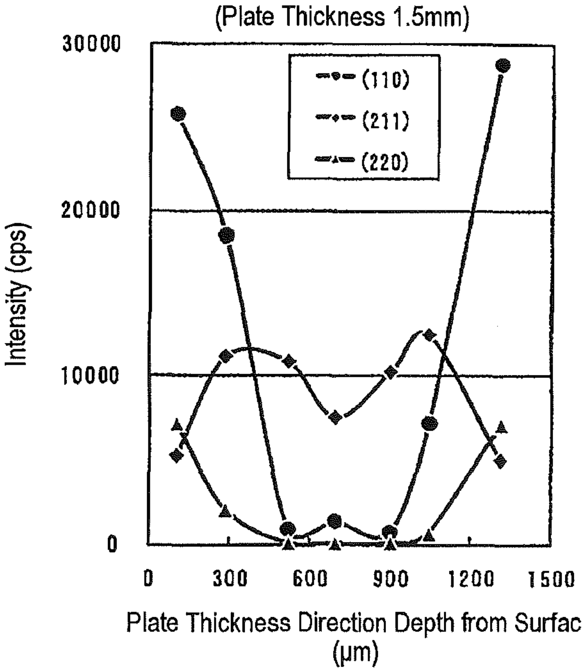
(Plate Thickness 1.5mm)
30000
20000
10000
0
Intensity (cps)
(110)
(211)
(220)
0
300
600
900
1200
1500
Plate Thickness Direction Depth from Surface (μm)

FIG. 6

Plate Thickness (mm)	Sintered Body Thickness (mm)		Crystal Grain Size per Temperature/Time																			
			1600°C				1700°C				1800°C				2000°C				2200°C			
			1h	2h	5h	10h	1h	2h	5h	10h	1h	2h	5h	10h	1h	2h	5h	10h	1h	2h	5h	10h
1.0	30	Example 1	40µm	50µm	55µm	60µm	50µm	4mm	10mm	>15mm	1mm	>15mm	>15mm	>15mm	10mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm
		Comparative Example 1	25µm	25µm	30µm	30µm	25µm	30µm	30µm	35µm	30µm	30µm	35µm	40µm	40µm	40µm	45µm	>15mm	>15mm	>15mm	>15mm	>15mm
1.5	30	Example 1	30µm	35µm	55µm	70µm	2mm	3.5mm	8mm	>15mm	1mm	>15mm	>15mm	>15mm	10mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm
		Comparative Example 1	25µm	25µm	25µm	30µm	25µm	25µm	30µm	30µm	30µm	30µm	30µm	40µm	40µm	40µm	45µm	45µm	>15mm	>15mm	>15mm	>15mm
2.0	30	Example 1	50µm	50µm	60µm	80µm	1mm	4mm	10mm	>15mm	2mm	10mm	>15mm	>15mm	12mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm
		Comparative Example 1	25µm	25µm	25µm	32µm	25µm	25µm	32µm	35µm	30µm	30µm	35µm	40µm	40µm	40µm	45µm	45µm	>15mm	>15mm	>15mm	>15mm
3.0	30	Example 1	45µm	55µm	55µm	70µm	50µm	2.5mm	8mm	>15mm	2mm	8mm	>15mm	>15mm	10mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm
		Comparative Example 1	25µm	25µm	25µm	30µm	25µm	25µm	30µm	35µm	30µm	30µm	35µm	35µm	35µm	40µm	45µm	1mm	>15mm	>15mm	>15mm	>15mm
10	150	Example 1	30µm	60µm	75µm	80µm	2.5mm	6mm	10mm	>15mm	4mm	10mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm
		Comparative Example 1	30µm	30µm	30µm	35µm	100µm	120µm	150µm	200µm	200µm	250µm	300µm	1mm	250µm	1mm	2mm	10mm	>15mm	>15mm	>15mm	>15mm
20	150	Example 1	35µm	40µm	65µm	100µm	2mm	6mm	8mm	>15mm	5mm	10mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm	>15mm
		Comparative Example 1	30µm	30µm	30µm	35µm	100µm	120µm	150µm	150µm	200µm	250µm	280µm	1.5mm	250µm	800µm	1mm	11mm	>15mm	>15mm	>15mm	>15mm

FIG. 7

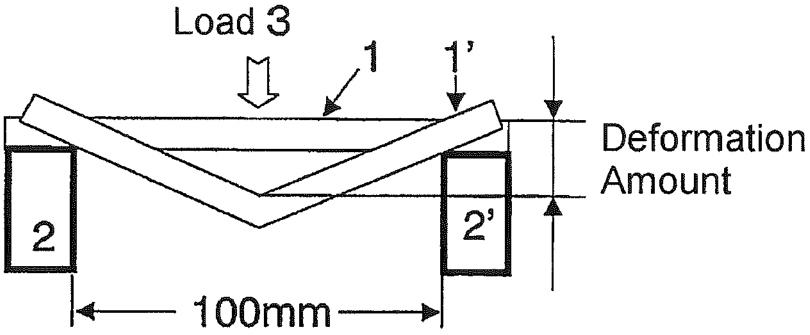

FIG. 8

Plate Thickness (mm)	Sintered Body Thickness (mm)		Crystal Grain Size	Deformation Amount per Time (mm)						
				1800°C						
				0h	10h	20h	40h	60h	80h	100h
1.0	30	Example 1	>15mm	0	0.01	0.03	0.05	0.10	0.13	0.15
		Comparative Example 1	35μm	0	8	20	stop	stop	stop	stop
1.5	30	Example 1	>15mm	0	0.01	0.02	0.06	0.12	0.18	0.20
		Comparative Example 1	30μm	0	10	20	stop	stop	stop	stop
2.0	30	Example 1	>15mm	0	0.01	0.05	0.06	0.15	0.20	0.25
		Comparative Example 1	35μm	0	10	20	stop	stop	stop	stop
3.0	30	Example 1	>15mm	0	0.02	0.06	0.08	0.16	0.23	0.25
		Comparative Example 1	35μm	0	12	20	stop	stop	stop	stop
10	150	Example 1	>15mm	0	0.01	0.02	0.05	0.09	0.12	0.15
		Comparative Example 1	300μm	0	8	20	stop	stop	stop	stop
20	150	Example 1	>15mm	0	0	0.01	0.03	0.06	0.08	0.10
		Comparative Example 1	280μm	0	6	20	stop	stop	stop	stop

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/050325

A. CLASSIFICATION OF SUBJECT MATTER
C22C27/04(2006.01)i, *C22F1/18*(2006.01)i, *C22F1/00*(2006.01)n, *C22F1/02*(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, C22F1/18, C22F1/00, C22F1/02

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

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 2008/084863 A1 (Nippon Steel Materials Co., Ltd.), 17 July 2008 (17.07.2008), paragraphs [0051] to [0057] & US 2010/0108501 A1 & KR 10-2009-0098908 A & CN 101611165 A	1-5 6-8
X A	JP 10-72602 A (Nippon Tangsten Co., Ltd.), 17 March 1998 (17.03.1998), paragraph [0017] (Family: none)	1-5,7,8 6
X	JP 5-140615 A (Toho Kinzoku Co., Ltd.), 08 June 1993 (08.06.1993), paragraphs [0001], [0007] to [0009] (Family: none)	1-8

☒ 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
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"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 29 March, 2012 (29.03.12)	Date of mailing of the international search report 17 April, 2012 (17.04.12)
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/JP2012/050325

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 9-196570 A (Tokyo Tungsten Co., Ltd.), 31 July 1997 (31.07.1997), entire text (Family: none)	1-8
A	JP 7-54093 A (Tokyo Tungsten Co., Ltd.), 28 February 1995 (28.02.1995), entire text (Family: none)	1-8

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

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- JP S61143548 A **[0011]**

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- **Y. FUKASAWA.** Very High Temperature Creep Behavior Of P/M Molybdenum Alloys. *Proceedings of the 11th International Plansee Seminar,* 1985, vol. 1, 295-308 **[0012]**
- Mechanical Properties of Oxide Dispersion Strengthened (ODS) Molybdenum. **R. BIANCO.** Molybdenum and Molybdenum Alloys. 1998, 125-142 **[0012]**
- Powder and Powder Metallurgy Glossary. The Nikkan Kogyo Shimbun, Ltd, 2001, 558-559 **[0012]**