

DESCRIPTION

TITLE OF INVENTION:

Molybdenum-Containing Material

5 TECHNICAL FIELD

[0001] The present disclosure relates to a molybdenum-containing material. The present application claims the priority based on Japanese Patent Application No. 2023-176718 filed on October 12, 2023. The entire contents of the description in this Japanese patent application are incorporated herein by reference.

10 BACKGROUND ART

[0002] Conventional molybdenum plates are disclosed in, for example, Japanese Patent Laying-Open No. 2002-69628 (PTL 1), International Publication No. 2019-176962 (PTL 2), Japanese Patent Laying-Open No. 2005-133198 (PTL 3), Japanese Patent Laying-Open No. 2015-221937 (PTL 4), Japanese Patent Publication No. 2-24901 (PTL 5), and Japanese Patent Laying-Open No. 2012-201930 (PTL 6).

CITATION LIST

PATENT LITERATURE

[0003] PTL 1: Japanese Patent Laying-Open No. 2002-69628

PTL 2: International Publication No. 2019-176962

20 PTL 3: Japanese Patent Laying-Open No. 2005-133198

PTL 4: Japanese Patent Laying-Open No. 2015-221937

PTL 5: Japanese Patent Publication No. 2-24901

PTL 6: Japanese Patent Laying-Open No. 2012-201930

SUMMARY OF INVENTION

25 [0004] A molybdenum-containing material of the present disclosure has a crystal grain size of 25 μm or more, a density of 10.15 g/cm^3 or more, a molybdenum content rate of 99.95 mass % or more, and a ratio between an intragranular tungsten content rate and a grain-boundary tungsten content rate (intragranular W/grain-boundary W) of 0.8 or less.

BRIEF DESCRIPTION OF DRAWINGS

[0005] Fig. 1 is a photograph showing a structure example of primary recrystallized grains of a molybdenum-containing material.

5 Fig. 2 is a photograph showing a structure example of secondary recrystallized grains of the molybdenum-containing material.

Fig. 3 is a diagram of an apparatus for measuring ease of deformation at high temperature.

DESCRIPTION OF EMBODIMENTS

[0006] [Problem to be Solved by the Present Disclosure]

10 A high-quality molybdenum material has been desired.

[0007] [Description of Embodiments of the Present Disclosure]

First, embodiments of the present disclosure will be listed and described.

15 [0008] PTL 1 discloses a technique of covering a side surface and a backing plate (BP) surface of a sputtering target with metal foil or a plate, thereby suppressing the generation of particles.

[0009] PTL 2 discloses that a molybdenum-containing material having a content rate of 99.999% or more, a relative density of 98% or more, an average grain size of 45 μm or less, and a radiation dose of 0.03 cph/cm² allows less particles to be generated.

20 [0010] PTL 3 discloses that a molybdenum-containing material having a content rate of 99.99% or more and a relative density of 98% or more allows less particles to be generated. The molybdenum-containing material is produced by HIP.

[0011] PTL 4 discloses that an aspect ratio of a crystal structure of a molybdenum-containing material is 3 or more, whereby a sputtering rate can be adjusted and a long-life target can be obtained.

25 [0012] PTL 5 discloses that an average grain size of a molybdenum-containing material is within the range of 15 to 150 μm and a thickness direction of crystal grains is 1/5 or more of a plate thickness.

[0013] PTL 6 discloses that a region where a peak intensity of each of (110) and (220) is less than a peak intensity of (211) in X-ray diffraction measurement is present at a

depth of 1/5 in a plate thickness direction from a surface of a molybdenum-containing material.

[0014] 1. (Description of Product)

5 The present disclosure relates to a molybdenum-containing material having a controlled amount of grain-boundary impurities, a controlled crystal grain size, a controlled density, and a controlled molybdenum content rate. It has been found that the molybdenum-containing material achieves effects when the following characteristic values are within the prescribed ranges.

<Crystal Grain Size>

10 A crystal grain size is 25 μm or more and less than 1 mm.

[0015] A preferable range is 45 μm or more and less than 1 mm as a primary recrystallized grain size.

A preferable range is 1 mm or more as a secondary recrystallized grain size.

15 [0016] A more preferable range is 10 mm or more as the secondary recrystallized grain size.

When the crystal grain size is within this range, intragranular W and K are reduced and the number of particles to be generated can be reduced.

<Ratio between Impurity Content Rates: Intragranular/Grain-Boundary>

20 A mass ratio between an intragranular tungsten content rate and a grain-boundary tungsten content rate (intragranular W/grain-boundary W) is 0.8 or less.

[0017] Preferably, in the case of primary recrystallization, a mass ratio between an intragranular potassium content rate and a grain-boundary potassium content rate (intragranular K/grain-boundary K) is 0.7 or less.

25 [0018] Preferably, in the case of secondary recrystallization, the intragranular W/grain-boundary W is 0.7 or less.

More preferably, in the case of secondary recrystallization, the intragranular K/grain-boundary K is 0.6 or less.

<Density>

A density is 10.15 g/cm^3 (relative density: 99.5%) or more.

[0019] A preferable range is 10.18 g/cm³ (relative density: 99.8%) or more.

When the density is within this range, voids in a target have less influence on a formed film.

<Molybdenum Content Rate>

5 A molybdenum content rate is 99.95 mass % or more.

[0020] A preferable range is 99.999 mass % or more.

When the molybdenum content rate is within this range, the number of particles caused by the impurities can be reduced.

<Tungsten Content Rate>

10 Preferably, a tungsten content rate is 200 ppm or less. More preferably, the tungsten content rate is 90 ppm or less. When the tungsten content rate is within this range, W segregated at a grain boundary does not have an adverse influence on the generation of particles.

<Potassium Content Rate>

15 Preferably, a potassium content rate is 20 ppm or less. Preferably, the potassium content rate is 10 ppm or less. When the potassium content rate is within this range, potassium segregated at a grain boundary does not have an adverse influence on the generation of particles.

20 [0021] One of the effects of the foregoing is that the number of particles to be generated in a thin film formed using a sputtering target fabricated according to the present disclosure is, for example, 35/mm² or less.

[0022] A thin film sheet resistance (thickness: 300 nm) of the thin film formed using the sputtering target fabricated according to the present disclosure is 1.5 Ω/□ or less.

[0023] Preferably, the following characteristics are provided.

25 Number of particles to be generated: 15/mm² or less

[0024] Thin film sheet resistance (thickness: 300 nm): 1.2 Ω/□ or less

Regarding the number of particles to be generated, a thin film having the quality suitable for a reflective mask blank can be obtained when the number of particles of 20 nm to 1 μm is 35 or less.

[0025] Furthermore, during heat treatment at 1800°C, secondary recrystallization occurs, which causes the crystal grains to grow to 1 mm or more, and more preferably 10 mm or more, and the grain boundaries to decrease. As a result, the number of particles to be generated is further reduced. Furthermore, the resistance to high temperature deformation of a plate is also increased.

[0026] 2. (Manufacturing Method and Examples)

<Manufacturing of Molybdenum Sputtering Target>

A molybdenum sputtering target is manufactured based on Step 1: molybdenum raw material powder, Step 2: CIP, Step 3: sintering, Step 4: hot rolling, Step 5: heat treatment, Step 6: cutting, Step 7: cutting and polishing, and Step 8: bonding.

[0027] Step 1: Molybdenum Raw Material Powder

A molybdenum powder having a molybdenum content rate of 99.95 mass % or more and a grain size measured by the FSSS method of 1 to 10 μm was used as a starting raw material.

[0028] When the molybdenum content rate is less than 99.95 mass %, the molybdenum content rate in a sputtered thin film decreases and a defect caused by the impurities also occurs.

[0029] When the FSSS grain size is smaller than 1 μm , the ignition risk of the powder increases. When the FSSS grain size exceeds 10 μm , sintering in powder metallurgy is difficult.

[0030] At this time, a molybdenum powder excellent in sinterability (e.g., a molybdenum-containing powder having an average grain size by the FSSS method of 0.1 μm or more and 10 μm or less, a molybdenum content rate of 99.99 mass % or more, and a compression deformation strength of 100 MPa or more and 200 MPa or less) may be used to cause slight grain boundary segregation of W and K due to grain boundary movement from the sintering stage.

[0031] Step 2: CIP

The above-described molybdenum powder is filled into a prescribed rubber container and pressure-molded by hydrostatic pressing (CIP). A CIP pressure was 1

to 3 ton/cm², and preferably 2.0 t/cm².

[0032] When the pressure is lower than this pressure, the strength of the pressed material is insufficient, which causes a sintering crack. The pressure higher than this pressure is not industrially realistic.

5 [0033] Step 3: Sintering

The pressed material obtained above is sintered at a sintering temperature equal to or higher than 1600°C and equal to or lower than 2300°C, and preferably 1800°C, for 3 to 20 hours in hydrogen atmosphere, to obtain a molybdenum sintered compact having a density of approximately 9.7 g/cm³.

10 [0034] When the temperature is lower than 1600°C, the density after sintering is insufficient. The temperature equal to or higher than 2300°C is not industrially realistic.

[0035] At this time, when a molybdenum powder that is not excellent in sinterability is used, slight grain boundary segregation of W and K due to grain boundary movement
15 from the sintering stage is less likely to occur. However, even when the molybdenum powder that is not excellent in sinterability is used, the same effect as that when the molybdenum powder excellent in sinterability is used can be obtained by adjusting the length of the sintering time. This is the effect that appears as a result of the progress of sintering, and the sintering conditions can be adjusted by adjusting not only the time
20 but also the amount of hydrogen and the temperature.

[0036] Step 4: Hot Rolling

The molybdenum sintered compact obtained above was inserted into a hydrogen heating furnace of 1100 to 1400°C, and then, was subjected to hot rolling processing. When the material becomes cold, heating is repeated as appropriate and
25 rolling is repeated to a target thickness. A density after hot rolling reaches 10.15 to 10.22 g/cm³ and a molybdenum plate having a fibrous structure extended in a rolling direction is obtained.

[0037] Step 5: Heat Treatment

The molybdenum plate obtained above is subjected to heat treatment at a

temperature equal to or higher than 950°C for 0.5 to 10 hours. The heat treatment causes recrystallization and a molybdenum plate having an equiaxed grain structure is obtained.

[0038] Fig. 1 is a photograph showing a structure example of primary recrystallized grains of the molybdenum-containing material. Fig. 2 is a photograph showing a structure example of secondary recrystallized grains of the molybdenum-containing material.

<Primary Recrystallization>

As shown in Fig. 1, a primary recrystallization temperature of the molybdenum plate is generally approximately 950°C to 1700°C, although the primary recrystallization temperature varies somewhat depending on the manufacturing conditions. The fibrous structure extended by hot rolling grows to equiaxed grains having a crystal grain size of several tens of micrometers to several hundreds of micrometers (several millimeters depending on the manufacturing conditions and the temperature).

[0039] <Secondary Recrystallization>

As shown in Fig. 2, secondary recrystallization of the molybdenum plate requires a temperature higher than that of primary recrystallization and generally occurs at a temperature equal to or higher than 1700°C. However, the likelihood of occurrence of secondary recrystallization varies depending on the manufacturing conditions. Secondary recrystallization is a phenomenon in which one of the adjacent primary recrystallized grains annexes the other and grows. When the grains are heated at a certain temperature or higher (e.g., 1800°C or 2000°C) for a long time (e.g., 5 hours or 10 hours), the grains grow rapidly to a macrocrystal of 10 mm or more. Generally, heat treatment at a high temperature such as 2000°C or higher causes secondary recrystallization in a shorter time. However, in view of energy cost and the like, secondary recrystallization was based on whether a crystal grain size of 1 mm or more is obtained at 1800°C × 5 h that is easily industrially implemented.

[0040] Step 6: Cutting

The recrystallized molybdenum plate obtained above is hollowed out into a circular plate by water jetting, to obtain a molybdenum circular plate. At this time, abrasive grains and the like may be used to increase the cutting efficiency. When a target shape is a rectangular shape, the molybdenum plate is cut into a rectangular plate.

[0041] Step 7: Cutting and Polishing

A surface of the above-described molybdenum circular plate is cut to a prescribed thickness by cutting processing, to remove an oxide film on the surface and increase the flatness. An outer circumference is also cut to a prescribed size.

Thereafter, the surface is polished to have Ra of 1.6 μm or less with the use of, for example, a GC grindstone.

[0042] Step 8: Bonding

A backing plate (made of Cu or the like) and a bonding material (made of In or the like) that are adapted to a sputtering apparatus are prepared, and the above-described molybdenum circular plate and the backing plate are heated with the use of a hot plate and bonded together by the bonding material. By performing this bonding, a molybdenum sputtering target is obtained.

[0043] <Overview of Examples>

Molybdenum plate materials were fabricated from various molybdenum raw material powders and subjected to heat treatment of $1300^{\circ}\text{C} \times 1 \text{ h}$, and evaluation was performed about crystal grain sizes thereof.

[0044] Furthermore, evaluation was also performed about whether the materials were secondary recrystallized by heat treatment of $1800^{\circ}\text{C} \times 5 \text{ h}$, without the above-described heat treatment of $1300^{\circ}\text{C} \times 1 \text{ h}$.

[0045] By using these materials, a sputtering target was produced. By using the target, a film formation test was performed to measure the number of particles to be generated and a film resistance of a thin film.

[0046] [Details of Embodiments of the Present Disclosure]

<Examples>

The molybdenum-containing powder was grouped into a plurality of molybdenum raw material powders as raw materials for each feature in Table 1 below.
[0047] [Table 1]

Powder group	Feature	W content rate in powder (ppm)	K content rate in powder (ppm)	Fsss grain size (μm)
1	amount of W is normal	70~200	13~35	4~5
2	amount of W is small	5~70	13~35	4~5
3	amount of K is normal	70~200	13~35	4~5
4	amount of K is small	70~200	3~13	4~5
5	Mo content rate is 99.999 mass % or more	less than 5	less than 3	4~5
6	amount of W is large	200~300	13~35	4~5
7	amount of K is large	70~200	35~80	4~5

5 [0048] “W content rate in powder” refers to a tungsten content rate in the molybdenum-containing powder. “K content rate in powder” refers to a potassium content rate in the molybdenum-containing powder. The powder raw material group 5 is a molybdenum-containing powder having an average grain size by the Fsss method of 0.1 μm or more and 10 μm or less, a molybdenum content rate of 99.99 mass % or
10 more, and a compression deformation strength of 100 MPa or more and 200 MPa or less, which is filed on the same date as the present application. “Fsss grain size” refers to an average grain size by the Fsss method.

[0049] In all of the raw materials, when sintering occurs, the potassium content rate decreases, although the tungsten content rate remains unchanged.

15 [0050] Each of the above-described molybdenum raw material powders was subjected to Steps 1 to 8, to obtain a molybdenum target having a diameter ϕ of 4 inches (4×2.54 cm). Details thereof are shown in Tables 2 to 5.

[0051] [Table 2]

Sample No.	Powder group	Sintering time h	Mo content rate %	Amount of W				Amount of K			
				Whole	Intragranular	Grain boundary	Intragranular W/grain-boundary W	Whole	Intragranular	Grain boundary	Intragranular K/grain-boundary K
				ppm	ppm	ppm		ppm	ppm	ppm	
101	1	15	99.95	200	160	230	0.70	6	4	7	0.57
102	1	20	99.95	200	160	230	0.70	7	4	7	0.57
103	2	10	99.99	27	24	30	0.80	4	4	5	0.80
104	2	15	99.98	54	46	59	0.78	7	5	8	0.63
105	2	20	99.99	16	12	22	0.55	4	3	5	0.60
106	3	10	99.98	130	90	120	0.75	20	16	22	0.73
107	3	15	99.95	70	56	80	0.70	20	15	23	0.65
108	3	20	99.96	150	120	170	0.71	18	13	21	0.62
109	4	6	99.99	80	60	90	0.67	2.3	1.1	2.7	0.41
110	4	10	99.98	130	100	150	0.67	1.5	1.0	1.9	0.53
111	4	15	99.98	150	120	170	0.71	1.4	0.9	1.8	0.50
112	4	20	99.99	80	50	90	0.56	2.0	1.0	2.5	0.40
113	5	3	99.999	2.2	1.6	2.4	0.67	0.5	0.4	0.6	0.67
114	5	6	99.999	0.8	0.5	1.2	0.42	0.3	0.2	0.4	0.50
115	5	10	99.999	0.7	0.5	1.2	0.42	0.3	0.2	0.4	0.50
116	5	15	99.999	2.8	2.0	3.2	0.63	0.4	0.3	0.5	0.60
117	5	20	99.999	2.3	1.7	2.9	0.59	0.4	0.2	0.5	0.40
201	1	3	99.96	180	170	190	0.89	8	7	9	0.78
202	1	6	99.95	200	180	220	0.82	9	7	9	0.78
203	1	10	99.96	170	150	180	0.83	8	6	9	0.67
204	2	3	99.98	25	22	27	0.81	4	3	4	0.75
205	2	6	99.97	62	54	64	0.84	8	6	9	0.67
206	3	3	99.97	130	120	140	0.86	14	12	15	0.80
207	3	6	99.95	80	70	80	0.88	19	16	21	0.76
208	4	3	99.97	70	60	70	0.86	1.5	1.1	1.8	0.61
209	6	15	99.94	220	200	230	0.87	9	7	10	0.70
210	6	20	99.93	210	180	230	0.78	10	8	11	0.73
211	7	15	99.95	120	120	130	0.92	21	18	22	0.82
212	7	20	99.93	120	100	120	0.83	21	17	24	0.71

heat treatment of 1300°C × 1 h

[0052] [Table 3]

Sample No.	Powder group	Sintering time	Mo content rate	Amount of W				Amount of K			
				Whole	Intragranular	Grain boundary	Intragranular W/grain-boundary W	Whole	Intragranular	Grain boundary	Intragranular K/grain-boundary K
		h	%	ppm	ppm	ppm		ppm	ppm	ppm	
118	1	15	99.95	200	160	230	0.70	6	4	7	0.57
119	1	20	99.95	200	150	250	0.60	7	5	9	0.56
120	2	6	99.97	62	52	75	0.69	8	5	9	0.56
121	2	10	99.99	27	17	30	0.57	4	3	5	0.60
122	2	15	99.98	54	40	68	0.59	7	4	7	0.57
123	2	20	99.99	16	13	21	0.62	4	2	4	0.50
124	3	6	99.95	80	67	96	0.70	19	12	21	0.57
125	3	10	99.98	130	110	160	0.69	20	13	22	0.59
126	3	15	99.95	70	53	86	0.62	20	12	24	0.50
127	3	20	99.96	150	120	180	0.67	18	11	20	0.55
128	4	6	99.99	80	50	90	0.56	2.3	1.2	2.2	0.55
129	4	10	99.98	130	100	160	0.63	1.5	0.8	1.5	0.53
130	4	15	99.98	150	110	180	0.61	1.4	0.7	1.5	0.47
131	4	20	99.99	80	61	110	0.55	2.0	1.1	2.1	0.52
132	5	3	99.999	2.2	1.2	2.2	0.55	0.5	0.3	0.6	0.50
133	5	6	99.999	0.8	0.5	0.9	0.56	0.3	0.1	0.4	0.25
134	5	10	99.999	0.7	0.3	0.7	0.43	0.3	0.2	0.4	0.50
135	5	15	99.999	2.8	1.8	3.0	0.60	0.4	0.2	0.5	0.40
136	5	20	99.999	2.3	1.2	2.5	0.48	0.4	0.1	0.5	0.20
213	1	3	99.96	180	170	190	0.89	8	7	9	0.78
214	1	6	99.95	200	180	220	0.82	9	8	10	0.80
215	1	10	99.96	170	160	190	0.84	8	6	9	0.67
216	2	3	99.98	25	23	28	0.82	4	3	4	0.75
217	3	3	99.97	130	120	140	0.86	14	12	15	0.80
218	4	3	99.97	70	65	80	0.81	1.5	1.1	1.6	0.69
219	6	15	99.94	220	210	240	0.88	9	8	11	0.73
220	6	20	99.93	210	190	230	0.83	10	7	10	0.70
221	7	15	99.95	120	110	130	0.85	21	18	21	0.86
222	7	20	99.93	120	100	120	0.83	21	17	22	0.77

heat treatment of 1800°C × 5 h

[0053] [Table 4]

Sample No.	Density	Oxygen	Crystal grain size	Sputtering film formation result	
	g/cm ³	ppm	μm	Number of particles to be generated number/mm ²	Thin film sheet resistance Ω/□
101	10.20	10	210	34	1.5
102	10.22	10	980	16	1.3
103	10.21	10	120	32	1.4
104	10.22	20	45	33	1.3
105	10.19	10	640	18	1.3
106	10.22	20	530	25	1.4
107	10.22	10	46	32	1.4
108	10.19	30	720	20	1.3
109	10.20	10	65	30	1.3
110	10.18	10	360	21	1.2
111	10.22	10	960	16	1.3
112	10.21	10	96	14	1.2
113	10.21	30	25	6	1.1
114	10.20	10	28	4	1.1
115	10.20	10	59	7	1.2
116	10.22	20	139	5	1.0
117	10.18	10	210	5	0.9
201	10.21	10	22	195	1.8
202	10.22	30	161	73	1.6
203	10.19	20	980	37	1.6
204	10.21	10	191	62	1.8
205	10.21	20	274	48	1.7
206	10.18	10	390	38	1.7
207	10.19	30	48	65	1.6
208	10.18	10	59	46	1.6
209	10.21	20	68	280	2.1
210	10.18	10	106	83	1.9
211	10.21	20	24	185	2.2
212	10.20	10	84	92	2.0

[0054] [Table 5]

Sample No.	Density	Oxygen	Crystal grain size	Sputtering film formation result		Secondary recrystallization	High temperature deformation 1800°C × 10 h
				Number of particles to be generated	Thin film sheet resistance		deformation by 1 mm or more A: not occur B: occur
	g/cm ³	ppm	μm	number/mm ²	Ω/□		
118	10.21	10	3700	18	1.4	A	A
119	10.22	10	15000	17	1.2	A	A
120	10.21	20	9900	21	1.5	A	A
121	10.22	10	22000	16	1.3	A	A
122	10.22	20	31000	15	1.2	A	A
123	10.19	10	33000	16	1.2	A	A
124	10.19	30	8000	29	1.5	A	A
125	10.22	20	2500	22	1.4	A	A
126	10.22	10	42000	19	1.2	A	A
127	10.19	30	26000	14	1.3	A	A
128	10.21	10	11000	13	1.2	A	A
129	10.18	10	39000	13	1.1	A	A
130	10.22	10	3000	16	1.2	A	A
131	10.21	10	21000	11	1.2	A	A
132	10.22	30	6000	4	0.9	A	A
133	10.20	10	14000	2	0.8	A	A
134	10.20	10	4000	2	1.0	A	A
135	10.22	20	19000	3	0.8	A	A
136	10.19	10	29000	2	0.7	A	A
213	10.22	10	36	89	1.7	B	B
214	10.22	30	250	70	1.6	B	B
215	10.19	20	990	55	1.6	B	B
216	10.21	10	360	72	1.8	B	B
217	10.19	10	510	57	1.8	B	B
218	10.18	10	120	39	1.6	B	B
219	10.22	20	65	156	2.0	B	B
220	10.18	10	620	122	1.8	B	B
211	10.22	20	80	183	2.1	B	B
212	10.20	10	320	81	2.0	B	B

[0055] In order to perform the heat treatment step (Step 5) under two conditions, the same plate was produced from Step 1 to hot rolling in Step 4, and this plate was cut into two circular plates of the same quality. Each of the circular plates was subjected to heat treatment under one of a first heat treatment condition and a second heat treatment condition.

[0056] First heat treatment condition: Sample Nos. 101 to 117 and 201 to 212

Second heat treatment condition: Sample Nos. 118 to 136 and 213 to 222

Step 1: Molybdenum Raw Material Powder

A molybdenum-containing powder having an Fsss average grain size of 4 to 5 μm was prepared.

[0057] Step 2: CIP

5 The CIP was performed at a pressure of 2.0 t/cm².

[0058] Step 3: Sintering

Sintering was performed at a temperature of 1800°C. The sintering time was adjusted to 3 hours, 6 hours, 10 hours, 15 hours, or 20 hours in hydrogen atmosphere, and a sintered compact having a thickness T of 10 to 40 mm was obtained. The
10 thickness of the sintered compact affects the density after hot rolling.

[0059] Step 4: Hot Rolling

The molybdenum sintered compact was heated at 1300°C and rolled to have thickness T of 7 mm.

[0060] Step 5: Heat Treatment

15 In order to recrystallize the obtained rolled material, the obtained rolled material was subjected to heat treatment under the two conditions. The first heat treatment condition is heat treatment at a temperature of 1300°C for the time of 1 h for primary recrystallization of molybdenum. The first heat treatment is not performed on the samples that are subjected to heat treatment under the second condition. The second
20 heat treatment is heat treatment at a temperature of 1800°C for the time of 5 h for the purpose of examining whether secondary recrystallization occurs.

[0061] Step 6: Cutting

The plate material after primary or secondary recrystallization was cut into a circular plate having a diameter ϕ of 4 inches by water jetting.

25 [0062] Step 7: Cutting and Polishing

Both surfaces of the circular plate having thickness T of 7 mm, which was produced in Step 6, were cut to thickness T of approximately 5.5 mm by cutting processing. The surfaces were polished to have thickness T of 5.0 mm with the use of a GC grindstone, to obtain a molybdenum circular plate of ϕ 4 inches $\times$ T 5.0 mm. At

this time, the flatness was 0.2 mm or less and a surface roughness Ra was approximately 1.0 μm .

[0063] Step 8: Bonding

5 The molybdenum circular plate as a molybdenum-containing material finished in Step 7 was bonded to a copper backing plate by using indium as a bonding material. A sputtering target was thus obtained.

<Evaluation Method>

<Molybdenum Content Rate, Impurity Content Rate>

The molybdenum content rate was calculated as follows:

10 Molybdenum content rate (mass %) = $100\% - 14 \text{ elements [Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si, Sn, Na, K, W]}$.

Tungsten (W) is an impurity.

[0064] Na, K: Atomic absorption spectrometry (contrAA300 manufactured by Analytik Jena Co., Ltd.) is used for content rate measurement.

15 [0065] Others: ICP emission spectroscopy (ICP-AES) (ICPS-8100CL type manufactured by Shimadzu Corporation) is used for content rate measurement.

[0066] Oxygen is measured as a reference value by an infrared absorption method (ON836 manufactured by LECO Corporation).

<Density>

20 The density is measured by an underwater gravimetric method (Archimedes method). The plate material subjected to heat treatment in Step 5 is cut into an arbitrary size of 10 g or more. An air weight, an underwater weight, and a temperature of water are measured. The following equation is used for calculation. This is a method described in JIS Z 8807.

25 [0067] $\text{Density} = \{\text{air weight}/(\text{air weight} - \text{underwater weight})\} \times (\text{density of water} - \text{density of air}) + \text{density of air}$

The relative density is expressed by the following equation, with a theoretical density of molybdenum being 10.22 g/cm³.

[0068] $\text{Relative density [\%]} = (\text{density}/10.22) \times 100$

<Crystal Grain Size (Less Than 1 mm)>

The crystal grain size is measured by using a cutting method defined in JIS G 0551 (2020).

[0069] A metal structure is observed with a microscope and a test line is 1500 μm .

5 The number of grain boundaries (P) that cross this test line is counted and an average line segment length per one crystal grain is defined as an average crystal grain size.

[0070] Specifically, an observation surface is a surface corresponding to a sputtered surface. In the case of the rolled material, the observation surface is an ND surface (rolled surface).

10 [0071] Four test lines in total, i.e., two vertical test lines and two horizontal test lines, are drawn on the observation surface. A region surrounded by the four test lines has a square shape of 1500 $\mu\text{m} \times 1500 \mu\text{m}$. The crystal grain size was calculated in accordance with the following equation.

[0072] Average crystal grain size per one test line = 1500 $\mu\text{m}/P$

15 Crystal grain size = an average value of an average grain size calculated from four test lines

When the crystal grain size is 1 mm or more, measurement cannot be performed in accordance with the above-described method. First, when the above-described crystal grain size is 1 mm, a crystal grain size is measured in accordance with the measurement method. When the crystal grain size exceeds 1 mm, a correct crystal grain size is determined in accordance with the following method.

20

<Crystal Grain Size (1 mm or More)>

Vertical and horizontal lengths of crystal grain boundaries of five crystal grains are measured visually or with a microscope of low power, to determine an average line segment length per one crystal grain similarly to the above. A value calculated by averaging the vertical and horizontal average line segment lengths is defined as a crystal grain size.

25

<Impurity Ratios W and K>

When the crystal grain size is less than 1 mm

Amount of intragranular impurity: The plate produced in Step 7 is crushed finely at an extremely low temperature. As a result, the grain boundaries are crushed. Thereafter, acid etching is performed, which causes the grain boundaries to corrode preferentially. As a result, an intragranular sample is obtained. This is collected,
 5 melted again and analyzed by the ICP, to determine a content rate of each of tungsten and potassium. This is defined as an intragranular impurity content rate.

[0073] Specifically, 10 samples of 1×20×20 mm are prepared. Each of the samples cooled with liquid nitrogen is crushed in a mortar. This is for exposing a grain boundary surface. Thereafter, sieving is performed with the use of a sieve having an
 10 opening size of 150 μm. Mixed acid is prepared as the acid by mixing hydrochloric acid (12.0 mole/dm³) and nitric acid (13.8 mole/dm³) at a volume ratio of 1:3 and diluting the mixture two times with pure water. Hereinafter, “mixed acid” in the present specification refers to this acid. The grains crushed and then sieved (under the sieve having an opening size of 150 μm) are introduced into the mixed acid and
 15 dissolved for 8 minutes. The undissolved remainder does not have any grain boundary surface and this is used as a sample for analyzing the intragranular impurities. The sample is further dissolved with the mixed acid and the solution is analyzed by the ICP.

[0074] Amount of grain-boundary impurity: The plate is crushed finely at an extremely
 20 low temperature. As a result, the grain boundaries are crushed. Thereafter, acid etching is performed, which causes the grain boundaries to corrode preferentially. Thereafter, the solution including the grain boundary component is analyzed by the ICP, to determine a content rate of each of tungsten and potassium. This is defined as a grain-boundary impurity content rate.

[0075] Specifically, 10 samples of 1×20×20 mm are prepared. Each of the samples cooled with liquid nitrogen is crushed in a mortar. This is for exposing a grain boundary surface. Sieving is performed with the use of a sieve having an opening size
 25 of 150 μm. Mixed acid including hydrochloric acid, nitric acid and water is used as the acid. The grains crushed and then sieved (under the sieve having an opening size

of 150 μm) are introduced into the mixed acid and dissolved for 15 minutes. The solution is used as a solution for analyzing the grain-boundary impurities. The solution is analyzed by the ICP.

[0076] When the crystal grain size is 1 mm or more

5 Amount of intragranular impurity: The plate is cut to a size of $1 \times 1 \times 1$ mm or more so as not to include a grain boundary, and a sample is thereby produced. The size of $1 \times 1 \times 1$ mm or more is selected in accordance with the size of the crystal grains. 1 g or more of samples are produced. For example, when the size of one sample is $1 \times 1 \times 1$ mm, 100 samples are produced. A total of 1 g or more of samples are
10 dissolved with acid. Mixed acid including hydrochloric acid, nitric acid and water is used as the acid. The solution is analyzed by the ICP.

[0077] Amount of grain-boundary impurity: The plate is cut to a size of $2 \times 2 \times 2$ mm or more so as to include one grain boundary, and a sample is thereby produced. The size of $2 \times 2 \times 2$ mm or more is selected in accordance with the size of the crystal grains. A
15 total of 1 g or more of samples are produced. For example, when the size of one sample is $2 \times 2 \times 2$ mm, 13 samples are produced. A total of 1 g or more of samples are dissolved with acid. Mixed acid including hydrochloric acid, nitric acid and water is used as the acid. The solution is analyzed by the ICP.

<Sputtering Film Formation Test>

20 A magnetron sputtering apparatus of SRV-4320 type manufactured by Shinko Seiki Co., Ltd. was used for sputtering of molybdenum. An Si substrate was provided to face a molybdenum target, and a molybdenum thin film was formed thereon to have a target thickness of 300 nm. A chamber is vacuumed to 5×10^{-4} Pa or less. Thereafter, an argon gas was supplied at 25 sccm and an output was 500 W. The
25 target had a size of ϕ 4 inches $\times$ T 5 mm.

[0078] <Number of Particles to be Generated>

A laser microscope OPTELICS HYBRID+ manufactured by Lasertech Co., Ltd. was used to measure the number of particles in the formed molybdenum thin film.

Surface irregularities were measured in a range of 1 mm × 1 mm, and irregularities having a height of 20 nm to 1 μm were defined as particles and the number thereof was counted.

[0079] <Thin Film Sheet Resistance>

5 RT-70V type manufactured by Napson Corporation was used to measure a film resistance. A sheet resistance was measured by bringing a measurement probe into contact with the formed molybdenum thin film of 300 nm.

[0080] <Evaluation>

10 “Powder group” in each of Tables 2 and 3 corresponds to the powder group in Table 1.

[0081] “Whole” in the column “amount of W” refers to a mass content rate of tungsten with respect to the whole of the molybdenum-containing material. “Intragranular” refers to a mass content rate of tungsten in a crystal grain. “Grain boundary” refers to a mass content rate of tungsten at a crystal grain boundary. “Intragranular W”/“grain-boundary W” refers to a ratio of W.

[0082] “Whole” in the column “amount of K” refers to a mass content rate of potassium with respect to the whole of the molybdenum-containing material. “Intragranular” refers to a mass content rate of potassium in a crystal grain. “Grain boundary” refers to a mass content rate of potassium at a crystal grain boundary.

20 “Intragranular K”/“grain-boundary K” refers to a ratio of K.

[0083] In Sample Nos. 101 to 117, the number of particles is 34 or less and the thin film sheet resistance is 1.5 Ω or less, and thus, Sample Nos. 101 to 117 show good results. In contrast, it can be seen that in Sample Nos. 201 to 212, the number of particles and the thin film resistance are larger.

25 [0084] In Sample Nos. 118 to 136, the number of particles is 29 or less and the thin film sheet resistance is 1.5 Ω or less, and thus, Sample Nos. 118 to 136 show good results. In contrast, it can be seen that in Sample Nos. 213 to 222, the number of particles and the thin film resistance are larger.

[0085] Evaluation was performed about secondary recrystallization and ease of

deformation at high temperature due to secondary recrystallization.

“Secondary recrystallization” in Table 5 is based on whether a crystal grain size of 1 mm or more is obtained at $1800^{\circ}\text{C} \times 5 \text{ h}$ that is easily industrially implemented, as described above. In Table 5, regardless of secondary recrystallization, a sample having a thickness T of 1 mm, a width B of 20 mm and a length L of 120 mm was produced in each of Sample Nos. 118 to 212.

[0086] Fig. 3 is a diagram of an apparatus for measuring the ease of deformation at high temperature. As shown in Fig. 3, a distance between two pillars 401 was set to 100 mm. A sample 402 was placed on pillars 401. A state in which the force of 150 g was applied to the center of the sample in a direction indicated by an arrow 403 was continued at a temperature of 1800°C for 10 hours. In the column “high temperature deformation $1800^{\circ}\text{C} \times 10 \text{ h}$ ” in Table 5, a sample in which an amount of deformation Z was less than 1 mm was denoted as “A”, and a sample in which the amount of deformation Z was 1 mm or more was denoted as “B”. It can be seen that when secondary recrystallization occurs, the amount of deformation decreases.

<Influence on Density>

Next, in order to examine an influence on the density, a sintered compact was produced by using each of Raw Materials 1 to 5 in Steps 1 to 3, with a thickness of the sintered compact being varied to T 15 mm, T 12 mm and T 10 mm. This was rolled to T 7 mm in Step 4, and examination was performed with the density after hot rolling being varied. The heat treatment temperature in Step 5 was $1300^{\circ}\text{C} \times 1 \text{ h}$, which was the first heat treatment condition. The obtained molybdenum plate was processed into a molybdenum target through Steps 5 to 8, and film formation was performed by sputtering.

[0087] [Table 6]

Sample No.	Powder group	Density adjustment method
137	1	T15mm sintered compact → rolling
138	2	T15mm sintered compact → rolling
139	3	T15mm sintered compact → rolling
140	3	T12mm sintered compact → rolling
141	4	T15mm sintered compact → rolling
142	5	T15mm sintered compact → rolling
223	1	T12mm sintered compact → rolling
224	1	T10mm sintered compact → rolling
225	1	HP
226	2	T12mm sintered compact → rolling
227	2	T10mm sintered compact → rolling
228	2	HP
229	3	T10mm sintered compact → rolling
230	3	HP
231	4	T12mm sintered compact → rolling
232	4	T10mm sintered compact → rolling
233	4	HP
234	5	T12mm sintered compact → rolling
235	5	T10mm sintered compact → rolling
236	5	HP

[0088] For further comparison, production by hot pressing (HP), which was commonly used as a method for producing a molybdenum target, was performed. The HP was performed under the condition of $1600^{\circ}\text{C} \times 40 \text{ MPa} \times 3 \text{ h}$, which was common in the HP for molybdenum, and a molybdenum sintered compact was obtained. The obtained sintered compact was processed into a molybdenum target through Steps 5 to 8 similarly to the rolled material, and film formation was performed by sputtering. The heat treatment temperature in Step 5 was $1300^{\circ}\text{C} \times 1 \text{ h}$, which was the first heat treatment condition.

[0089] [Table 7]

Sample No.	Mo content rate	Amount of W				Amount of K			
		Whole	Intragranular	Grain boundary	Intragranular W/grain-boundary W	Whole	Intragranular	Grain boundary	Intragranular K/grain-boundary K
	%	ppm	ppm	ppm		ppm	ppm	ppm	
137	99.95	200	170	230	0.74	6	5	7	0.71
138	99.98	57	50	63	0.79	8	6	9	0.67
139	99.97	130	110	140	0.79	19	16	21	0.76
140	99.97	140	120	150	0.80	19	15	22	0.68
141	99.99	82	75	100	0.75	2.2	1.6	2.3	0.70
142	99.999	2.8	2.5	3.3	0.76	0.4	0.2	0.4	0.50
223	99.95	200	180	220	0.82	6	5	7	0.71
224	99.95	210	180	210	0.86	6	5	6	0.83
225	99.95	210	190	210	0.90	6	6	7	0.86
226	99.98	57	51	62	0.82	9	7	9	0.78
227	99.98	56	51	60	0.85	8	8	9	0.89
228	99.98	58	56	59	0.95	8	8	8	1.00
229	99.97	130	120	140	0.86	20	18	21	0.86
230	99.97	130	130	130	1.00	20	19	21	0.90
231	99.99	80	78	85	0.92	2.0	1.8	2.1	0.86
232	99.99	83	81	84	0.96	2.1	2.0	2.1	0.95
233	99.99	80	79	80	0.99	2.0	1.9	2.0	0.95
234	99.999	2.8	2.6	3.1	0.84	0.4	0.3	0.4	0.75
235	99.999	2.9	2.6	3.0	0.87	0.4	0.3	0.4	0.75
236	99.999	2.9	2.7	3.1	0.87	0.4	0.4	0.4	1.00

[0090] [Table 8]

Sample No.	Density	Oxygen	Crystal grain size	Sputtering film formation result	
				Number of particles to be generated	Thin film sheet resistance
	g/cm ³	ppm	μm	number/mm ²	Ω/□
137	10.16	20	260	35	1.5
138	10.15	10	410	31	1.4
139	10.17	10	180	34	1.4
140	10.15	10	190	32	1.5
141	10.16	10	320	28	1.5
142	10.15	10	94	22	1.5
223	10.14	20	290	73	1.7
224	10.08	10	330	170	2.3
225	10.08	250	58	650	2.4
226	10.14	20	460	46	1.8
227	10.09	30	760	180	2.2
228	10.06	330	82	530	2.1
229	10.10	10	260	140	1.9
230	10.09	210	43	490	2.2
231	10.13	30	450	95	1.8
232	10.11	20	530	110	2.2
233	10.07	240	35	450	2.3
234	10.14	30	210	41	1.6
235	10.11	10	370	88	1.9
236	10.11	200	51	160	2.1

[0091] As a result, it could be seen that when the density was 10.15 g/cm³ or less, the number of particles to be generated increased. In addition, the number of particles to be generated in the HP product was larger than that in the rolled material, even when the same raw material powder as that for the rolled material was used.

[0092] Significant grain boundary movement occurred in the rolled material when recrystallization occurred in heat treatment after rolling, whereas grain boundary segregation of W and K was insufficient in the HP product because only sintering was performed.

(Additional Aspect 1)

A molybdenum-containing material having a crystal grain size of 25 μm or more, a density of 10.15 g/cm³ or more, a molybdenum content rate of 99.95 mass % or more, and a mass ratio between an intragranular tungsten content rate and a grain-boundary tungsten content rate (intragranular W/grain-boundary W) of 0.8 or less.

(Additional Aspect 2)

The molybdenum-containing material according to Additional Aspect 1,
wherein

the crystal grain size is 1 mm or more and a value of the intragranular W/grain-
5 boundary W is 0.7 or less.

(Additional Aspect 3)

The molybdenum-containing material according to Additional Aspect 1 or 2,
wherein

a value of intragranular K/grain-boundary K is 0.7 or less, the intragranular
10 K/grain-boundary K being a ratio between an intragranular potassium content rate and
a grain-boundary potassium content rate.

(Additional Aspect 4)

The molybdenum-containing material according to Additional Aspect 3,
wherein

15 the value of the intragranular K/grain-boundary K is 0.6 or less.

(Additional Aspect 5)

The molybdenum-containing material according to any one of Additional
Aspects 1 to 4, wherein

the density is 10.18 g/cm^3 (99.8%) or more.

20 (Additional Aspect 6)

The molybdenum-containing material according to any one of Additional
Aspects 1 to 5, wherein

the molybdenum content rate is 99.999 mass % or more.

(Additional Aspect 7)

25 The molybdenum-containing material according to any one of Additional
Aspects 1 to 6, wherein

a tungsten content rate is 200 ppm or less.

(Additional Aspect 8)

The molybdenum-containing material according to any one of Additional

Aspects 1 to 7, wherein

a potassium content rate is 20 ppm or less.

(Additional Aspect 9)

The molybdenum-containing material according to any one of Additional

5 Aspects 1 to 8, wherein

the molybdenum-containing material has a shape of a plate or a target.

[0093] It should be understood that the embodiments and examples disclosed herein are illustrative and non-restrictive in every respect. The scope of the present invention is defined by the terms of the claims, rather than the description above, and is intended to
10 include any modifications within the scope and meaning equivalent to the terms of the claims.

CLAIMS

[Claim 1] A molybdenum-containing material having a crystal grain size of 25 μm or more, a density of 10.15 g/cm^3 or more, a molybdenum content rate of 99.95 mass % or more, and a mass ratio between an intragranular tungsten content rate and a grain-boundary tungsten content rate (intragranular W/grain-boundary W) of 0.8 or less.

[Claim 2] The molybdenum-containing material according to claim 1, wherein the crystal grain size is 1 mm or more and a value of the intragranular W/grain-boundary W is 0.7 or less.

[Claim 3] The molybdenum-containing material according to claim 1 or 2, wherein a value of intragranular K/grain-boundary K is 0.7 or less, the intragranular K/grain-boundary K being a ratio between an intragranular potassium content rate and a grain-boundary potassium content rate.

[Claim 4] The molybdenum-containing material according to claim 3, wherein the value of the intragranular K/grain-boundary K is 0.6 or less.

[Claim 5] The molybdenum-containing material according to claim 1 or 2, wherein the density is 10.18 g/cm^3 (99.8%) or more.

[Claim 6] The molybdenum-containing material according to claim 1 or 2, wherein the molybdenum content rate is 99.999 mass % or more.

[Claim 7] The molybdenum-containing material according to claim 1 or 2,
wherein

a tungsten content rate is 200 ppm or less.

5 [Claim 8] The molybdenum-containing material according to claim 1 or 2,
wherein

a potassium content rate is 20 ppm or less.

10 [Claim 9] The molybdenum-containing material according to claim 1 or 2,
wherein

the molybdenum-containing material has a shape of a plate or a target.