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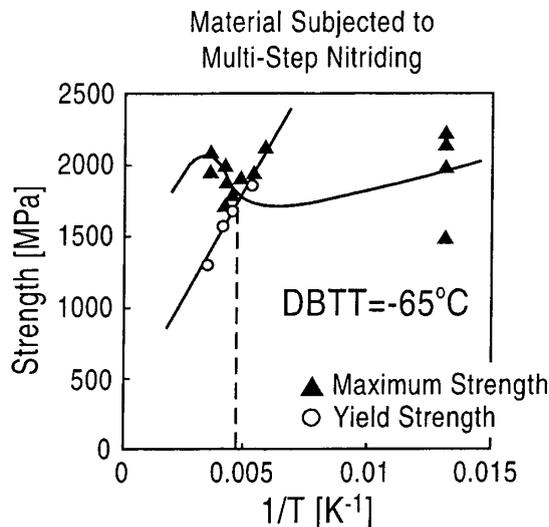
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(54) **HIGH MELTING POINT METAL BASED ALLOY MATERIAL EXHIBITING HIGH STRENGTH AND HIGH CRYSTALLIZATION TEMPERATURE AND METHOD FOR PRODUCTION THEREOF**

(57) A refractory metal-based alloy material exhibiting high strength and high recrystallization temperature includes a worked material obtained by carburizing, while using a carbon source and coexisted oxygen, a material containing nitride particles of a solute metal dispersed and precipitated in a matrix by multi-step nitriding of a

worked alloy material containing one metal selected from Mo, W, and Cr as a matrix and at least one element selected from Ti, Zr, Hf, V, Nb, and Ta as the solute metal, wherein the worked material contains carbon segregated at grain boundaries as a result of the carburizing and oxide particles converted from the nitride particles.

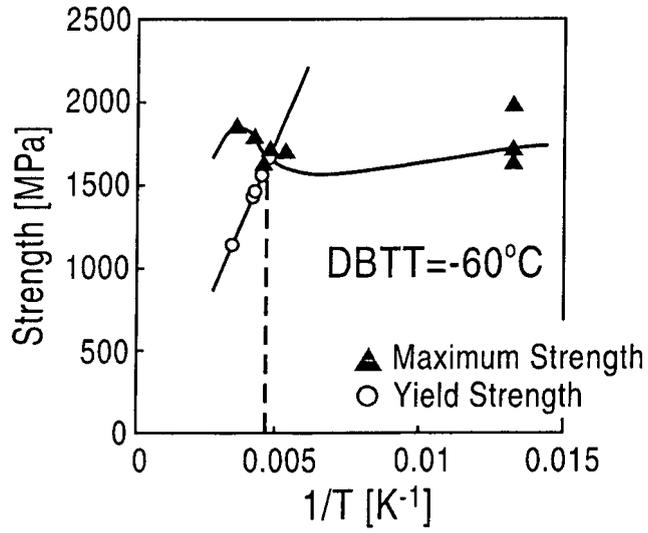
FIG.3A



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FIG.3B

Material Subjected to
Multi-Step Nitriding
and CO Treatment



Description

Technical Field

[0001] The present invention relates to high-temperature resistant materials, in particular to an oxide dispersion-strengthened refractory metal-based alloy material exhibiting high strength and high recrystallization temperature, the alloy material having one refractory metal selected from Mo, W, and Cr as a matrix.

[0002] Today, TZM alloys (maximum allowable working temperature: 1,400°C), in which Ti, Zr, and C are added to Mo and which is produced by Plansee AG, are almost exclusively used as a refractory metal-based heat-resistant alloy. However, these alloys have low workability.

[0003] Mo alloys, which are a representative example of refractory metal-based alloy materials, have a significant drawback in that, once Mo alloys are heated to the recrystallization temperature (1,000°C to 1,300°C) or more, the Mo alloys exhibit cold brittleness and decreased strength at high temperature as a result of recrystallization. In order to overcome this drawback, the present inventors have developed a multi-step internal nitriding process of first nitriding a Mo-Ti alloy at a temperature not more than a recrystallization upper limit temperature, and then nitriding the alloy by increasing the temperature stepwise to form TiN particles (patent document 1). The Mo alloy material obtained through this process exhibits a recrystallization temperature as high as 1,600°C by the pinning effect of the precipitated TiN particles (patent document 1).

[0004] The present inventors also developed a process of conducting a multi-step internal nitriding process on a worked alloy material containing Mo as a matrix and at least one of Ti, Zr, Hf, V, Nb, and Ta as a solid solution, and then conducting an external nitriding process (patent document 2). By this process, Mo worked alloy materials having high corrosion resistance, high strength, and high toughness are obtained. Furthermore, the present inventors have made a report of a study on a carburizing process as a process for strengthening crystal grain boundaries of Mo-based materials, the carburizing process including vapor-depositing a trace amount of carbon and vacuum heating the worked material to allow the carbon to disperse in grain boundaries (nonpatent document 1). The present inventor also made a report of a study on the process of controlling and strengthening material structures by carburizing TZM alloys using diluted CO gas (nonpatent document 2). The present inventors also made a report of a study on material structures produced by heating recrystallized Mo-Ti-based alloys with CO gas (nonpatent document 3).

[0005]

Patent document 1: Japanese Unexamined Patent Application Publication No. 2001-073060

Patent document 2: Japanese Unexamined Patent

Application Publication No. 2003-293116

Nonpatent document 1: Tetsuji HOSHIKA et al., Journal of the Japan Society of Powder and Powder Metallurgy, 49 (2002) 32-36

Nonpatent document 2: Naoki NOMURA et al., Abstracts of 2002 Japan Society of Powder and Powder Metallurgy autumn conference, (2002) 201

Nonpatent document 3: Abstracts of 2003 Japan Society of Powder and Powder Metallurgy autumn conference, (2003) 31

Disclosure of Invention

Problems to be Solved by the Invention

[0006] Although Mo-Ti-based alloys with a recrystallization temperature as high as 1,600°C can be obtained by the above-described multi-step internal nitriding process developed by the present inventors, the stability of TiN particles at high temperature and high vacuum is not sufficient. As a result, degradation and denitration reaction of TiN particles gradually progress from the surface of the alloys, thereby leading to recrystallization and embrittlement in a long-term service.

Means for Solving the Problems

[0007] The present inventors have for many years studied the control and strengthening of microstructures by nitriding or carburizing Mo-based materials, and have successfully developed a refractory metal-based alloy material which does not recrystallize and maintains stability for long time even when it is used at a high temperature of at least 1,600°C and in high vacuum and which exhibits excellent strength at room temperature and high temperatures (for example, 1,500°C) in comparison with commercially available Mo alloys. This refractory metal-based alloy material is obtained by carburizing an alloy material already subjected to a multi-step internal nitriding process in nitriding at a temperature not more than the recrystallization upper limit temperature is conducted, followed by further nitriding while increasing the temperature stepwise.

[0008] In particular, the present invention provides: (1) A refractory metal-based alloy material exhibiting high strength and high recrystallization temperature, including a worked material obtained by carburizing, while using a carbon source and coexisted oxygen, a material containing nitride particles of a solute metal dispersed and precipitated in a matrix by multi-step nitriding of a worked alloy material containing one metal selected from Mo, W, and Cr as a matrix and at least one element selected from Ti, Zr, Hf, V, Nb, and Ta as the solute metal, wherein the worked material contains carbon segregated at grain boundaries as a result of the carburizing and oxide particles converted from the nitride particles.

[0009] The present invention also provides: (2) the refractory metal-based alloy material exhibiting high

strength and high recrystallization temperature according to (1) above, in which a worked structure is maintained in the surface of the alloy material, and the interior of the alloy material includes a recrystallized structure.

[0010] The present invention also provides: (3) the refractory metal-based alloy material according to (1) or (2) above, in which the matrix is Mo, the solute metal is Ti, and the recrystallization temperature is 1,600°C or more.

[0011] The present invention also provides: (4) a process of producing the refractory metal-based alloy material according to (1) or (2) above, including subjecting an alloy material containing one metal selected from Mo, W, and Cr as a matrix and at least one element selected from Ti, Zr, Hf, V, Nb, and Ta as a solute metal to multi-step internal nitriding so that nitride particles of the solute metal are dispersed in the matrix, and then carburizing the resulting worked alloy material by using a carbon source and coexisted oxygen.

[0012] The present invention also provides: (5) the process of producing the refractory metal-based alloy material according to (4) above, in which a first nitriding step is conducted at a temperature not more than a recrystallization upper limit temperature of the worked alloy material but not less than a temperature 200°C lower than a recrystallization lower limit temperature so as to produce and diffuse nitride particles of the solute metal, and then a second nitriding step is conducted at a temperature not less than a recrystallization lower limit temperature of the resulting worked alloy material after the first step nitriding so as to allow the nitride particles produced and dispersed in the first nitriding step to grow into grains and be stabilized.

[0013] The present invention also provides: (6) the process of producing the refractory metal-based alloy material according to (4) or (5) above, in which the carburizing is conducted by using inert gas containing 0.1 to 5 percent by volume of CO.

[0014] The present inventors have found that, by carburizing a refractory metal worked material containing nitride particles dispersed in a matrix while using a carbon source and coexisted oxygen, not only the grain boundaries are strengthened due to grain boundary segregation of carbon, but also the nitride particles are converted to oxide particles by dispersion of oxygen, thereby causing dispersion segregation of oxide particles of the solute metal (internal oxidation).

[0015] The reason for formation of oxide particles by carburizing using a carbon source and coexisted oxygen is not clear but is presumed as follows: When the heating temperature is low, a very thin Mo₂C film is formed on a surface of the worked material and inhibits dispersion of oxygen into the interior of the worked material. As a result, dispersion of carbon is possible only from the interface between the Mo₂C film and the worked material, thereby causing internal carburization. However, when the heating is conducted at a high temperature, a Mo₂C film is rarely formed on the surface of the worked material, and this leads to dispersion of oxygen. For example, when

similar heat treatment is conducted using argon gas containing 2 percent by volume of CH₄ gas, a very thick MoC₂ film is formed irrespective of the temperature of heat treatment, and the resulting material becomes brittle.

When oxygen coexists, formation of a MoC₂ film (i.e., carburizing reaction of Mo itself) is inhibited, and this causes grain boundary dispersion of carbon and intraparticle dispersion of oxygen to occur simultaneously.

[0016] The oxide particles produced thereby have a pinning effect of inhibiting migration of crystal grain boundaries as do the nitride particles; however, since the oxide particles are more thermodynamically stable compared to the nitride particles, the oxide particles dispersed and precipitated in the refractory metal do not degrade at high temperature and high vacuum but remain stable for long time. Moreover, since recrystallization embrittlement, which is observed in nitride particles, is improved and the recrystallization temperature is increased, resistance to high-temperature deformation can be enhanced.

[0017] The alloy material obtained by the multi-step nitriding and carburizing retains a rolled structure at least in the surface and contains the oxide particles of the solute metal dispersed and precipitated across the region from the surface to the inner layer. Thus, the strength is increased as a result of grain boundary segregation of carbon, and the recrystallization temperature is improved by precipitation hardening of the oxide particles. For example, a Mo-Ti alloy will exhibit strength two to three fold that of commercially available Mo alloys over a wide range from room temperature to 1,600°C, and will show superior heat resistance that can completely prevent recrystallization at a temperature as high as 1,700°C (the temperature at which the material subjected to the multi-step internal nitriding is recrystallized) under high vacuum.

Advantages

[0018] The present invention provides a refractory metal-based heat-resistant alloy material exhibiting excellent heat resistance such that the material remains stable and does not recrystallize at high temperature under high vacuum for long time. Since the rolled structure maintained in the surface portion of the alloy material has an effect of inhibiting propagation of cracks, impact resistance is also high. Since the production process of the present invention includes heating an alloy material in a nitriding atmosphere after the alloy material is worked into a desired shape, followed by heating using a carbon source and coexisted oxygen, the process can be easily used to produce a previously worked product having a complicated shape.

Best Mode for Carrying Out the Invention

[0019] For the refractory metal-based alloy material of the present invention, Ti, Zr, Hf, V, Nb, and Ta are suitable

as the solute metal. These metals all form stable nitrides compared to group 6A elements such as Mo and W; thus, they are necessary for controlling the structure by a multi-step internal nitriding of the first step. Their oxides are also more stable than their nitrides; thus, the nitride particles are converted to oxide particles by CO gas heat treatment conducted after the multi-step nitriding process. The content thereof is about 0.1 to 5.0 wt%, preferably about 0.3 to 2.0 wt%. At a content less than 0.1 wt%, the precipitated particles are too few to inhibit recrystallization. At a content exceeding 5.0 wt%, the material after nitriding-CO gas heat treatment becomes brittle, and the material is not suitable for practical use.

[0020] The refractory metal-based alloy material containing the solute metal is worked into a desired shape and then subjected to a multi-step internal nitriding process. The material obtained by the multi-step internal nitriding and the production process therefor are known in the art as shown in patent document 1 (Japanese Unexamined Patent Application Publication No. 2001-073060).

[0021] In other words, the material obtained by the multi-step internal nitriding is a worked alloy material which contains fine nitrides dispersed in a matrix, the fine nitrides being formed by internally nitriding, in a nitriding atmosphere, the metal element dissolved in a worked alloy material containing one of Mo, W, and Cr as a matrix. This worked alloy material has a structure in which nitride precipitated particles are grown into grains while maintaining the worked structure, such as a rolled structure, in at least the surface thereof.

[0022] The production process therefor includes: subjecting the worked alloy material to a first nitriding step at a temperature not more than the recrystallization upper limit temperature of the alloy but not less than a temperature 200°C lower than the recrystallization lower limit temperature to produce and diffuse nitride particles of the solute metal; and subjecting the resulting worked alloy material to a second nitriding step at a temperature not more than the recrystallization lower limit temperature of the alloy worked material after the first nitriding step so that the nitride particles formed and dispersed in the first nitriding step are grown into grains and are stabilized.

[0023] The recrystallization temperature of the worked alloy material depends on the conditions, such as working ratio, during preparation of the alloy material, and has a certain breadth between the upper limit value and the lower limit value. For example, a Mo-1.0 wt% Ti worked alloy material has a recrystallization temperature ranging from about 950°C to about 1,020°C. The recrystallization onset temperature decreases as the working ratio increases.

[0024] The reason for conducting the first nitriding step at a temperature not more than the recrystallization upper limit temperature is because the material will recrystallize and become brittle if nitrided at a temperature beyond this value. The reason for conducting the step at a temperature not less than a temperature 200°C lower than

the recrystallization lower limit temperature is because the nitrogen dispersion rate will be too low to internally nitride the material down to a depth sufficient for practical application if the temperature is below this value.

[0025] The number of steps in the multi-step nitriding process needs to be at least two. From the third nitriding step and on, the material may be heated at a temperature not less than the recrystallization lower limit temperature of the worked alloy material obtained in the previous nitriding step so that the nitride particles formed and dispersed in the preceding nitriding step can be further grown into grains and stabilized.

[0026] For example, when the first nitriding step is conducted at 900°C, in the resulting inner nitride layer, the distribution density of the precipitated TiN particles exhibits a gradient from the surface toward the interior (i.e., the number of particles is high in the surface and low inside). As a result, recrystallization temperature of the inner nitride layer obtained by the first nitriding step in a nitriding atmosphere is highest (e.g., 1,400°C (recrystallization upper limit temperature)) near the surface and lowest (e.g., 950°C (recrystallization lower limit temperature)) (at the end of the internal nitride layer).

[0027] The thickness of the internal nitride layer obtained by the first nitriding step defines the theoretical maximum thickness of the worked structure, such as rolled structure, that remains at the end. In order to allow the worked structure, such as rolled structure, to remain as much as possible, it is necessary to increase the precipitation density of the TiN particles near the end of the internal nitride layer obtained in the first nitriding step by conducting the second nitriding step at a temperature slightly above the recrystallization lower limit temperature and to increase the size of TiN particles. This increases the recrystallization lower limit temperature of the material (i.e., the recrystallization temperature near the end of the inner nitride layer) after the second nitriding step. It is of course possible to allow the worked structure, such as rolled structure, to remain as thick as possible by conducting the second nitriding step at a temperature above the temperature of the first nitriding step but below the recrystallization lower limit temperature; however, this increases the number of nitriding steps and the time required therefor. The same applies to cases where three or more nitriding steps are conducted.

[0028] The morphology of the nitride particles depends on the nitriding temperature. For example, according to a three-step nitriding process of 900°C, 1,200°C, and 1,600°C, the particles after the first nitriding step are disk-shaped particles with a diameter of about 1 to 2 nm, the number of precipitated particles decreasing toward inside the specimen. Near the outermost surface portion, nearly all alloyed elements are precipitated as nitrides. After the second nitriding step, the particles are grown into grains of ten and several nanometers, and the distribution density gradient of the precipitated TiN particles inside the worked structure such as rolled structure becomes moderate. After the third nitriding step, the TiN

particles are grown into bar-shaped particles with a length of about 50 to 150 nm, and nearly all Ti exists as nitrides in the worked structure, such as rolled structure, remaining in the surface of the material.

[0029] As discussed above, the refractory metal-based alloy material having a recrystallization temperature increased by the multi-step internal nitriding, is carburized by using a carbon source and coexisted oxygen. As a result of the carburization, the rolled structure remains in the material surface, and a characteristic two-layer structure, which is a recrystallized structure, is formed inside. By the carburization process, only the nitride particles precipitated by the multi-step internal nitriding can be converted to oxide particles without affecting the microstructure of the matrix in any way.

[0030] The amount of carbon segregated at grain boundaries is about 30 to 150 ppm (wt%). At an amount below this range, the effect of strengthening the grain boundaries cannot be expected. The nitrides inside the worked structure, such as rolled structure, remaining after the multi-step nitriding are all converted to oxide particles. During the conversion, size and morphology are changed. For example, bar-shaped TiN particles (aspect ratio: 4 to 7) with a length of 50 to 150 nm are converted to oxide particles having a length of 30 to 60 nm (aspect ratio: 2 to 3). The number of particles increases as their size is reduced.

[0031] An example of the carbon source and coexisted oxygen used is diluted CO gas. Diluted CO gas is preferably inert gas containing 0.1 to 5 percent by volume of CO. If the CO concentration is higher than 5 percent by volume, the refractory metal is excessively carburized, which is problem. The carbon potential of diluted CO gas can be easily controlled, and formation of a hard, brittle carbide layer on the surface of the alloy material can be suppressed by adjusting the concentration of carbon.

[0032] The carburization is possible not only by using diluted CO gas but also by placing a solid carbon, hydrocarbon, or the like around the refractory metal-based alloy material in the presence of oxygen. For example, reaction similar to the reaction induced by using diluted CO gas can be conducted by heating the material while placing carbon powder near the worked material and while vacuuming with a rotary pump or the like without bringing the worked material into direct contact with the carbon source. Under a condition where the degree of vacuum is unsatisfactory, a trace amount of oxygen in the atmosphere reacts with carbon to generate CO gas, which contributes to the reaction. A similar reaction also occurs by burying the worked material in a powder mixture of carbon powder and alumina powder to conduct reaction under a low vacuum condition. However, if a solid carbon source is used and the heating temperature is low, a hard, brittle carbide layer of the refractory metal is easily formed on the surface of the worked material. Thus, a carburizing process that uses diluted CO gas is more preferable.

EXAMPLE 1

[0033] Two pieces of a Mo-1.0 wt% Ti alloy rolled material (1.0 mm in thickness, 2.5 mm in width, 25 mm in length) were used as test specimens. The recrystallization lower limit temperature and the recrystallization upper limit temperature of this alloy rolled material were 900°C and 1,020°C, respectively. Each test specimen was subjected to a multi-step internal nitriding process including a first nitriding step at 900°C for 64 hours, a second nitriding step at 1,200°C for 25 hours, and a third nitriding step at 1,500°C for 25 hours. The recrystallization upper and lower limit temperatures were 950°C and 1,400°C, respectively, after the first step, 1,250°C and 1,600°C after the second step, and 1,600°C and 1,800°C after the third step (in nitrogen atmosphere). The nitriding was conducted in a N₂ gas stream at 1 atm. One of the two test specimens was directly used as a comparative example. The other test specimen was carburized at 1,500°C for 16 hours in a diluted CO gas atmosphere. The concentration of CO gas was Ar/CO = 49/1 (CO concentration: 2 vol%).

[0034] Fig. 1 includes optical micrographs showing the structures of the test specimens after the processing. The micrographs showed that a rolled structure was maintained in either of the surfaces of the test specimens subjected to the multi-step nitriding and to the multi-step nitriding followed by carburizing, respectively. Fig. 2 shows TEM structures of the test specimens after the processing. Fig. 2 shows that bar-shaped TiN particles of the test specimen subjected to the multi-step nitriding are converted to a Ti oxide having an elliptical shape. Fig. 3 shows the results of the three-point bending test. Fig. 3 shows that their mechanical properties do not change after the processing with CO gas. The ductile-to-brittle transition temperature (DBTT) also remains the same.

[0035] Fig. 4 includes optical micrographs showing the structures of the test specimens vacuum processed at 1,600°C for 1 hour in the first step and 1,700°C for 1 hour in the second step to examine the recrystallization temperature of the test specimens. The comparative example subjected to the multi-step nitriding underwent recrystallization as apparent from the existence of a white portion directly below the rolled structure. In contrast, the sample subjected to the multi-step nitriding and carburizing did not recrystallize even when it was heated at 1,700°C. Fig. 5 shows the results of high-temperature three-point bending test at 1,500°C conducted on the test specimen before processing, the test specimen subjected to the multi-step nitriding, and the test specimen subjected to the multi-step nitriding and carburizing. The results show that test specimens subjected to the multi-step nitriding and the multi-step nitriding and carburizing exhibit significantly improved strength compared with the unprocessed test specimen.

Industrial Applicability

[0036] The refractory metal-based alloy material of the present invention exhibits heat resistance that surpasses that of existing TZM alloys and are used for heat-resistant structural materials compatible with very high temperature environment. Concrete examples thereof include bolts and nuts for ultra-high temperature parts, heaters of ultra-high temperature furnaces, filaments, reflector plates, boats and heat-sinks for baking semiconductor components, molds and dies for hot working, gas jet nozzles for aerospace applications, and rapid solidification molds and injection molding dies for molten metal.

Brief Description of the Drawings

[0037]

[Fig. 1] Fig. 1 includes optical micrographs, i.e., substitutes for a drawing, that show the structures of the test specimens after processing in a first embodiment.

[Fig. 2] Fig. 2 includes photographs, i.e., substitutes for a drawing, that show TEM structures of the test specimens after the processing in the first embodiment.

[Fig. 3] Fig. 3 includes graphs showing the results of the three-point bending test of the test specimens after the processing in the first embodiment.

[Fig. 4] Fig. 4 includes optical micrographs, i.e., substitutes for a drawing, that show the structures of the processed test specimens after heating at high temperature in the first embodiment.

[Fig. 5] Fig. 5 includes graphs showing the results of high-temperature three-point bending test at 1,500°C conducted on an unprocessed specimen, a specimen subjected to multi-step nitriding, and a specimen subjected to multi-step nitriding and carburizing.

Claims

1. A refractory metal-based alloy material exhibiting high strength and high recrystallization temperature, comprising a worked material obtained by carburizing, while using a carbon source and coexisted oxygen, a material containing nitride particles of a solute metal dispersed and precipitated in a matrix by multi-step nitriding of a worked alloy material containing one metal selected from Mo, W, and Cr as a matrix and at least one element selected from Ti, Zr, Hf, V, Nb, and Ta as the solute metal, wherein as a result of the carburizing, the worked material contains carbon segregated at grain boundaries and oxide particles converted from the nitride particles.
2. The refractory metal-based alloy material exhibiting high strength and high recrystallization temperature according to claim 1, wherein a worked structure is maintained in the surface of the alloy material, and the interior of the alloy material includes a recrystallized structure.
3. The refractory metal-based alloy material exhibiting high strength and high recrystallization temperature according to claim 1, wherein the matrix is Mo, the solute metal is Ti, and the recrystallization temperature is 1,600°C or more.
4. A process of producing the refractory metal-based alloy material exhibiting high strength and high recrystallization temperature according to claim 1, comprising subjecting a worked alloy material containing one metal selected from Mo, W, and Cr as a matrix and at least one element selected from Ti, Zr, Hf, V, Nb, and Ta as a solute metal to multi-step internal nitriding so that nitride particles of the solute metal are dispersed in the matrix, and then carburizing the resulting worked alloy material by using a carbon source and coexisted oxygen.
5. The process of producing the refractory metal-based alloy material according to claim 4, wherein a first nitriding step is conducted at a temperature not more than a recrystallization upper limit temperature of the worked alloy material but not less than a temperature 200°C lower than a recrystallization lower limit temperature so as to produce and diffuse nitride particles of the solute metal, and then a second nitriding step is conducted at a temperature not less than a recrystallization lower limit temperature of the resulting worked alloy material after the first step nitriding so as to allow the nitride particles produced and dispersed in the first nitriding step to grow into grains and be stabilized.
6. The process of producing the refractory metal-based alloy material according to claim 4, wherein the carburizing is conducted by using inert gas containing 0.1 to 5 percent by volume of CO.

FIG.1A

Material Subjected to
Multi-Step Nitriding

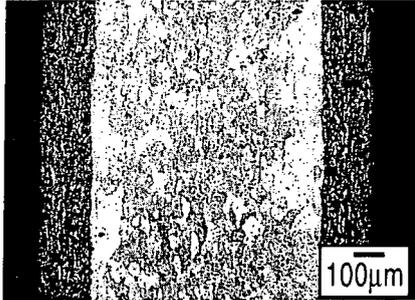


FIG.1B

Material Subjected to
Multi-Step Nitriding
and CO Treatment

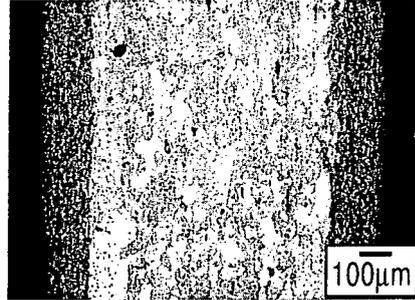


FIG.2A

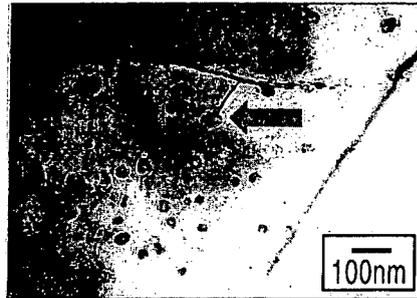
Material Subjected to
Multi-Step Nitriding



Bar-Shaped TiN Particles

FIG.2B

Material Subjected to
Multi-Step Nitriding
and CO Treatment



Ti Oxide Particles Having
Elliptical Shape



FIG.3A

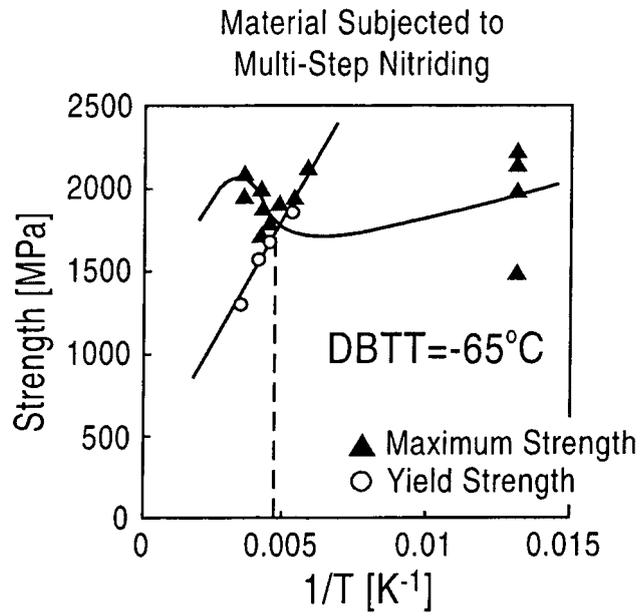


FIG.3B

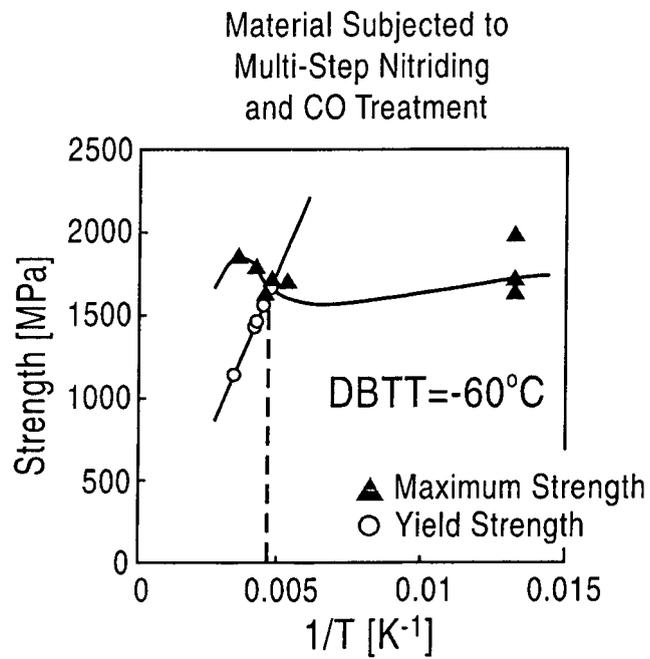
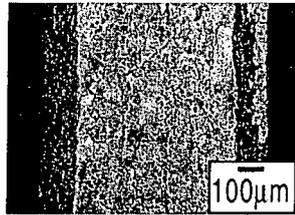


FIG.4A

Material Subjected to
Multi-Step Nitriding



Vacuum
Treatment
at
1600°C-1h

FIG.4B

Material Subjected to
Multi-Step Nitriding
and CO Treatment

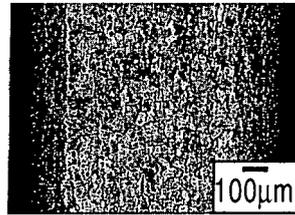
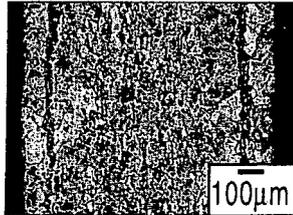


FIG.4C

Material Subjected to
Multi-Step Nitriding



Vacuum
Treatment
at
1700°C-1h

FIG.4D

Material Subjected to
Multi-Step Nitriding
and CO Treatment

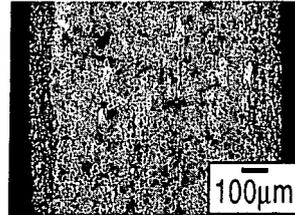


FIG.5A

M0-1.0 Ti Alloy
Recrystallized Material

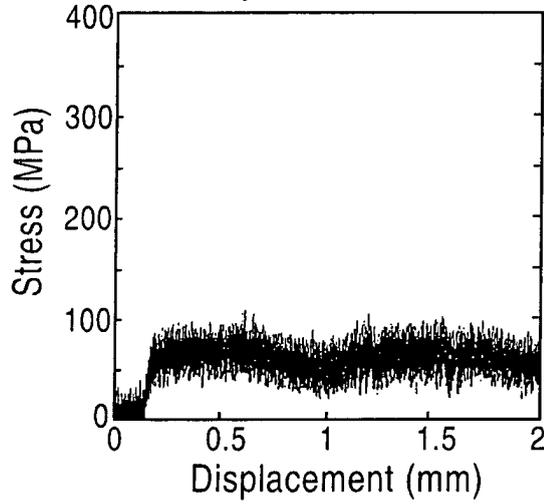


FIG.5B

M0-1.0 Ti Alloy Subjected
to Multi-Step Nitriding

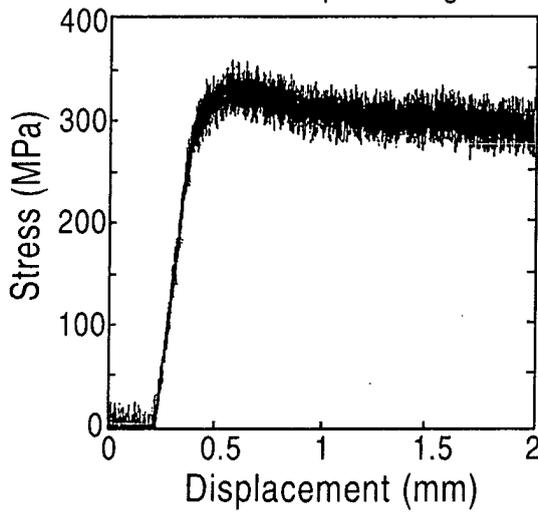
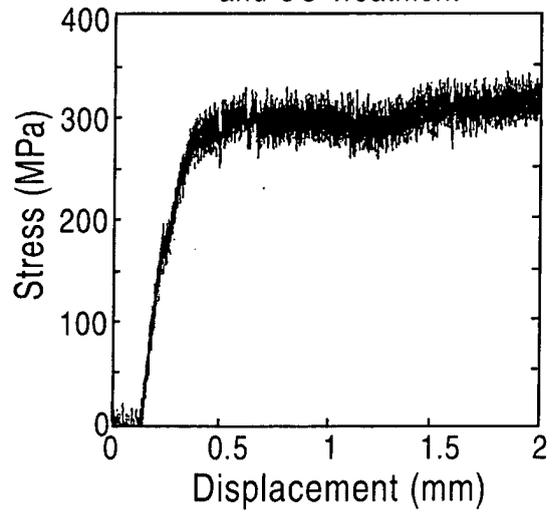


FIG.5C

M0-1.0 Ti Alloy Subjected
to Multi-Step Nitriding
and CO Treatment



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/008069

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C22C1/10, 27/04, C23C8/34		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ C22C1/10, 27/04, C23C8/34		
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 1996-2005 Kokai Jitsuyo Shinan Koho 1971-2005 Toroku Jitsuyo Shinan Koho 1994-2005		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-293070 A (Japan Science and Technology Corp.), 15 October, 2003 (15.10.03) & EP 1491652 A1	1-6
A	JP 2001-73060 A (Japan Science and Technology Corp.), 21 March, 2001 (21.03.01) & EP 1219722 A1	1-6
A	JP 2001-295023 A (A.L.M.T. Corp.), 26 October, 2001 (26.10.01) (Family: none)	1-6
A	JP 5-263179 A (Kubota Corp.), 12 October, 1993 (12.10.93) (Family: none)	1-6
<input type="checkbox"/> Further documents are listed in the continuation of Box C.		<input type="checkbox"/> See patent family annex.
* Special categories of cited documents:	"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	
"A" document defining the general state of the art which is not considered to be of particular relevance	"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	
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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		
Date of the actual completion of the international search 16 August, 2005 (16.08.05)	Date of mailing of the international search report 06 September, 2005 (06.09.05)	
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	
Facsimile No.	Telephone No.	

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REFERENCES CITED IN THE DESCRIPTION

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- **TETSUJI HOSHIKA et al.** *Journal of the Japan Society of Powder and Powder Metallurgy*, 2002, vol. 49, 32-36 [0005]
- **NAOKI NOMURA et al.** *Abstracts of 2002 Japan Society of Powder and Powder Metallurgy autumn conference*, 2002, vol. 201 [0005]
- *Abstracts of 2003 Japan Society of Powder and Powder Metallurgy autumn conference*, 2003, vol. 31 [0005]