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(54) **TUNGSTEN ALLOY, TUNGSTEN ALLOY PART USING SAME, DISCHARGE LAMP, TRANSMISSION TUBE, AND MAGNETRON**

(57) It is an object to provide a tungsten alloy containing no thorium which is a radioactive material, which is equal to or higher in emission characteristics than a thorium-containing tungsten alloy, and a discharge lamp, a transmitting tube and a magnetron which use the tungsten alloy. According to one embodiment, a tungsten alloy includes a Hf component within a range of 0.1 wt% or more and 3 wt% or less in terms of HfO₂.

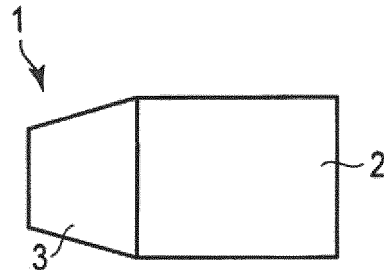


FIG. 1

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Description

Technical Field

5 **[0001]** Embodiments described herein relate to a tungsten alloy, a tungsten alloy part using the same, a discharge lamp electrode part, a discharge lamp, a transmitting tube, and a magnetron.

Background Art

10 **[0002]** A tungsten alloy part is used in various fields utilizing tungsten having a strength at a high temperature. Examples thereof include a discharge lamp, a transmitting tube, and a magnetron. The tungsten alloy part is used for a cathode electrode, an electrode supporting rod, and a coil part or the like in the discharge lamp (HID lamp). The tungsten alloy part is used for a filament and a mesh grid or the like in the transmitting tube. The tungsten alloy part is used for the coil part or the like in the magnetron. These tungsten alloy parts include a sintered body having a predetermined shape, a wire rod, and a coil part obtained by processing the wire rod into a coil form.

15 **[0003]** Conventionally, as described in Jpn. Pat. Appln. KOKAI Publication No. 2002-226935 (Patent Literature 1), a tungsten alloy containing thorium (or a thorium compound) is used for these tungsten alloy parts. In the tungsten alloy of Patent Literature 1, deformation resistance is improved by finely dispersing thorium particles and thorium compound particles which have the average particle diameter of 0.3 μm or less. Since the thorium-containing tungsten alloy has excellent emitter characteristics and mechanical strength at a high temperature, the thorium-containing tungsten alloy is used in the above fields.

20 **[0004]** However, since thorium or the thorium compound is a radioactive material, a tungsten alloy part using no thorium is desired in consideration of the influence on the environment. In Jpn. Pat. Appln. KOKAI Publication No. 2011-103240 (Patent Literature 2), a tungsten alloy part containing boride lanthanum (LaB_6) has been developed as the tungsten alloy part using no thorium.

25 **[0005]** On the other hand, a short arc type high-pressure discharge lamp using a tungsten alloy containing lanthanum trioxide (La_2O_3) and HfO_2 or ZrO_2 is described in Patent Literature 3. According to the tungsten alloy described in Patent Literature 3, sufficient emission characteristics are not obtained. This is because lanthanum trioxide has a low melting point of about 2300°C, and lanthanum trioxide is evaporated in an early stage when a part is subjected to a high temperature by increasing an applied voltage or a current density, which causes deterioration in emission characteristics.

Citation List

Patent Literature

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[0006]

Patent Literature 1: Jpn. Pat. Appln. KOKAI Publication No. 2002-226935

Patent Literature 2: Jpn. Pat. Appln. KOKAI Publication No. 2011-103240

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Patent Literature 3: Japanese Patent No. 4741190

Summary of Invention

Technical Problem

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[0007] For example, discharge lamps, parts which use a tungsten alloy, are roughly divided into two kinds (a low-pressure discharge lamp and a high-pressure discharge lamp). Examples of the low-pressure discharge lamp include various arc-discharge type discharge lamps such as for general lighting, special lighting used for a road or a tunnel or the like, a coating material curing apparatus, a UV curing apparatus, a sterilizer, and a light cleaning apparatus for a semiconductor or the like. Examples of the high-pressure discharge lamp include a processing apparatus for water supply and sewerage, general lighting, outdoor lighting for a stadium or the like, a UV curing apparatus, an exposure device for a semiconductor and a printed circuit board or the like, a wafer inspection apparatus, a high-pressure mercury lamp such as a projector, a metal halide lamp, an extra high pressure mercury lamp, a xenon lamp, and a sodium lamp.

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[0008] A voltage of 10 V or more is applied to the discharge lamp according to the application. When a voltage is less than 100 V, a life equal to that of the thorium-containing tungsten alloy is obtained for the tungsten alloy containing boride lanthanum described in Patent Literature 2. However, if the voltage is 100 V or more, the emission characteristics are deteriorated. As a result, the life is also largely decreased.

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[0009] Similarly, there is a problem that sufficient characteristics are not obtained also for the transmitting tube or the

magnetron if the applied voltage is increased.

[0010] The present invention was made in consideration of the above problem. It is an object of the present invention to provide a tungsten alloy equal to or higher in characteristics than a thorium-containing tungsten alloy without using thorium which is a radioactive material, and a tungsten alloy part, a discharge lamp, a transmitting tube, and a magnetron which use the tungsten alloy.

Solution to Problem

[0011] An embodiment provides a tungsten alloy containing a W component and at least two kinds selected from the group consisting of Hf, HfO₂, HfC, and C. The Hf component is within a range of 0.1 wt% or more and 3 wt% or less in terms of HfO₂. An embodiment provides a tungsten alloy containing a W component, and a Hf component containing HfO₂ particles. The amount of the Hf component is within a range of 0.1 wt% or more and 5 wt% or less in terms of HfO₂. The average primary particle diameter of the HfO₂ particles is 15 μm or less.

[0012] A tungsten alloy part of the embodiment containing Hf of 0.1 wt% to 3 wt% in terms of HfO₂ contains at least two kinds of Hf, HfO₂, HfC, and C.

[0013] The contents of Hf and O are preferably represented by HfO_x, where $x < 2$. The contents of Hf and O are preferably represented by HfO_x, where $0 < x < 2$.

[0014] When the amount of carbon in a surface part in the tungsten alloy part is defined as C1 (wt%) and the amount of carbon in a central part is defined as C2 (wt%), $C1 < C2$ is preferably set. The tungsten alloy part preferably contains 0.01 wt% or less of at least one kind of K, Si, and Al. When the content of Hf is defined as 100 parts by mass, the content of Zr is preferably 10 parts by mass or less. The average crystal particle diameter of tungsten is preferably 1 to 100 μm.

[0015] The tungsten alloy part is preferably used for at least one kind of a discharge lamp part, a transmitting tube part, and a magnetron part.

[0016] A discharge lamp of the embodiment includes the tungsten alloy part of the embodiment. A transmitting tube of the embodiment includes the tungsten alloy part of the embodiment. A magnetron of the embodiment includes the tungsten alloy part of the embodiment.

[0017] The discharge lamp electrode part of the embodiment is made of a tungsten alloy. The tungsten alloy contains 0.1 to 5 wt% of the Hf component in terms of HfO₂, and the HfO₂ particles in the Hf component have an average particle diameter of 15 μm or less.

[0018] The HfO₂ particles preferably have an average particle diameter of 5 μm or less and a maximum diameter of 15 μm or less. Two kinds (HfO₂ and metal Hf) preferably exist as the Hf component. Metal Hf preferably exists as the Hf component on the surfaces of the HfO₂ particles. Preferably, metal Hf of the Hf component is partly or wholly solid-solved in tungsten. When the total content of the Hf component is defined as 100 parts by mass, the ratio of Hf in the HfO₂ particles is preferably 30 to 98 mass. The tungsten alloy preferably contains 0.01 wt% or less of a dope material made of at least one kind of K, Si, and Al. The tungsten alloy preferably contains 2 wt% or less of at least one kind of Ti, Zr, V, Nb, Ta, Mo, and rare earth elements. A wire diameter is preferably 0.1 to 30 mm. The tungsten alloy preferably has a Vickers hardness of within a range of Hv 330 to 700. The discharge lamp electrode part preferably has a tip part having a tapered tip and a cylindrical body part.

[0019] When the crystal structure of the circumferential section of the body part is observed, the area ratio of tungsten crystals per unit area of 300 μm × 300 μm is preferably 90% or more, and the tungsten crystals have a crystal particle diameter of 1 to 80 μm. When the crystal structure of the side section of the body part is observed, the area ratio of tungsten crystals per unit area of 300 μm × 300 μm is preferably 90% or more, and the tungsten crystals have a crystal particle diameter of 2 to 120 μm.

[0020] The discharge lamp of the embodiment includes the discharge lamp electrode part of the embodiment. The applied voltage of the discharge lamp is preferably 100 V or more.

Advantageous Effects of Invention

[0021] Since a tungsten alloy of an embodiment does not contain thorium (containing thoria) which is a radioactive material, the tungsten alloy does not exert a bad influence on the environment. In addition, the tungsten alloy has characteristics equal to or higher than those of a thorium-containing tungsten alloy. For this reason, a tungsten alloy part, a discharge lamp electrode part, a discharge lamp, a transmitting tube, and a magnetron which use the tungsten alloy can be used as environment-friendly products.

Brief Description of Drawings

[0022]

FIG. 1 shows an example of a tungsten alloy part of a first embodiment.

FIG. 2 shows another example of the tungsten alloy part of the first embodiment.

FIG. 3 shows an example of a discharge lamp of the first embodiment.

FIG. 4 shows an example of a magnetron part of the first embodiment.

5 FIG. 5 shows an example of a discharge lamp electrode part of a second embodiment.

FIG. 6 shows another example of the discharge lamp electrode part of the second embodiment.

FIG. 7 shows an example of a circumferential section of a body part of the discharge lamp electrode part of the second embodiment.

10 FIG. 8 shows an example of a side section of the body part of the discharge lamp electrode part of the second embodiment.

FIG. 9 shows an example of a discharge lamp of the second embodiment.

FIG. 10 shows the relationship between an emission current density and an applied voltage of Example 1 and Comparative Example 1.

15 Description of Embodiments

(First Embodiment)

20 **[0023]** A first embodiment provides a tungsten alloy containing a W component and at least two kinds selected from the group consisting of Hf, HfO₂, HfC, and C. The content of the Hf component is within a range of 0.1 wt% or more and 3 wt% or less in terms of HfO₂. Examples of the Hf component include Hf, HfO₂, and HfC. The Hf component preferably contains Hf and HfO₂.

[0024] A tungsten alloy part of the embodiment contains 0.1 to 3 wt% of Hf in terms of HfO₂. The tungsten alloy part contains at least two kinds of Hf, HfO₂, HfC, and C.

25 **[0025]** The tungsten alloy part contains 0.1 to 3 wt% of Hf (hafnium) in terms of HfO₂ (hafnium oxide), and thereby characteristics such as emission characteristics and strength can be improved. That is, when the content of Hf is less than 0.1 wt% in terms of HfO₂, the addition effect of Hf is insufficient. When the content of Hf is more than 3 wt%, the characteristics are deteriorated. The content of the Hf component is preferably 0.5 to 2.5 wt% in terms of HfO₂.

30 **[0026]** The HfO₂ component contained in the tungsten alloy needs to contain at least two kinds of Hf, HfO₂, HfC, and C. That is, the tungsten alloy contains the HfO₂ component as a combination of Hf and HfO₂, a combination of HfO₂ and HfC (hafnium carbide), a combination of HfO₂ and C (carbon), a combination of Hf, HfO₂, and HfC, a combination of HfO₂, HfC, and C, a combination of Hf, HfO₂ and C, or a combination of Hf, HfO₂, HfC, and C (carbon). When the melting points are compared, the melting points of metal Hf, HfO₂, HfC, and tungsten are respectively 2222°C, 2758°C, 3920°C, and 3400°C (see Iwanami Shoten "Rikagakujiten (Dictionary of Physics and Chemistry)"). The melting points of metal thorium and thorium oxide (ThO₂) are respectively 1750°C and 3220 ± 50°C. Since hafnium has a melting point higher than that of thorium, the tungsten alloy of the embodiment can have a high-temperature strength equal to or higher than that of a thorium-containing tungsten alloy.

35 **[0027]** When the contents of Hf and O are converted into HfO_x, $x < 2$ is preferably set. $x < 2$ means that the HfO₂ component contained in the tungsten alloy does not always exist as HfO₂, and a part thereof exist as metal Hf and HfC. Since the work function of metal Hf is 3.9, and greater than the work function (3.4) of metal Th, the emission characteristics are considered to be deteriorated. However, this is not particularly problematic in the application for the discharge lamp or the like. Since metal hafnium forms a solid solution with tungsten, metal hafnium is a component effective in enhancing strength.

40 **[0028]** When the contents of Hf and O are converted into HfO_x, $0 < x < 2$ is preferably set. $x < 2$ is described above. $0 < x$ means that either HfC or C exists as the HfO₂ component contained in the tungsten alloy. HfC or C has a deoxidation effect for removing an oxygen impurity contained in the tungsten alloy. Since the electrical resistance value of the tungsten alloy part can be decreased by reducing the oxygen impurity, the tungsten alloy part has improved characteristics as an electrode. In this range, metal Hf, HfO₂, HfC, or C exists in a good balance, to improve characteristics such as emission characteristics, strength, electrical resistance, and a life.

45 **[0029]** The contents of Hf, HfO₂, HfC, and O in the tungsten alloy part are measured by using an ICP analysis method and an inert gas fusion-infrared absorption method. In the ICP analysis method, a Hf amount obtained by adding a Hf amount of Hf and a Hf amount of HfO₂ and HfC can be measured. An amount of oxygen is obtained by adding an amount of O (oxygen) of HfO_x and an amount of oxygen which independently exists or an amount of oxygen which exists as another oxide, and the amount of oxygen can be measured by the inert gas fusion-infrared absorption method. In the embodiment, the amount of Hf and the amount of O are measured by the ICP analysis method and the inert gas fusion-infrared absorption method, and converted into HfO_x.

55 **[0030]** The tungsten alloy part may contain 0.01 wt% or less of at least one kind of K, Si, and Al. K (potassium), Si (silicon), and Al (aluminum) are so-called dope materials. Recrystallization characteristics can be improved by adding

these dope materials. The recrystallization characteristics are improved, and thereby a uniform recrystal structure is likely to be obtained when a recrystallization heat treatment is performed. Although the lower limit of the content of the dope material is not particularly limited, the lower limit is preferably 0.001 wt% or more. When the lower limit is less than 0.001 wt%, the addition effect is small. When the lower limit is more than 0.01 wt%, sinterability and processability are deteriorated, which may cause a decrease in a mass production property.

[0031] When the content of Hf is defined as 100 parts by mass, the content of Zr is preferably 10 parts by mass or less. The content of Hf represents the total Hf amount of Hf, HfO₂, and HfC. Since Zr (zirconium) has a high melting point of 1855°C, Zr hardly exerts an adverse influence even when Zr is contained in the tungsten part. Commercially available Hf powder or the like may contain several percent of Zr, depending on the grade of the powder. It is effective to use high-purity Hf powder or high-purity HfO₂ powder from which impurities have been removed in order to improve the characteristics. On the other hand, highly-purified raw material causes a cost increase. If the content of Zr (zirconium) is 10 parts by mass or less when the content of Hf is defined as 100 parts by weight, excessive deterioration of the characteristics can be prevented.

[0032] When the amount of carbon in a surface part in the tungsten alloy part is defined as C1 (wt%) and the amount of carbon in a central part is defined as C2 (wt%), C1 < C2 is preferably set. The surface part means a portion located between the surface of the tungsten alloy and a point distant by 20 μm from the surface. The central part is a central portion in the section of the tungsten alloy part. The amount of carbon is a value obtained by adding both carbon of carbide such as HfC, and independently existing carbon, and is analyzed by the combustion-infrared absorption method. The amount of carbon C1 in the surface part is smaller than the amount of carbon C2 in the central part means that carbon in the surface part is oxidized into CO₂, which is discharged to the outside of the system. The decrease in the amount of carbon in the surface part causes a relative increase in the Hf amount in the surface part. For this reason, it is particularly effective when Hf is used as an emitter material.

[0033] The average crystal particle diameter of tungsten is preferably 1 to 100 μm. The tungsten alloy part is preferably a sintered body. When the tungsten alloy part is the sintered body, parts having various shapes can be prepared by utilizing a molding process. The sintered body is subjected to a forging process, a rolling process, and a wiredrawing process or the like, and thereby the sintered body is likely to be processed into a wire rod (including a filament) and a coil part or the like.

[0034] The tungsten crystals have an isotropic crystal structure in which the ratio of crystals having an aspect ratio of less than 3 is 90% or more in the sintered body. When the sintered body is subjected to the wiredrawing process, the tungsten crystals have a flat crystal structure in which the ratio of crystals having an aspect ratio of 3 or more is 90% or more. The particle diameters of the tungsten crystals are obtained as follows. A photograph of a crystal structure is taken by use of a metallurgical microscope or the like. A maximum Feret diameter is measured for one tungsten crystal imaged therein, and defined as a particle diameter. This measurement is performed for 100 arbitrary tungsten crystals, and the average value thereof is defined as an average crystal particle diameter.

[0035] When the average of the maximum Feret diameters of the tungsten crystals is a small value of less than 1 μm, it is difficult to form a uniform dispersion state of a dispersed component such as Hf, HfO₂, HfC, or C. The dispersed component exists in the grain boundary between the tungsten crystals. Therefore, the grain boundary is small when the average of the maximum Feret diameters of the tungsten crystals is a small value of less than 1 μm, which makes it difficult to uniformly disperse the dispersed component. On the other hand, when the average of the maximum Feret diameters of the tungsten crystals is a large value of more than 100 μm, the strength as the sintered body is decreased. Therefore, the average of the maximum Feret diameters of the tungsten crystals is preferably 1 to 100 μm, and more preferably 10 to 60 μm.

[0036] From the viewpoint of uniform dispersion, the average value of the maximum Feret diameters of the dispersed component such as Hf, HfO₂, HfC, or C is preferably smaller than the average value of the maximum Feret diameters of tungsten. When the average value of the maximum Feret diameters of the tungsten crystals is defined as A (μm) and the average value of the maximum Feret diameters of the dispersed component is defined as B (μm), B/A ≤ 0.5 is preferably set. The dispersed component such as Hf, HfO₂, HfC, or C exists in the grain boundary between the tungsten crystals, and functions as an emitter material or a grain boundary reinforcing material. The average particle diameter of the dispersed component is decreased to 1/2 or less of the average crystal particle diameter of tungsten, and thereby the dispersed component is more likely to be uniformly dispersed in the grain boundary between the tungsten crystals, which can reduce variation in the characteristics.

[0037] The above tungsten alloy part is preferably used for at least one kind of a discharge lamp part, a transmitting tube part, and a magnetron part.

[0038] Examples of the discharge lamp part include a cathode electrode, an electrode supporting rod, and a coil part which are used for a discharge lamp. FIGS. 1 and 2 show an example of a discharge lamp cathode electrode. In FIGS. 1 and 2, numeral number 1 designates a cathode electrode; numeral number 2 designates an electrode body part; and numeral number 3 designates an electrode tip part. The cathode electrode 1 is formed by the sintered body of the tungsten alloy. The electrode tip part 3 may have a tip formed into a trapezoidal shape (truncated cone shape) as shown

in FIG. 1 or a tip formed into a triangular shape (cone shape) as shown in FIG. 2. The tip part is subjected to polishing processing if needed. Preferably, the electrode body part 2 has a cylindrical shape, and has a diameter of 2 to 35 mm and a length of 10 to 600 mm.

5 [0039] FIG. 3 shows an example of the discharge lamp. In FIG. 3, numeral number 1 designates a cathode electrode; numeral number 4 designates a discharge lamp; numeral number 5 designates an electrode supporting rod; and numeral number 6 designates a glass tube. In the discharge lamp 4, the pair of cathode electrodes 1 are disposed in a state where electrode tip parts face each other. The cathode electrode 1 is joined to the electrode supporting rod 5. A phosphor layer which is not shown is provided in the glass tube 6. A mercury, halogen, or argon gas (or neon gas) or the like are enclosed in the glass tube if needed. When the tungsten alloy part of the embodiment is used as the electrode supporting rod 5, the whole electrode supporting rod may be the tungsten alloy of the embodiment. The tungsten alloy of the embodiment may be used for a portion of the electrode supporting rod joined to the cathode electrode and the remaining portion may be joined to another lead material.

10 [0040] The coil part may be attached to the electrode supporting rod depending on the kind of the discharge lamp, to produce the electrode. The tungsten alloy of the embodiment can also be applied to the coil part.

15 [0041] The tungsten alloy or tungsten alloy part of the embodiment is used for the discharge lamp of the embodiment. The kind of the discharge lamp is not particularly limited. The discharge lamp can be applied to both a low-pressure discharge lamp and a high-pressure discharge lamp. Examples of the low-pressure discharge lamp include various arc-discharge type discharge lamps such as for general lighting, special lighting used for a road or a tunnel or the like, a coating material curing apparatus, a UV curing apparatus, a sterilizer, and a light cleaning apparatus for a semiconductor or the like. Examples of the high-pressure discharge lamp include a processing apparatus for water supply and sewerage, general lighting, outdoor lighting for a stadium or the like, a UV curing apparatus, an exposure device for a semiconductor and a printed circuit board or the like, a wafer inspection apparatus, a high-pressure mercury lamp such as a projector, a metal halide lamp, an extra high pressure mercury lamp, a xenon lamp, and a sodium lamp.

20 [0042] The tungsten alloy part of the embodiment is suitable also for the transmitting tube part. Examples of the transmitting tube part include a filament or a mesh grid. The mesh grid may be obtained by knitting a wire rod in a mesh form or forming a plurality of holes in a sintered body plate. Since the tungsten alloy part of the embodiment is used as the transmitting tube part in the transmitting tube of the embodiment, the transmitting tube has good emission characteristics or the like.

25 [0043] The tungsten alloy part of the embodiment is suitable also for the magnetron part. Examples of the magnetron part include a coil part. FIG. 4 shows a magnetron cathode structure as an example of the magnetron part. In FIG. 4, numeral number 7 designates a coil part; numeral number 8 designates an upper supporting member; numeral number 9 designates a lower supporting member; numeral number 10 designates a supporting rod; and numeral number 11 designates a magnetron cathode structure. The upper supporting member 8 and the lower supporting member 9 are integrated with each other with the supporting rod 10 provided therebetween. The coil part 7 is disposed around the supporting rod 10, and integrated with the upper supporting member 8 and the lower supporting member 9. The magnetron part is suitable for a microwave oven. A tungsten wire material having a wire diameter of 0.1 to 1 mm is preferably used for the coil part. The diameter of the coil part is preferably 2 to 6 mm. When the tungsten alloy part of the embodiment is used for the magnetron part, the magnetron part exhibits excellent emission characteristics and excellent strength at a high temperature. Therefore, the reliability of the magnetron using the magnetron part can be improved.

30 [0044] Next, a method for producing the tungsten alloy and tungsten alloy part of the embodiment will be described. As long as the tungsten alloy and tungsten alloy part of the embodiment have the above constitution, the method for producing the tungsten alloy and the tungsten alloy part is not particularly limited. However, examples of the method for efficiently producing the tungsten alloy and the tungsten alloy part include the following method.

35 [0045] First, tungsten powder used as a raw material is prepared. The average particle diameter of the tungsten powder is preferably 1 to 10 μm . When the average particle diameter is less than 1 μm , the tungsten powder is apt to be aggregated, which makes it difficult to uniformly disperse the HfO_2 component. When the average particle diameter is more than 10 μm , the average crystal particle diameter of the sintered body may be more than 100 μm . Although the purity of the tungsten powder depends on the intended application, the tungsten powder preferably has a high purity of 99.0 wt% or more, and more preferably 99.9 wt% or more.

40 [0046] Next, HfO_2 powder is prepared as the HfO_2 component. HfC powder is prepared as the HfC component. A mixture of Hf powder and carbon powder may be used instead of the HfC powder. Instead of HfC powder, a mixture obtained by mixing one or two kinds of the Hf powder or carbon powder with the HfC powder may be used. Of these, the HfO_2 powder or the HfC powder is preferably used. The HfC powder is partially decomposed in a sintering process, and carbon reacts with an oxygen impurity in the tungsten powder to be oxidized into carbon dioxide. Carbon dioxide is discharged to the outside of the system. The HfC powder contributes to uniformity of the tungsten alloy, which is preferable. When the mixed powder of the Hf powder and carbon powder is used, a load in a production process is increased since both the Hf powder and the carbon powder must be uniformly mixed. Since metal Hf is apt to be oxidized, the HfC powder is preferably used.

[0047] The HfO₂ component powder preferably has an average particle diameter of 0.5 to 5 μm. When the average particle diameter is less than 0.5 μm, the aggregation of the HfO₂ powder is large, which makes it difficult to uniformly disperse the HfO₂ powder. When the average particle diameter is more than 5 μm, it is difficult to uniformly disperse the HfO₂ powder in the grain boundary between the tungsten crystals. The HfC component powder preferably has an average particle diameter of 0.5 to 5 μm. When the average particle diameter is less than 0.5 μm, the aggregation of the HfC powder is large, which makes it difficult to uniformly disperse the HfC powder. When the average particle diameter is more than 5 μm, it is difficult to uniformly disperse the HfC powder in the grain boundary between the tungsten crystals. From the viewpoint of a uniform dispersion, the average particle diameter of the HfO₂ powder or HfC powder which is equal to or smaller than the average particle diameter of the tungsten powder is preferably set.

[0048] When the Hf amount of the HfO₂ powder, HfC powder, or Hf powder is defined as 100 parts by mass, the amount of Zr is preferably 10 parts by mass or less. A Zr component may be contained as an impurity in the HfO₂ powder, the HfC powder, or the Hf powder. When the amount of Zr is 10 parts by mass or less based on the Hf amount, degradation of excellent Hf component characteristics can be prevented. Although the amount of Zr is preferably small, highly-purified raw material causes a cost increase. Therefore, the amount of Zr is more preferably 0.1 to 3 parts by mass.

[0049] At least one dope material selected from K, Si, and Al is added if needed. The addition amount is preferably 0.01 wt% or less.

[0050] Next, raw powders are uniformly mixed. A mixing process is preferably performed by using a mixing machine such as a ball mill. The mixing process is preferably performed for 8 hours or more, and more preferably 20 hours or more. The raw powders may be mixed with an organic binder or an organic solvent if needed to produce a slurry. A granulation process may be performed if needed.

[0051] Next, the raw powders are pressed in a mold to prepare a molded body. The molded body is subjected to a degreasing process if needed. Next, a sintering process is performed. The sintering process is preferably performed under an inert atmosphere such as a hydrogen atmosphere or a nitrogen atmosphere, or in a vacuum. A sintering condition is preferably performed at a temperature of 1400 to 3000°C for 1 to 20 hours. When the sintering temperature is less than 1400°C or the sintering time is less than 1 hour, the sintering is insufficient, which decreases the strength of the sintered body. When the sintering temperature is more than 3000°C or the sintering time is more than 20 hours, the tungsten crystals may overgrow. Carbon in the surface part of the sintered body can be likely to be discharged to the outside of the system by sintering under a hydrogen atmosphere, under an inert atmosphere, or in a vacuum. The sintering process is not particularly limited to electric sintering, and pressureless sintering, pressure sintering or the like can also be used.

[0052] Next, a process of processing the sintered body (tungsten alloy) into a part is performed. Examples of the process of processing the sintered body into a part include a forging process, a rolling process, a wiredrawing process, a cutting process, and a polishing process. Examples of the process when the sintered body is processed into a coil part include a coiling process. Examples of the process when the mesh grid is prepared as the transmitting tube part include a process of weaving the filament in a mesh form.

[0053] Next, after the sintered body is processed into the part, the part is subjected to a stress relief heat treatment if needed. The stress relief heat treatment is preferably performed at 1300 to 2500°C under an inert atmosphere or in a vacuum. The stress relief heat treatment is performed, and thereby an internal stress generated in the processing process to the part can be suppressed, which can enhance the strength of the part.

(Second Embodiment)

[0054] A second embodiment provides a tungsten alloy containing a W component, and a Hf component containing HfO₂ particles. The amount of the Hf component is within a range of 0.1 wt% or more and 5 wt% or less in terms of HfO₂. The average primary particle diameter of the HfO₂ particles is 15 μm or less.

[0055] A discharge lamp electrode part of the embodiment is made of a tungsten alloy. The tungsten alloy contains 0.1 to 5 wt% of the Hf component in terms of HfO₂, and the HfO₂ primary particles in the Hf component have an average particle diameter of 15 μm or less.

[0056] FIGS. 5 and 6 show an example of the discharge lamp electrode part of the embodiment. In FIGS. 5 and 6, numeral number 21 designates a discharge lamp electrode part; numeral number 22 designates a discharge lamp electrode part having a taper-shaped tip part; numeral number 23 designates a tip part; and numeral number 24 designates a body part. The discharge lamp electrode part 21 has a cylindrical shape. The tip part 23 of the discharge lamp electrode part 21 is tapered to produce the discharge lamp electrode part 22. Although the discharge lamp electrode part 21 before being tapered usually has a cylindrical shape, the discharge lamp electrode part 21 may have a quadrangular prism shape.

[0057] First, the tungsten alloy contains 0.1 to 5 wt% of the Hf component in terms of HfO₂. Examples of the Hf component include two kinds (HfO₂ and Hf). The atomic ratio of O/Hf for HfO₂ (hafnium oxide) is not limited to 2, and is within a range of 1.6 to 2. The tungsten alloy contains 0.1 to 5 wt% of the Hf component in terms of HfO₂ (O/Hf atomic ratio = 2). The Hf component is a component functioning as an emitter material in the discharge lamp electrode part.

When the content of the Hf component is less than 0.1 wt% in terms of HfO₂, emission characteristics are insufficient. On the other hand, when the content of the Hf component is more than 5 wt%, a strength decrease or the like may be caused. Therefore, the amount of the Hf component is preferably 0.3 to 3.0 wt% in terms of HfO₂, and more preferably 0.5 to 2.5 wt%.

[0058] The Hf component exists as HfO₂ or Hf as described above. Of these, the primary particles of HfO₂ need to have an average particle diameter of 15 μm or less. That is, it is important that HfO₂ component comprises the HfO₂ particles. The HfO₂ particles exist in the grain boundary between tungsten crystal particles. Therefore, when the HfO₂ particles are too large, a clearance between the tungsten crystal particles is enlarged, which causes a density decrease and a strength decrease. When the HfO₂ particles exist in the grain boundary between the tungsten crystal particles, the HfO₂ particles function as not only an emission material but also as a dispersion reinforcing material. Therefore, the strength enhancement of an electrode part is also obtained.

[0059] The primary particles of the HfO₂ particles preferably have an average particle diameter of 5 μm or less and a maximum diameter of 15 μm or less. The HfO₂ particles preferably have an average particle diameter of 0.1 to 3 μm. The HfO₂ particles preferably have a maximum diameter of 1 to 10 μm. The small HfO₂ particles having an average particle diameter of less than 0.1 μm or a maximum diameter of less than 1 μm may be consumed quickly and disappear due to emission. The HfO₂ particles preferably have an average particle diameter of 0.1 μm or more or a maximum diameter of 1 μm or more in order to achieve a life improvement of the electrode.

[0060] For the dispersion state of the HfO₂ particles, 2 to 30 particles preferably exist on an arbitrary straight line of 200 μm. When the number of the HfO₂ particles is less than 2 (0 to 1 particle) per straight line of 200 μm, the HfO₂ particles are partially decreased, which increases the variation in emission. On the other hand, when the number of the HfO₂ particles is more than 30 (31 particles or more) per straight line of 200 μm, a part of the HfO₂ particles may be unevenly distributed, to cause an adverse influence such as a strength decrease. The dispersion state of the HfO₂ particles is measured by subjecting the arbitrary section of the tungsten alloy to magnification photography. The magnification ratio of the magnified photograph is set to 1000 times or more. An arbitrary straight line of 200 μm (line thickness: 0.5 mm) is drawn on the magnified photograph, and the number of the HfO₂ particles existing on the line is counted.

[0061] The secondary particles of the HfO₂ particles preferably have a maximum diameter of 100 μm or less. The secondary particle of the HfO₂ particles is an agglomerate of the primary particles. When the diameter of the secondary particle is more than 100 μm, the strength of the tungsten alloy part is decreased. Therefore, the maximum diameter of the secondary particles of the HfO₂ particles is preferably 100 μm or less, more preferably 50 μm or less, and still more preferably 20 μm or less.

[0062] Hf (metal Hf) of the Hf component has various dispersion states.

[0063] In a first dispersion state, metal Hf exists as particles. Metal Hf particles exist in the grain boundary between the tungsten crystal particles as in the HfO₂ particles. The metal Hf particles exist in the grain boundary between the tungsten crystal particles, and thereby the metal Hf particles also function as the emission material and the dispersion reinforcing material. Therefore, the metal Hf primary particles have preferably an average particle diameter of 15 μm or less, more preferably 10 μm or less, and still more preferably 0.1 to 3 μm. The maximum diameter is preferably 15 μm or less, and more preferably 10 μm or less. When the tungsten alloy is prepared, the HfO₂ particles and the metal Hf particles may be previously mixed, or the HfO₂ particles may be deoxidized in the production process. When a method for deoxidizing the HfO₂ particles is used, an effect for discharging oxygen in tungsten to the outside of the system is also obtained, which is preferable. When the deoxidation is possible, the electrical resistance of the tungsten alloy can be decreased, which improves the conductivity as the electrode.

[0064] In a second dispersion state, metal Hf exists on the surfaces of the HfO₂ particles. As in the first dispersion state, when the sintered body of the tungsten alloy is prepared, oxygen is deoxidized from the surfaces of the HfO₂ particles, which leads to a state in which a metal Hf film is formed on the surface. The HfO₂ particles with the metal Hf film exhibit excellent emission characteristics. The primary particle diameter of the HfO₂ particles with the metal Hf film is preferably an average particle diameter of 15 μm or less, more preferably 10 μm or less, and still more preferably 0.1 to 3 μm. The maximum diameter is preferably 15 μm or less, and more preferably 10 μm or less.

[0065] In a third dispersion state, metal Hf is partly or wholly solid-solved in tungsten. Metal Hf forms a solid solution with tungsten. The strength of the tungsten alloy can be enhanced by forming the solid solution. The presence or absence of the solid solution can be measured by XRD analysis. First, the contents of the Hf component and oxygen are measured. The amounts of Hf and oxygen in the Hf component are converted into HfO₂, to confirm HfO_x (x < 2). Next, the XRD analysis is performed to confirm that the peak of metal Hf is not detected. Although HfO_x (x < 2) is confirmed, and hafnium which is not oxidized into hafnium oxide exists, the peak of metal Hf is not detected. This means that metal Hf is solid-solved in tungsten.

[0066] On the other hand, HfO_x (x < 2) is set; hafnium which is not oxidized into hafnium oxide exists; and the peak of metal Hf is detected. This means the first dispersion state where metal Hf is not solid-solved and exists in the grain boundary between the tungsten crystals. The second dispersion state can be analyzed by using EPMA (electron beam microanalyzer) or TEM (transmission electron microscope).

[0067] The dispersion state of metal Hf may be any one kind or a combination of two or more kinds of the first dispersion state, the second dispersion state, and the third dispersion state.

[0068] When the total content of the Hf component (the content of Hf) is defined as 100 parts by mass, the ratio of Hf existing into the HfO₂ particles is preferably 30 to 98 parts by mass. Naturally, all of the Hf component may be oxidized into the HfO₂ particles. The emission characteristics are obtained by use of the HfO₂ particles. On the other hand, the conductivity and strength of the tungsten alloy can be enhanced by dispersing metal Hf. However, when the Hf component is metal Hf, the emission characteristics and the strength at a high temperature are decreased. Metal Hf has a melting point of 2230°C; HfO₂ has a melting point of 2758°C; and metal tungsten has a melting point of 3400°C. Since HfO₂ has a higher melting point, the high-temperature strength of the tungsten alloy containing a predetermined amount of HfO₂ is enhanced. Since HfO₂ has a surface current density nearly equal to that of ThO₂, electric current equal to that of a thorium dioxide-containing tungsten alloy can be passed through the tungsten alloy. Therefore, a current density equal to that of a thorium dioxide-containing tungsten alloy electrode can be set as the discharge lamp, which eliminates the design change of a control circuit or the like. Therefore, when the total content of the Hf component is defined as 100 parts by mass, the ratio of the HfO₂ particles is preferably 30 to 98 parts by mass, and more preferably 60 to 95 parts by mass.

[0069] In a method for analyzing the contents of HfO₂ and metal Hf, the total amount of Hf in the tungsten alloy is measured according to the ICP analysis method. Next, the total amount of oxygen in the tungsten alloy is measured by an inert gas fusion-infrared absorption method. When the tungsten alloy is a binary system containing the Hf component, the measured total amount of oxygen may be considered to be substantially and wholly contained in HfO₂. The amount of HfO₂ in the Hf component can be measured by comparison of the measured total amount of Hf with the total amount of oxygen. In the case of using this method, the amount of HfO₂ is calculated by $O/Hf = 2$.

[0070] For the measurement of the sizes of the HfO₂ particles, a magnified photograph of an arbitrary section of the tungsten alloy sintered body is taken, and the longest diagonal line of the HfO₂ particles imaged therein is measured as the particle diameter of the HfO₂ particle. In this work, 50 HfO₂ particles are measured, to define the average value thereof as the average particle diameter of the HfO₂ particles. The maximum value of the particle diameters (the longest diagonal lines) of the HfO₂ particles is defined as the maximum diameter of the HfO₂ particles.

[0071] The tungsten alloy may contain 0.01 wt% or less of a dope material made of at least one kind of K, Si, and Al. K (potassium), Si (silicon), and Al (aluminum) are so-called dope materials. Recrystallization characteristics can be improved by adding these dope materials. The recrystallization characteristics are improved, and thereby a uniform recrystal structure is likely to be obtained when a recrystallization heat treatment is performed. Although the lower limit of the content of the dope material is not particularly limited, the lower limit is preferably 0.001 wt% or more. When the lower limit is less than 0.001 wt%, the addition effect is small. When the lower limit is more than 0.01 wt%, sinterability and processability are deteriorated, which causes a decrease in a mass production property.

[0072] The tungsten alloy may contain 2 wt% or less of at least one element selected from the group consisting of Ti, Zr, V, Nb, Ta, Mo, and rare earth elements. Ti, Zr, V, Nb, Ta, Mo, and rare earth elements can take any one form of a metal simple substance, oxide, and carbide. The tungsten alloy may contain two or more kinds of elements. Even if the tungsten alloy contains two or more kinds of elements, the total amount thereof is preferably 2 wt% or less. These contained components mainly function as the dispersion reinforcing material. Since the HfO₂ particles function as the emission material, the HfO₂ particles are consumed when the discharge lamp is used for a long time. Since Ti, Zr, V, Nb, Ta, Mo, and rare earth elements have weak emission characteristics, these are less consumed by emission, and can maintain their function as the dispersion reinforcing material over a long period of time. Although the lower limits of the contents thereof are not particularly limited, the lower limits are preferably 0.01 wt% or more. Of these components, Zr or the rare earth elements are preferable. Since these components have a large atomic radius of 0.16 nm or more, the components have a large surface current density. In other words, a metal simple substance containing an element having an atomic radius of 0.16 nm or more or a compound thereof is said to be preferable.

[0073] The discharge lamp electrode part preferably includes a tip part having a tapered tip and a cylindrical body part. The characteristics of the discharge lamp electrode part are improved by tapering, that is, sharpening the tip part. As shown in FIG. 6, the ratio of the length of the tip part 23 to that of the body part 24 is not particularly limited, and is determined in accordance with the application.

[0074] The wire diameter ϕ of the discharge lamp electrode part is preferably 0.1 to 30 mm. When the wire diameter ϕ is less than 0.1 mm, the strength of the electrode part cannot be maintained, which may lead to breakage of the electrode part when the electrode part is incorporated into the discharge lamp or breakage of the electrode part when the tip part is tapered. When the wire diameter ϕ is a large value of more than 30 mm, it is difficult to control the uniformity of the tungsten crystal structure, as described below.

[0075] When the crystal structure of the circumferential section (transverse section) of the body part is observed, the area ratio of the tungsten crystals per unit area of $300 \mu\text{m} \times 300 \mu\text{m}$ is preferably 90% or more, and the tungsten crystals have a crystal particle diameter of 1 to 80 μm . FIG. 7 shows an example of the circumferential section of the body part. In FIG. 7, numeral number 24 designates a body part; and numeral number 25 designates a circumferential section.

When the crystal structure of the circumferential section is measured, a magnified photograph of the section in the center of the length of the body part is taken. When the wire diameter is thin, and a unit area of $300\ \mu\text{m} \times 300\ \mu\text{m}$ cannot be measured in one viewing field, a plurality of arbitrary circumferential sections are photographed. In the magnified photograph, the longest diagonal line of the tungsten crystal particles imaged therein is defined as the maximum diameter. The area percent of the tungsten crystal particles having a maximum diameter falling within a range of 1 to $80\ \mu\text{m}$ is measured.

[0076] The area ratio of the tungsten crystals per unit area of the circumferential section of the body part is 90% or more, and the tungsten crystals have a crystal particle diameter of 1 to $80\ \mu\text{m}$. This shows that the small tungsten crystals having a crystal particle diameter of less than $1\ \mu\text{m}$ and the large tungsten crystals having a crystal particle diameter of more than $80\ \mu\text{m}$ are few. When the tungsten crystals of less than $1\ \mu\text{m}$ are too many, the grain boundary between the tungsten crystal particles is too small. When the ratio of the HfO_2 particles is increased in the grain boundary, and the HfO_2 particles are consumed by emission, large defects are formed, which decreases the strength of the tungsten alloy. On the other hand, when the number of large tungsten crystal particles of more than $80\ \mu\text{m}$ are increased, the grain boundary is too large, which decreases the strength of the tungsten alloy. The area ratio of the tungsten crystals having a crystal particle diameter of 1 to $80\ \mu\text{m}$ is more preferably 96% or more, and still more preferably 100%.

[0077] The average particle diameter of the tungsten crystal particles in the circumferential section is preferably $50\ \mu\text{m}$ or less, and more preferably $20\ \mu\text{m}$ or less. The average aspect ratio of the tungsten crystal particles is preferably less than 3. The aspect ratio is measured as follows. A magnified photograph of unit area of $300\ \mu\text{m} \times 300\ \mu\text{m}$ is taken; the maximum diameter (Ferret diameter) of the tungsten crystal particles imaged therein is defined as a major axis L; the particle diameter vertically extending from the center of the major axis L is defined as a minor axis S; and the aspect ratio is obtained by dividing major axis L by minor axis S (major axis L / minor axis S). This measurement is performed for 50 tungsten crystal particles, and the average value thereof is defined as the average aspect ratio. When the average particle diameter is obtained, and the particle diameter is obtained by dividing a total value of major axis L and minor axis S by 2 ((major axis L + minor axis S)/2 = particle diameter), the average value of the 50 tungsten crystal particles is defined as the average particle diameter.

[0078] When the crystal structure of the side section (vertical section) of the body part is observed, the area ratio of the tungsten crystals per unit area of $300\ \mu\text{m} \times 300\ \mu\text{m}$ is preferably 90% or more, and the tungsten crystals have a crystal particle diameter of 2 to $120\ \mu\text{m}$. FIG. 8 shows an example of the side section. In FIG. 8, numeral number 24 designates a body part; and numeral number 26 designates a side section. When the crystal structure of the side section is measured, the section passing through the center of the wire diameter of the body part is measured. When a unit area of $300\ \mu\text{m} \times 300\ \mu\text{m}$ cannot be measured in one viewing field, a plurality of arbitrary side sections are photographed. In the magnified photograph, the longest diagonal line of the tungsten crystal particles imaged therein is defined as the maximum diameter. The area percent of the tungsten crystal particles having a maximum diameter falling within a range of 2 to $120\ \mu\text{m}$ is measured.

[0079] The area ratio of the tungsten crystals per unit area of the side section of the body part is 90% or more, and the tungsten crystals have a crystal particle diameter of 2 to $120\ \mu\text{m}$. This shows that the small tungsten crystals having a crystal particle diameter of less than $2\ \mu\text{m}$ and the large tungsten crystals having a crystal particle diameter of more than $120\ \mu\text{m}$ are few. When the tungsten crystals of less than $2\ \mu\text{m}$ are too many, the grain boundary between the tungsten crystal particles is too small. When the ratio of the HfO_2 particles is increased in the grain boundary, and the HfO_2 particles are consumed by emission, large defects are formed, which decreases the strength of the tungsten alloy. On the other hand, when the number of large tungsten crystal particles of more than $120\ \mu\text{m}$ is increased, the grain boundary is too large, which decreases the strength of the tungsten alloy. The area ratio of the tungsten crystals having a crystal particle diameter of 2 to $120\ \mu\text{m}$ is more preferably 96% or more, and still more preferably 100%.

[0080] The average particle diameter of the tungsten crystal particles in the side section is preferably $70\ \mu\text{m}$ or less, and more preferably $40\ \mu\text{m}$ or less. The average aspect ratio of the tungsten crystal particles is preferably 3 or more. A method for measuring the average particle diameter and the average aspect ratio is the same as that used for the circumferential section.

[0081] As described above, a tungsten alloy having excellent discharge characteristics and strength, particularly strength at a high temperature can be provided by controlling the sizes of the tungsten crystal particles, and the size and ratio of the Hf component. Therefore, the characteristics of the discharge lamp electrode part are also improved.

[0082] The tungsten alloy preferably has a relative density of 95.0% or more, and more preferably 98.0% or more. When the relative density is less than 95.0%, air bubbles are increased, which may cause influences such as a strength decrease and partial discharge. The relative density is a value obtained by dividing a measured density according to an Archimedes method by a theoretical density. (Measured density/theoretical density) $\times 100$ (%) = relative density is set. The theoretical density is obtained by calculation according to the mass ratios of tungsten, hafnium, and hafnium oxide. The theoretical density of tungsten is $19.3\ \text{g/cm}^3$; the theoretical density of hafnium is $13.31\ \text{g/cm}^3$; and the theoretical density of hafnium oxide is $9.68\ \text{g/cm}^3$. For example, in the case of a tungsten alloy containing 1 wt% of HfO_2 , 0.2 wt% of Hf, and the remainder being tungsten, the theoretical density is $9.68 \times 0.01 + 13.31 \times 0.002 + 19.3 \times 0.988 =$

19.19182 g/cm³. When the theoretical density is calculated, the existence of impurities may not be considered.

[0083] The tungsten alloy preferably has a Vickers hardness of Hv 330 or more, and more preferably Hv 330 to 700. When the Vickers hardness is less than Hv 330, the tungsten alloy is too soft, which decreases the strength. On the other hand, when the Vickers hardness is more than Hv 700, the tungsten alloy is too hard, which makes it difficult to process the tip part into a taper shape. When the tungsten alloy is too hard, an electrode part having a long body part has no flexibility, and may be apt to be broken. The three point bending strength of the tungsten alloy can be increased to 400 MPa or more.

[0084] The surface roughness Ra of the discharge lamp electrode part is preferably 5 μm or less. Particularly, the tip part preferably has a surface roughness Ra of 5 μm or less, and more preferably 3 μm or less. When surface unevenness is large, emission characteristics are deteriorated.

[0085] The above discharge lamp electrode part can be applied to various discharge lamps. Therefore, even if a large voltage of 100 V or more is applied as an applied voltage, a long life can be achieved. The discharge lamps to be used are not particularly limited to the low-pressure discharge lamp and the high-pressure discharge lamp or the like. The wire diameter of the body part is within a range of 0.1 to 30 mm. The wire diameter capable of being applied is a thin size of 0.1 mm or more and 3 mm or less, a medium size of more than 3 mm and 10 mm or less, and a thick size of more than 10 mm and 30 mm or less. The length of the electrode body part is preferably 10 to 600 mm.

[0086] FIG. 9 shows an example of the discharge lamp. In FIG. 9, numeral number 22 designates an electrode part (having a tapered tip part); numeral number 27 designates a discharge lamp; numeral number 28 designates an electrode supporting rod; and numeral number 29 designates a glass tube. In the discharge lamp 27, the pair of electrode parts 22 are disposed in a state where electrode tip parts face each other. The electrode parts 22 are joined to the electrode supporting rod 28. A phosphor layer which is not shown is provided on the inner surface of the glass tube 29. A mercury, halogen, or argon gas (or neon gas) or the like is enclosed in the glass tube if needed.

[0087] The tungsten alloy or electrode part of the embodiment is used for the discharge lamp of the embodiment. The kind of the discharge lamp is not particularly limited. The discharge lamp can be applied to both a low-pressure discharge lamp and a high-pressure discharge lamp. Examples of the low-pressure discharge lamp include various arc-discharge type discharge lamps such as for general lighting, special lighting used for a road and a tunnel or the like, a coating material curing apparatus, a UV curing apparatus, a sterilizer, and a light cleaning apparatus for a semiconductor or the like. Examples of the high-pressure discharge lamp include a processing apparatus for water supply and sewerage, general lighting, outdoor lighting for a stadium or the like, a UV curing apparatus, an exposure device for a semiconductor and a printed circuit board or the like, a wafer inspection apparatus, a high-pressure mercury lamp such as a projector, a metal halide lamp, an extra high pressure mercury lamp, a xenon lamp, and a sodium lamp. Since the strength of the tungsten alloy is improved, the discharge lamp can also be applied to a field involving movement (vibration) such as an automotive discharge lamp.

[0088] Next, a production method will be described. As long as the tungsten alloy and discharge lamp electrode part of the embodiment have the above constitution, the production method is not particularly limited. However, examples of the production method for efficiently obtaining the tungsten alloy and the discharge lamp electrode part include the following method.

[0089] First, tungsten alloy powder containing a Hf component is prepared as a method for producing a tungsten alloy.

[0090] First, HfO₂ powder is prepared as the Hf component. The primary HfO₂ particles have an average particle diameter of 15 μm or less, and more preferably an average particle diameter of 5 μm or less. Preferably, HfO₂ particles having a maximum diameter of more than 15 μm are previously removed by using a sieve. When a maximum diameter is desired to be set to 10 μm or less, large HfO₂ particles are removed by using a sieve having an intended mesh diameter. When the HfO₂ particles having a small particle diameter are desired to be removed, the HfO₂ particles are removed by using a sieve having an intended mesh diameter. Before sieving, the HfO₂ particles are preferably subjected to a pulverizing process in a ball mill or the like. Since the aggregate can be broken by performing the pulverizing process, particle diameter control according to sieving is likely to be performed.

[0091] Next, a process of mixing metal tungsten powder is performed. The metal tungsten powder preferably has an average particle diameter of 0.5 to 10 μm. The tungsten powder preferably has purity of 98.0 wt% or more, an oxygen content of 1 wt% or less, and an impurity metal component of 1 wt% or less. It is preferable that the metal tungsten powder is previously pulverized in a ball mill or the like as in the HfO₂ particles, and small particles and large particles are removed in a sieving process.

[0092] The metal tungsten powder is added so that the amount of the Hf component is set to an intended amount (0.1 to 5 wt% in terms of HfO₂) when being converted into HfO₂. A mixed powder of HfO₂ particles and metal tungsten powder is put into a mixing vessel, and the mixing vessel is rotated, to uniformly mix the mixed powder. At this time, the mixed powder can be smoothly mixed by using a cylindrical mixing vessel as the mixing vessel, and rotating the cylindrical mixing vessel in a circumferential direction. The tungsten powder containing the HfO₂ particles can be prepared by this process. In consideration of deoxidation during a sintering process to be described below, a small amount of carbon powder may be added.

[0093] Next, a molded body is prepared by using the obtained tungsten powder containing the HfO₂ particles. When the molded body is formed, a binder is used if needed. When a cylindrical molded body is formed, the diameter of the molded body is preferably 0.1 to 40 mm. When a molded body is cut out from a plate-like sintered body as described below, the size of the molded body is arbitrary. The length (thickness) of the molded body is arbitrary.

[0094] Next, a process of presintering the molded body is performed. The presintering is preferably performed at 1250 to 1500°C. A presintered body can be obtained by this process. Next, a process of subjecting the presintered body to electric sintering is performed. The electric sintering is preferably performed so that the temperature of the sintered body is set to 2100 to 2500°C. When the temperature is less than 2100°C, the sintered body cannot be sufficiently densified, which decreases the strength. When the temperature is more than 2500°C, the HfO₂ particles and the tungsten particles overgrow, and the intended crystal structure is not obtained.

[0095] Examples of another method include a method for sintering the molded body at a temperature of 1400 to 3000°C for 1 to 20 hours. When the sintering temperature is less than 1400°C or the sintering time is less than 1 hour, the sintering is insufficient, which decreases the strength of the sintered body. When the sintering temperature is more than 3000°C or the sintering time is more than 20 hours, the tungsten crystals may overgrow.

[0096] Examples of the sintering atmosphere include an inert atmosphere such as a nitrogen or argon atmosphere, a reducing atmosphere such as a hydrogen atmosphere, and a vacuum. Under any of these atmospheres, carbon in the HfO₂ particles is removed during the sintering process. Since an oxygen impurity in the tungsten powder is also removed during decarbonization, the oxygen content in the tungsten alloy can be decreased to 1 wt% or less, and further to 0.5 wt% or less. When the oxygen content in the tungsten alloy is decreased, the conductivity is improved.

[0097] A Hf component-containing tungsten sintered body can be obtained by the sintering process. When the presintered body has a cylindrical shape, the sintered body is also a cylindrical sintered body (ingot). In the case of the plate-shaped sintered body, a process of cutting out the plate-shaped sintered body into a predetermined size is performed. The cylindrical sintered body (ingot) is obtained by the cutting-out process.

[0098] Next, there is performed a process of subjecting the cylindrical sintered body (ingot) to forging processing, rolling processing, and wiredrawing processing or the like, to adjust the wire diameter. A processing ratio in that case is preferably within a range of 30 to 90%. When the sectional area of the cylindrical sintered body before processing is defined as A and the sectional area of the cylindrical sintered body after processing is defined as B, the processing ratio is obtained by dividing (A - B) by A, the processing ratio of $[(A - B)/A] \times 100\%$. The wire diameter is preferably adjusted by a plurality of such processes. The pores of the cylindrical sintered body before processing can be crushed by performing the plurality of such processes, to obtain a high-density electrode part.

[0099] Next will be described a case where a cylindrical sintered body having a diameter of 25 mm is processed into a cylindrical sintered body having a diameter of 20 mm, for example. Since the sectional area A of a circle having a diameter of 25 mm is 460.6 mm² and the sectional area B of a circle having a diameter of 20 mm is 314 mm², the processing ratio is 32% = $[(460.6 - 314)/460.6] \times 100\%$. At this time, the diameter of the cylindrical sintered body is preferably processed to 20 mm from 25 mm by a plurality of wiredrawing processings or the like.

[0100] When the processing ratio is a low value of less than 30%, the crystal structure is not sufficiently stretched in the processing direction, which makes it difficult to set the tungsten crystals and the thorium component particles at the intended size. When the processing ratio is a small value of less than 30%, the pores in the cylindrical sintered body before processing are not sufficiently crushed, and may remain as is. The remaining internal pores cause a decrease in the durability or the like of a cathode part. On the other hand, when the processing ratio is a large value of more than 90%, the sintered body is excessively processed, which may cause disconnections and decrease the yield. For this reason, the processing ratio is 30 to 90%, and preferably 35 to 70%.

[0101] When the relative density of the sintered tungsten alloy is 95% or more, the sintered tungsten alloy may not be necessarily processed at a predetermined processing ratio.

[0102] After the wire diameter is processed to 0.1 to 30 mm, the electrode part is prepared by cutting the sintered body to a required length. The tip part is processed into a taper shape if needed. Polishing processing, a heat treatment (recrystallization heat treatment or the like), and shape processing are performed if needed.

[0103] The recrystallization heat treatment is preferably performed at 1300 to 2500°C under a reducing atmosphere, under an inert atmosphere, or in a vacuum. The effect of the stress relief heat treatment suppressing the internal stress generated in the processing process to the electrode part is obtained by performing the recrystallization heat treatment, and the strength of the part can be enhanced.

[0104] The above production method can efficiently produce the tungsten alloy and discharge lamp electrode part of the embodiment.

[0105] In the tungsten alloy of the first embodiment, further improvement in the emission characteristics can be expected by specifying the physical properties described in the second embodiment, or specifying the physical properties described in the first embodiment in the tungsten alloy of the second embodiment. For example, in the tungsten alloy of the first embodiment, the emission characteristics can be improved by specifying any of the primary particle diameter and secondary particle diameter of the HfO₂ particles, the dispersion state of the HfO₂ particles, the dispersion state of metal

Hf, the ratio of Hf contained in HfO₂, the dispersion reinforcing material, the relative density, and the Vickers hardness as in the second embodiment. In the tungsten alloy part of the first embodiment, the emission characteristics can be improved by specifying the crystal structure of the section and the surface roughness Ra as in the second embodiment.

5 Examples

(Example 1)

10 **[0106]** As raw powders, 1.5 wt% of HfO₂ powder (purity: 99.0%) having an average particle diameter of 2 μm was added to tungsten powder (purity: 99.99 wt%) having an average particle diameter of 2 μm. When the amount of Hf for the HfO₂ powder was defined as 100 parts by mass, the amount of impurity Zr was 1.0 part by mass.

15 **[0107]** The raw powders were mixed in a ball mill for 10 hours, to prepare a mixed raw powder. Next, the mixed raw powder was put into a mold, to produce a molded body. The obtained molded body was subjected to furnace sintering in hydrogen at 1800°C for 10 hours. A sintered body having a height of 16 mm, a width of 16 mm, and a length of 420 mm was obtained by the process.

[0108] A rod having a square shape section or a round shape section was prepared by forging processing or the like. Next, a cylindrical sample having a diameter of 2.4 mm and a length of 150 mm was cut out. The sample was subjected to centerless polishing processing, to set a surface roughness Ra to 5 μm or less. Next, as a stress relief heat treatment, a heat treatment was performed in hydrogen at 1600°C.

20 **[0109]** Thereby, an electrode for measuring emission characteristics was prepared as a tungsten alloy part according to Example 1, and emission current measurement was performed.

(Comparative Example 1)

25 **[0110]** A discharge lamp cathode part was prepared, which was made of a tungsten alloy containing 2 wt% of ThO₂ and had the same size.

30 **[0111]** The content of a HfO₂ component (the amount in terms of HfO₂), an x value when the contents of Hf and O are converted into HfOx, the amounts of carbon in a surface part and a central part, and the average particle diameter of tungsten crystals were investigated for the tungsten alloy part according to Example 1. For the content of the HfO₂ component, the amount of Hf and amount of oxygen were analyzed by ICP analysis and an inert gas fusion-infrared absorption method, and converted into HfOx. The amounts of carbon in the surface part and the central part were analyzed as follows. Measurement samples were cut out from a range between a surface and a position distant by 10 μm from the surface, and from a cylindrical section, and the amounts of carbon were measured by the combustion-infrared absorption method. The average value of the crystal particle diameters of 100 tungsten crystals measured in an arbitrary section was defined as the average crystal particle diameter of tungsten. The results are shown in Table 1.

[Table 1]

	In terms of HfO ₂ (wt%)	x value when converted into HfOx	Amount of carbon in surface part (wt%)	Amount of carbon in central part (wt%)	Average crystal particle diameter of tungsten (μm)
40 Example 1	1.5	1.82	0.001	0.002	30

45 **[0112]** Next, there were investigated the emission characteristics of the discharge lamp cathode parts according to Example 1 and Comparative Example 1. For the measurement of the emission characteristics, emission current densities (mA/mm²) were measured by changing an applied voltage (V) to 100 V, 200 V, 300 V, and 400 V. The emission current densities were measured under conditions of an electric current load of 18 ± 0.5 A/W applied to the cathode part and an applied time of 20 ms. The results are shown in FIG. 10.

50 **[0113]** As can be seen from FIG. 10, it was found that Example 1 has more excellent emission characteristics than those of Comparative Example 1. As a result, it is found that the discharge lamp cathode part of Example 1 exhibits excellent emission characteristics without using thorium oxide which is a radioactive material. The temperature of the cathode part was 2100 to 2200°C during measurement. For this reason, it is found that the cathode part according to Example 1 has excellent strength at a high temperature and an excellent life or the like.

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(Examples 2 to 6)

[0114] Next, there were prepared raw mixed powders in which the addition amount of HfO₂, the addition amount of HfC, and the addition amount of K as a dope material were changed as shown in Table 2. The raw mixed powders were subjected to metal molding, and sintered in hydrogen at 1500 to 1900°C for 7 to 16 hours, to obtain sintered bodies. In Examples 2 and 3, a cutting-out process was performed under a condition where the size of the sintered body was the same as that of Example 1. In Examples 4 and 5, the sizes of the molded bodies were adjusted, to directly obtain sintered bodies having a diameter of 2.4 mm and a length of 150 mm. In Examples 6, 0.5 wt% of HfC powder (purity: 99.0%) having an average particle diameter of 2 μm was added. When the Hf amount of HfO₂ powder was defined as 100 parts by mass, the amount of impurity Zr was 1.0 part by mass. When the HfO₂ powder and HfC powder of Example 6 were used, and the Hf amount was defined as 100 parts by mass, the amount of impurity Zr was 1.0 part by mass.

[0115] Each of the samples was subjected to centerless polishing processing to set a surface roughness Ra to 5 μm or less. Next, a tip part was processed into a shape having a triangle section having 45 degrees. Next, as a stress relief heat treatment, a heat treatment was performed in hydrogen at 1400 to 1700°C. Thereby, discharge lamp cathode parts according to Examples 2 to 5 were prepared, and measured in the same manner as in Example 1. The results are shown in Table 3.

[Table 2]

	Addition amount of HfO ₂	Addition amount of K	Addition amount of HfC
Example 2	0.5	none	none
Example 3	1.0	none	none
Example 4	2.3	0.005	none
Example 5	1.2	none	none
Example 6	1.0	none	0.5

[Table 3]

	In terms of HfO ₂ (wt%)	x value when converted into HfO _x	Amount of carbon in surface part (wt%)	Amount of carbon in central part (wt%)	Average crystal particle diameter of tungsten (μm)
Example 2	0.5	1.85	0.001	0.002	60
Example 3	1.0	1.83	0.001	0.002	40
Example 4	2.3	1.86	0.002	0.003	50
Example 5	1.2	1.81	0.001	0.002	30
Example 6	1.5	0.95	0.005	0.009	10

[0116] Next, emission characteristics were estimated under the same condition as that of Example 1. The results are shown in Table 4.

[Table 4]

	Emission current density (mA/mm ²)			
	Applied voltage 100V	Applied voltage 200V	Applied voltage 300V	Applied voltage 400V
Example 2	1.0	29.6	41.0	43.2
Example 3	1.5	30.7	44.4	45.6

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(continued)

	Emission current density (mA/mm ²)			
	Applied voltage 100V	Applied voltage 200V	Applied voltage 300V	Applied voltage 400V
Example 4	5.7	35.0	47.1	49.0
Example 5	3.5	31.5	45.0	46.5
Example 6	2.2	36.2	43.2	49.8

[0117] As can be seen from Table 4, the discharge lamp cathode parts according to the present Examples exhibited excellent characteristics. The temperatures of the cathode parts were 2100 to 2200°C during measurement. For this reason, it is found that the cathode parts according to Examples 2 to 6 have excellent strength at a high temperature and an excellent life or the like. Examples 1 to 5 contained two kinds (Hf and HfO₂). Examples 6 contained three kinds (Hf, HfO₂, and HfC).

(Examples 11 to 20 and Comparative Example 11)

[0118] Tungsten powder (purity: 99.0 wt% or more) and HfO₂ powder shown in Table 5 were prepared as raw powders. The powders were sufficiently loosened in a ball mill, and subjected to a sieving process so that the maximum diameters thereof were set to values shown in Table 5 if needed.

[Table 5]

	Tungsten powder				HfO ₂ powder	
	Average particle diameter (μm)	Maximum diameter (μm)	Oxygen content (wt%)	Carbon content (wt%)	Average particle diameter of primary particles (μm)	Maximum diameter of secondary particles (μm)
Example 11	1	5	0.2	<0.01	1.2	7.0
Example 12	2	8	0.2	<0.01	2.5	8.0
Example 13	3	10	0.2	<0.01	4.5	10.0
Example 14	5	18	0.8	<0.01	4.7	10.0
Example 15	8	30	0.8	<0.01	8.3	13.0
Example 16	2	10	0.5	<0.01	2.4	6.0
Example 17	3	12	0.5	<0.01	3.2	8.5
Example 18	2	6	0.1	<0.01	0.7	3.5
Example 19	2	6	0.1	<0.01	0.7	3.5
Example 20	2	6	0.1	<0.01	0.7	3.5
Comparative Example 11	5	40	0.8	<0.01	20	50

[0119] Next, the tungsten powder and the HfO₂ powder were mixed so that the ratios of the Hf component in the tungsten alloy were as shown in Table 6 in terms of HfO₂, and mixed in the ball mill again. Next, the mixtures were molded to prepare molded bodies. Next, a sintering process was performed under conditions shown in Table 6. Sintered bodies having a height of 16 mm, a width of 16 mm, and a length of 420 mm were obtained.

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[Table 6]

	Amount of Hf component (in terms of HfO ₂ , wt%)	Sintering process	
5	Example 11	0.5	under nitrogen atmosphere, presintering, 1400°C → electric sintering, 2300°C
	Example 12	1.0	under hydrogen atmosphere, presintering, 1350°C → electric sintering, 2200°C
10	Example 13	1.5	under hydrogen atmosphere, furnace sintering, 1900°C
	Example 14	2.0	under nitrogen atmosphere, prosintering, 1450°C → electric sintering, 2200°C
15	Example 15	2.6	under hydrogen atmosphere, furnace sintering, 1800°C
	Example 16	1.5	under hydrogen atmosphere, presintering, 1400°C → electric sintering, 2250°C
20	Example 17	1.0	under hydrogen atmosphere, furnace sintering, 1950°C
	Example 18	0.8	under hydrogen atmosphere, presintering, 1380°C → electric sintering 2250°C
25	Example 19	0.2	under hydrogen atmosphere, presintering, 1430°C → electric sintering, 2230°C
	Example 20	4.5	under hydrogen atmosphere, furnace sintering, 2000°C
30	Comparative Example 11	2.5	hydrogen atmosphere, furnace sintering, 1800°C

[0120] Next, cylindrical sintered bodies (ingots) were cut out from the obtained tungsten alloy sintered bodies, and the wire diameters were adjusted by appropriately combining forging processing, rolling processing, and wire drawing processing. Processing ratios were as shown in Table 7. The wire diameters were adjusted. Then, the sintered bodies were cut to a predetermined length, and the tip parts were processed into a taper shape. Then, the sintered bodies were subjected to surface polishing, to set surface roughnesses Ra to 5 μm or less. Next, the sintered bodies were subjected to a recrystallization heat treatment at 1600°C under a hydrogen atmosphere. Thereby, discharge lamp electrode parts were completed.

[Table 7]

	Cylindrical sintered body (ingot)		Wire diameter of electrode part (mm)	Processing ratio (%)
	Kind of cylindrical sintered body	Diameter mm × Length mm		
45	Example 11	diameter 5mm × 50mm	diameter 3mm	64
	Example 12	diameter 10mm × 100mm	diameter 8mm	36
50	Example 13	diameter 20mm × 100mm	diameter 16mm	36
	Example 14	diameter 26mm × 100mm	diameter 20mm	41
55	Example 15	diameter 35mm × 100mm	diameter 25mm	49

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(continued)

	Cylindrical sintered body (ingot)		Wire diameter of electrode part (mm)	Processing ratio (%)
	Kind of cylindrical sintered body	Diameter mm × Length mm		
5	Example 16	diameter 22.4mm×100mm	diameter 10mm	80
10	Example 17	diameter 1.2mm×50mm	diameter 1mm	70
	Example 18	diameter 5mm×50mm	diameter 3mm	64
	Example 19	diameter 10mm×100mm	diameter 8mm	36
15	Example 20	diameter 35mm×100mm	diameter 25mm	49
	Comparative Example 11-1	diameter 10mm×50mm	diameter 3mm	91
20	Comparative Example 11-2	diameter 9mm×100mm	diameter 8mm	21

[0121] Next, magnified photographs of the circumferential section and side section were taken of the body part of each of the discharge lamp electrode parts. The average particle diameter of the primary particles of the HfO₂ component, the maximum diameters of the primary particles and secondary particles, and the ratio, average particle diameter and aspect ratio of the tungsten crystal particles were then measured. For the magnified photographs, the circumferential section and side section passing through the center of the body part were cut out, and arbitrary unit areas of 300 μm × 300 μm were investigated. The results are shown in Table 8.

[Table 8]

	Tungsten crystal particle diameter						HfO ₂ particles		
	Circumferential section			Side section			Average particle diameter of primary particles μm	Maximum diameter of primary particles μm	Maximum diameter of secondary particles μm
	Ratio of 1 to 80 μm %	Average particle diameter μm	Average aspect ratio	Ratio of 2 to 120 μm %	Average particle diameter μm	Average aspect ratio			
Example 11	100	11.8	2.7	100	19.3	4.3	1.2	2.0	7.0
Example 12	100	24.8	2.2	100	35.7	3.4	2.5	3.7	8.0
Example 13	98	33.1	2.4	97	44.7	3.6	4.5	6.5	10.0
Example 14	94	49.9	2.6	93	72.2	3.7	4.7	6.9	10.0
Example 15	90	56.0	2.8	92	80.8	3.8	8.3	10.7	13.0
Example 16	100	25.1	2.4	100	36.0	3.6	2.4	4.1	6.0
Example 17	100	33.7	2.5	100	53.6	3.9	3.2	5.3	8.5
Example 18	100	22.5	2.3	100	36.2	3.6	0.7	1.5	3.4
Example 19	100	26.9	2.4	100	37.2	3.5	0.7	1.5	3.4
Example 20	100	25.5	2.3	100	35.0	3.5	0.7	1.5	3.4
Comparative Example 11-1	74	52.0	3.8	68	112.0	5.3	20	28.3	50
Comparative Example 11-2	90	57.6	1.9	93	58.5	2.0	20	28.3	50

[0122] Next, the x value when the contents of Hf and O are converted into HfO_x and the ratio of HfO₂ in the Hf component were measured for each of the discharge lamp electrode parts. An oxygen content, a relative density (%), a Vickers hardness (Hv), and a three point bending strength were obtained.

[0123] The ratio of HfO₂ in the Hf component was obtained by measuring the amount of Hf in the tungsten alloy according to an ICP analysis method and the amount of carbon in the tungsten alloy according to a combustion-infrared absorption method. Carbon in the tungsten alloy may be considered to be contained in HfO₂. Therefore, the detected total amount of Hf was defined as 100 parts by weight, and the amount of Hf contained in HfO₂ was converted. The mass ratio thereof was obtained. The oxygen content in the tungsten alloy was analyzed by an inert gas combustion-infrared absorption method. The relative density was obtained by dividing a measured density analyzed by an Archimedes method by a theoretical density. The theoretical density was obtained by the above calculation. The Vickers hardness (Hv) was obtained according to JIS-Z-2244. The three point bending strength was obtained according to JIS-R-1601. The results are shown in Table 9.

[Table 9]

	x value when converted into HfO _x	Parts by mass of Hf in HfO ₂ when the total amount of Hf is defined as 100 parts by mass	Oxygen content in tungsten alloy (wt%)	Relative density (%)	Vickers hardness (Hv)	Three point bending strength (MPa)
Example 11	0.19	96	0.1	99.5	487	509
Example 12	0.18	90	<0.01	96.2	423	443
Example 13	0.14	70	<0.01	96.8	433	464
Example 14	0.12	60	0.4	98.4	484	484
Example 15	0.16	80	<0.01	99.2	492	500
Example 16	0.18	92	<0.01	99.8	500	513
Example 17	0.19	93	<0.01	99.3	499	505
Example 18	0.18	90	<0.01	99.6	495	513
Example 19	0.17	86	<0.01	97.0	433	451
Example 20	0.15	76	<0.01	98.8	482	492
Comparative Example 11-1	0.19	96	0.2	99.0	822	388
Comparative Example 11-2	0.19	96	0.2	92.2	283	326

[0124] The discharge lamp electrode part according to the present Examples had high density, and an excellent Vickers hardness (Hv). This was because a part of HfO₂ was deoxidized. The Hf component which was not contained into HfO₂ was in any state of a state of metal Hf particles, a state where a part of surfaces of HfO₂ particles were metal Hf, and a state of a solid solution of tungsten and hafnium. That is, two kinds (Hf and HfO₂) are contained as the Hf component.

(Examples 21 to 25)

[0125] Next, the same tungsten powder and HfO₂ powder as those in Example 12 were used, and a second component changed to a composition shown in Table 10 was prepared. These were subjected to furnace sintering at 2000°C under a sintering condition of a hydrogen atmosphere, to obtain ingots. The ingots were processed at a processing ratio of 50%, to obtain electrode parts having a wire diameter of 10 mm. The electrode parts were subjected to a recrystallization heat treatment at 1600°C under a hydrogen atmosphere. The same measurement was performed for each of Examples. The results were as shown in Tables 10 to 12.

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[Table 10]

	Amount of Hf component (in terms of HfO ₂ , wt%)	Addition component (material/wt%)	
5	Example 21	1.0	K/0.005
	Example 22	1.0	Zr/0.01
	Example 23	1.0	Zr/0.5
	Example 24	1.0	ZrC/0.1
10	Example 25	1.0	Ta/0.2

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[Table 11]

	Tungsten crystal particle diameter						HfO ₂ particles		
	Circumferential section			Side section			Average particle diameter of primary particles μm	Maximum diameter of primary particles μm	Maximum diameter of secondary particles μm
	Ratio of 1 to 80 μm	Average particle diameter μm	Average aspect ratio	Ratio of 2 to 120 μm %	Average particle diameter μm	Average aspect ratio			
Example 21	100	28.8	2.3	100	39.1	3.5	2.5	4.0	8.0
Example 22	100	27.2	2.3	100	36.5	3.5	2.5	4.0	8.0
Example 23	100	25.6	2.4	100	35.9	3.6	2.5	4.0	8.0
Example 24	100	27.8	2.4	100	37.3	3.6	2.5	4.0	8.0
Example 25	100	27.5	2.3	100	38.0	3.3	2.5	4.0	8.0

[Table 12]

	x value when converted into HfO _x	Parts by mass of Hf in HfO ₂ when the total amount of Hf is defined as 100 parts by mass	Oxygen content in tungsten alloy (wt%)	Relative density (%)	Vickers hardness (Hv)	Three point bending strength (MPa)
Example 21	0.18	92	<0.01	98.1	443	454
Example 22	0.18	90	<0.01	98.4	440	445
Example 23	0.18	91	<0.01	98.7	438	458
Example 24	0.18	88	<0.01	98.5	443	450
Example 25	0.18	90	<0.01	98.3	440	454

[0126] As can be seen from the Tables, since the use of the addition elements strengthened a dispersion strengthening function and suppressed the grain growth of the tungsten crystals, enhancement of the strength was observed.

(Examples 11A to 25A, Comparative Examples 11-1A to 11-2A, and Comparative Example 12A)

[0127] The emission characteristics of discharge lamp electrode parts of Examples 11A to 25A, Comparative Example 11-1A, and Comparative Example 11-2A were investigated. For the measurement of the emission characteristics, emission current densities (mA/mm²) were measured by changing an applied voltage (V) to 100 V, 200 V, 300 V, and 400 V. The emission current densities were measured under conditions of an electric current load of 18 ± 0.5 A/W applied to the discharge lamp electrode part and an application time of 20 ms.

[0128] A discharge lamp electrode part which was made of a tungsten alloy containing 2 wt% of ThO₂ and had a wire diameter of 8 mm was prepared as Comparative Example 12A. The results are shown in Table 13.

[Table 13]

	Electrode part	Emission current density (mA/mm ²)			
		Applied voltage 100V	Applied voltage 200V	Applied voltage 300V	Applied voltage 400V
Example 11A	Example 11	1.0	30.3	43.7	45.6
Example 12A	Example 12	1.3	31.6	44.3	46.0
Example 13A	Example 13	3.3	36.6	45.2	51.0
Example 14A	Example 14	3.5	37.8	47.1	53.5
Example 15A	Example 15	5.9	38.8	49.0	55.1
Example 16A	Example 16	3.3	37.0	46.7	52.2
Example 17A	Example 17	3.3	37.5	46.9	51.8
Example 18A	Example 18	1.2	30.5	43.9	45.9
Example 19A	Example 19	1.0	29.9	41.8	43.6
Example 20A	Example 20	4.1	42.7	48.5	53.3
Example 21A	Example 21	1.3	32.2	44.4	46.0
Example 22A	Example 22	1.3	32.2	44.4	46.0
Example 23A	Example 23	1.3	32.2	44.6	46.5

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(continued)

	Electrode part	Emission current density (mA/mm ²)				
		Applied voltage 100V	Applied voltage 200V	Applied voltage 300V	Applied voltage 400V	
5	Example 24A	Example 24	1.3	32.3	44.9	46.8
	Example 25A	Example 25	1.3	32.5	44.8	46.4
10	Comparative Example 11-1A	Comparative Example 11-1	1.2	28.8	40.0	42.7
	Comparative Example 11-2A	Comparative Example 11-2	1.0	25.0	35.3	37.1
15	Comparative Example 12A	Comparative Example 12	1.1	31.1	43.0	45.0

[0129] The discharge lamp electrode parts according to Example exhibited emission characteristics equal to or higher than those of Comparative Example 12 using thorium oxide in spite of the nonuse of thorium oxide. The temperatures of the electrode parts were 2100 to 2200°C during measurement. For this reason, the discharge lamp electrode parts according to Examples have excellent strength at a high temperature.

(Examples 26 to 28)

[0130] Next, there were prepared Example 26 (the recrystallization heat treatment condition of Example 11 was changed to 1800°C), Example 27 (the recrystallization heat treatment condition of Example 13 was changed to 1800°C), and Example 28 (the recrystallization heat treatment condition of Example 18 was changed to 1800°C) produced by the same production method except that the recrystallization heat treatment condition was changed to 1800°C in the discharge lamp electrodes of Example 11, Example 13, and Example 18. The same measurement was performed. The results are shown in Tables 14 and 15.

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[Table 14]

	Tungsten crystal particle diameter						HfO ₂ particles		
	Circumferential section			Side section			Average particle diameter of primary particles μm	Maximum diameter of primary particles μm	Maximum diameter of secondary particles μm
	Ratio of 1 to 80 μm %	Average particle diameter μm	Average aspect ratio	Ratio of 2 to 120 μm %	Average particle diameter μm	Average aspect ratio			
Example 26	100	14.2	2.9	100	25.1	4.7	1.2	2.0	7.0
Example 27	98	37.1	2.6	96	49.4	4.0	4.5	6.5	10.0
Example 28	100	25.7	2.7	100	40.3	3.8	0.7	1.5	3.4

[Table 15]

	x value when converted into HfO _x	Parts by mass of Hf in HfO ₂ when the total amount of Hf is defined as 100 parts by mass	Oxygen content in tungsten alloy (wt%)	Relative density (%)	Vickers hardness (Hv)	Three point bending strength (MPa)
Example 26	0.19	94	0.04	99.5	480	500
Example 27	0.14	69	<0.01	97.2	427	460
Example 28	0.18	88	<0.01	99.7	490	502

[0131] The discharge lamp electrode parts according to Example exhibited emission characteristics equal to or (Hv), and an excellent three point bending strength. This was because a part of HfO₂ was deoxidized. As a result of analyzing the Hf component which was not contained in HfO₂, the Hf component became a solid solution of tungsten and hafnium. That is, two kinds (Hf and HfO₂) existed as the Hf component. For this reason, when the recrystallization heat treatment temperature was set to 1700°C or more, metal Hf was found to be likely to be solid-solved in tungsten. The emission characteristics were measured by the same method as that in the case of Table 13.

[Table 16]

	Electrode part	Emission current density (mA/mm ²)			
		Applied voltage 100V	Applied voltage 200V	Applied voltage 300V	Applied voltage 400V
Example 26A	Example 26	1.2	31.5	45.0	47.1
Example 27A	Example 27	3.5	37.3	46.6	53.8
Example 28A	Example 28	1.6	33.3	46.3	48.9

[0132] It was found that metal Hf is wholly solid-solved in tungsten as described above, which improves the emission characteristics. This is considered to be because the existence of metal Hf on the surface of the tungsten alloy is likely to be caused by the solid solution.

[0133] Since the present invention has excellent emission characteristics as described above, the present invention can be used for not only the discharge lamp electrode part but also fields such as the magnetron part (coil part) and the transmitting tube part (mesh grid) requiring the emission characteristics.

Reference Signs List

[0134]

1...Cathode electrode; 2... Electrode body part; 3... Electrode tip part; 4... Discharge lamp; 5... Electrode supporting rod; 6... Glass tube; 7...Coil part; 8... Upper supporting member; 9...Lower supporting member; 10... Supporting rod; 11...Magnetron cathode structure; 21...Discharge lamp electrode part; 22... Discharge lamp electrode part having a taper-shaped tip part; 23...Tip part; 24...Body part; 25...Circumferential section; 26... Side section; 27...Discharge lamp; 28...Electrode supporting rod; 29...Glass tube.

Claims

1. A tungsten alloy comprising a W component and at least two kinds selected from the group consisting of Hf, HfO₂, HfC, and C,

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wherein an amount of the Hf component is within a range of 0.1 wt% or more and 3 wt% or less in terms of HfO₂.

2. A tungsten alloy comprising a W component, and a Hf component comprising HfO₂ particles,
wherein an amount of the Hf component is within a range of 0.1 wt% or more and 5 wt% or less in terms of HfO₂,
and an average primary particle diameter of the HfO₂ particles is 15 μm or less.
3. The tungsten alloy according to claim 2, wherein the HfO₂ particles have an average primary particle diameter of 5 μm or less, and a maximum diameter of 15 μm or less.
4. The tungsten alloy according to any one of claims 2 and 3, wherein a maximum value of secondary particle diameters of the HfO₂ particles is 100 μm or less.
5. The tungsten alloy according to any one of claims 1 to 4, wherein contents of Hf and O are represented by HfO_x, where $x < 2$.
6. The tungsten alloy according to any one of claims 1 to 4, wherein contents of Hf and O are represented by HfO_x, where $0 < x < 2$.
7. The tungsten alloy according to any one of claims 1 to 6, wherein the tungsten alloy comprises 0.01 wt% or less of at least one kind selected from the group consisting of K, Si, and Al.
8. The tungsten alloy according to any one of claims 1 to 7, wherein when a content of Hf is defined as 100 parts by mass, a content of Zr is 10 parts by mass or less.
9. The tungsten alloy according to any one of claims 1 to 8, wherein the Hf component comprises metal Hf solid-solved in W.
10. The tungsten alloy according to any one of claims 1 to 9, wherein the Hf component comprises metal Hf on a surface of the Hf component.
11. The tungsten alloy according to any one of claims 1 to 10, wherein when a content of Hf is defined as 100 parts by mass, a ratio of Hf in HfO₂ particles is 30 parts by mass or more and 98 parts by mass or less.
12. The tungsten alloy according to any one of claims 1 to 11, wherein the tungsten alloy has a Vickers hardness of Hv 330 or more.
13. The tungsten alloy according to any one of claims 1 to 12, wherein the W component comprises tungsten particles having an average crystal particle diameter of 1 μm or more and 100 μm or less.
14. A tungsten alloy part comprising the tungsten alloy according to any one of claims 1 to 13.
15. A tungsten alloy part comprising the tungsten alloy according to any one of claims 1 to 13, wherein the tungsten alloy part is a wire rod having a wire diameter of 0.1 mm or more and 30 mm or less.
16. The tungsten alloy part according to claim 15, wherein a crystal structure of a transverse section of the wire rod has an area ratio of tungsten crystals of 90% or more per unit area of 300 μm × 300 μm, the tungsten crystals having a crystal particle diameter of 1 μm or more and 80 μm or less.
17. The tungsten alloy part according to claim 15, wherein a crystal structure of a vertical section of the wire rod has an area ratio of tungsten crystals of 90% or more per unit area of 300 μm × 300 μm, the tungsten crystals having a crystal particle diameter of 2 μm or more and 120 μm or less.
18. The tungsten alloy part according to any one of claims 14 to 17, wherein the tungsten alloy part is used for at least one part selected from the group consisting of a discharge lamp part, a transmitting tube part, and a magnetron part.
19. A discharge lamp comprising the tungsten alloy part according to any one of claims 14 to 18.
20. A transmitting tube comprising the tungsten alloy part according to any one of claims 14 to 18.

21. A magnetron comprising the tungsten alloy part according to any one of claims 14 to 18.

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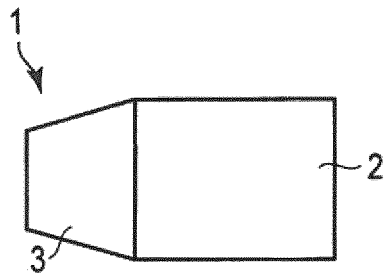


FIG. 1

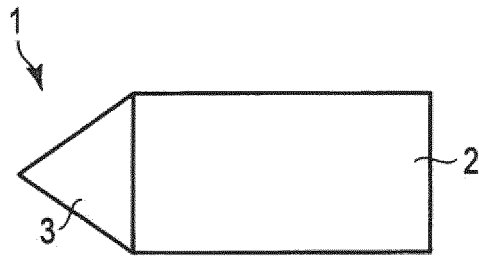


FIG. 2

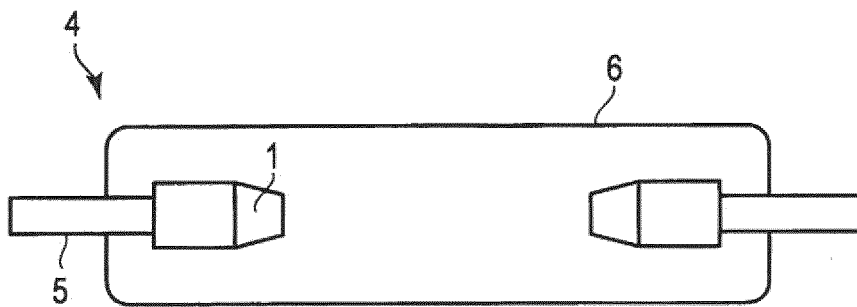


FIG. 3

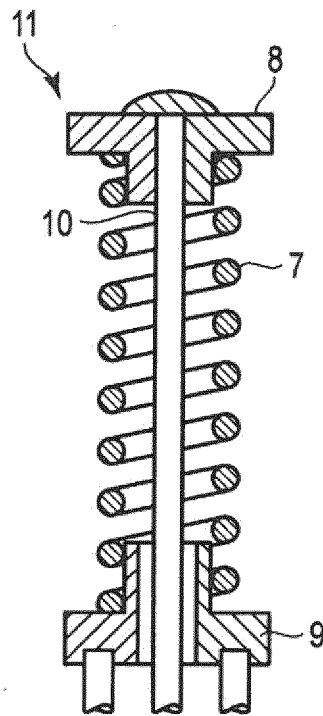


FIG. 4

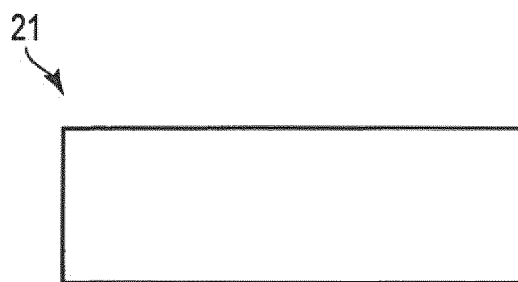


FIG. 5

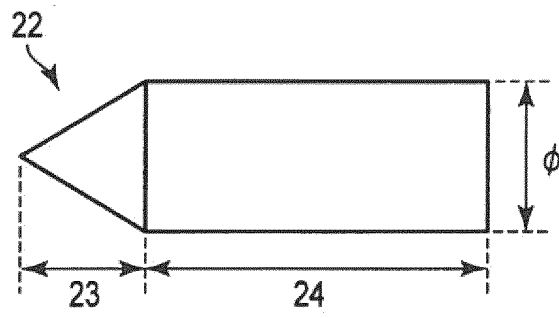


FIG. 6

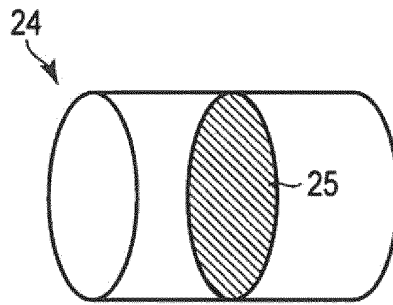


FIG. 7

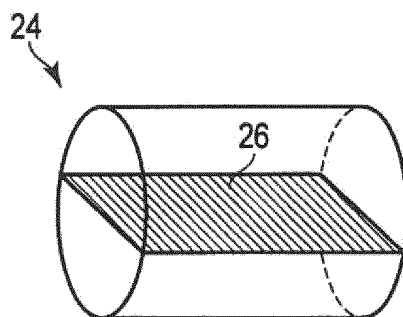


FIG. 8

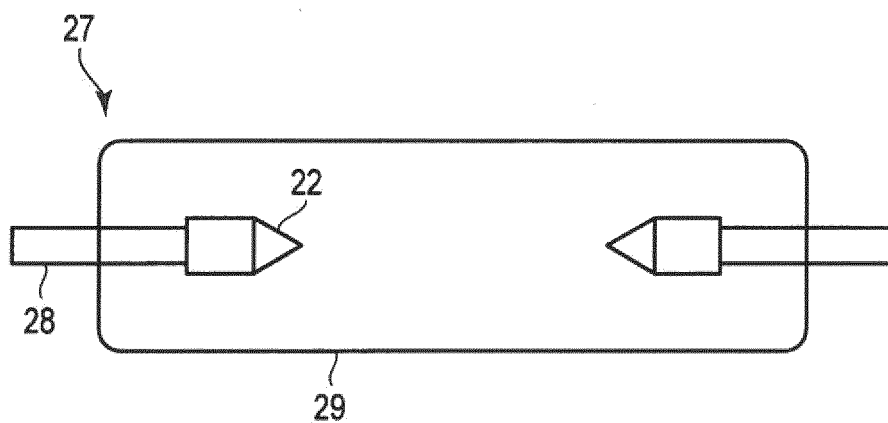


FIG. 9

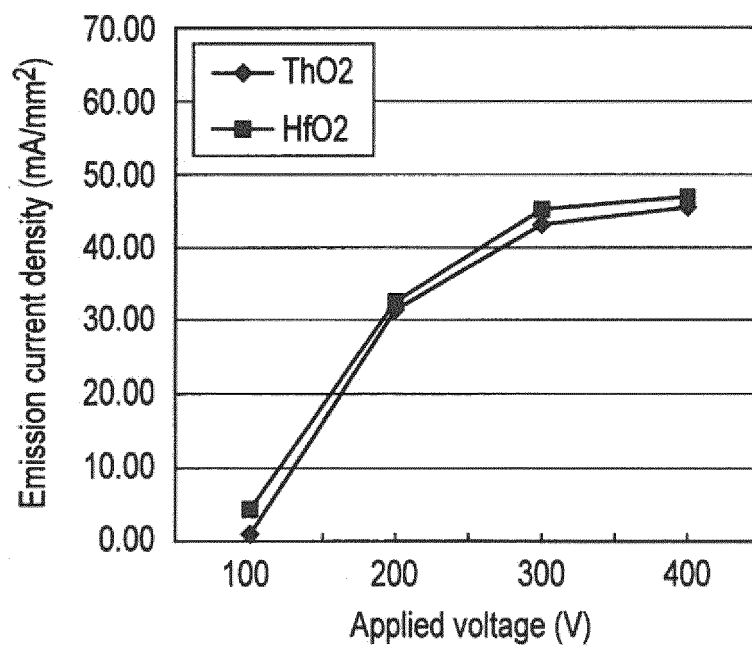


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/083257

5	A. CLASSIFICATION OF SUBJECT MATTER C22C1/04(2006.01)i, C22C1/05(2006.01)i, C22C1/10(2006.01)i, C22C27/04(2006.01)i, H01J1/14(2006.01)i, H01J23/04(2006.01)i, H01J61/06(2006.01)i, B22F3/10(2006.01)n, B22F3/24(2006.01)n According to International Patent Classification (IPC) or to both national classification and IPC	
10	B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C22C1/04, C22C1/05, C22C1/10, C22C27/04, H01J1/14, H01J23/04, H01J61/06, B22F3/10, B22F3/24	
15	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2013 Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013	
20	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)	
25	C. DOCUMENTS CONSIDERED TO BE RELEVANT	
30	Category*	Citation of document, with indication, where appropriate, of the relevant passages
35	Y	JP 2006-102775 A (Nippon Tangsten Co., Ltd.), 20 April 2006 (20.04.2006), claims; paragraphs [0011], [0013], [0024]; table 3 & WO 2006/004073 A1
40	Y	JP 2005-285676 A (Nippon Tangsten Co., Ltd.), 13 October 2005 (13.10.2005), claims (Family: none)
45	<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.	
50	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
55	Date of the actual completion of the international search 04 March, 2013 (04.03.13)	Date of mailing of the international search report 12 March, 2013 (12.03.13)
	Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
	Facsimile No.	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/083257

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
5 10	Y JP 2005-519435 A (Patent-Treuhand-Gesellschaft fuer Elektrische Gluehlampen mbH), 30 June 2005 (30.06.2005), claims & US 2005/0104521 A1 & EP 1481418 A & WO 03/075310 A1 & DE 10209426 A & CN 1639833 A & TW 288943 A	1-21
15	Y JP 2010-159484 A (Allied Material Corp.), 22 July 2010 (22.07.2010), claims & EP 2375438 A1 & WO 2010/067781 A1 & CN 102246260 A	1-21
20	Y JP 2008-539332 A (Koninklijke Philips Electronics N.V.), 13 November 2008 (13.11.2008), claims & WO 2006/114770 A1 & US 2009/0128039 A1 & EP 1894227 A & CN 101167156 A	1-21
25 30	Y JP 2007-113104 A (Toshiba Corp.), 10 May 2007 (10.05.2007), claims; paragraph [0001] (Family: none)	1-21
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- JP 2011103240 A [0004] [0006]
- JP 4741190 B [0006]