A method of preparing a tungsten metal material with high purity, comprising the steps of (A) providing a tungsten metal powder to mix with a metal nitrate to form a mixed powder slurry; (B) ball-grinding the mixed powder slurry to obtain a uniformly mixed powder; (C) sintering the uniformly mixed powder to obtain the tungsten metal material with high purity. Accordingly, the tungsten metal material with purity more than 99.9% can be prepared, so as to prepare the tungsten metal target.
providing a tungsten metal powder to mix with a metal nitrate to form a mixed powder slurry → $S101$

ball-grinding the mixed powder slurry to obtain a uniformly mixed powder → $S102$

sintering the uniformly mixed powder to obtain the tungsten metal material with high purity → $S103$

**FIG. 1**
FIG. 2
FIG. 3
FIG. 4

[Graph showing X-ray diffraction patterns for different W/NiW/Ni ratios with relative intensity on the y-axis and two theta (degree) on the x-axis. Thenotated labels S/L=88/12, S/L=92/8, S/L=96/4, S/L=98/2, S/L=99/1, and S/L=99.95/0.05 are indicated.]
FIG. 5
METHOD OF PREPARING TUNGSTEN METAL MATERIAL AND TUNGSTEN TARGET WITH HIGH PURITY

CROSS-REFERENCE TO RELATED APPLICATION


FIELD OF THE INVENTION

[0002] The present invention relates to a method of preparing the metal material and, more particularly, to a method of preparing the tungsten metal material with high purity and a method of preparing the tungsten target.

BACKGROUND OF THE INVENTION

[0003] Tungsten has the highest melting point among the metals. Since tungsten has the properties such as high strength, high density, good toughness of matrix phase, low coefficient of expansion, and good wear-resistant ability, tungsten is usually used in the fields of national defense and electronics industry. In the military industry, particularly in the aspect used for manufacturing weapons, tungsten exhibits its good property. Tungsten is principally used in manufacturing all kinds of warhead of armor piercing shell in the weapon industry. With coming of nano-era which requires that the electronic products have light weight and thin volume, the applications of thin film sputtering develops continuously, and so does the applications of tungsten sputtering target that can be used in relevant industries such as optical recording media, flat panel displays, semiconductors. Therefore, for the application of the tungsten material used as target, the industries have put a lot of labors and money in researching and developing of the tungsten target in order to get good tungsten sputtering thin film.

[0004] In addition to having good inherent properties, tungsten can be subject to powder pre-treatment technique and large deformation strengthening technique to fine the grains of the material and elongate the orientation of the grains, and thus further enhance toughness and erosion-resisting ability of the tungsten material. Smelting casing technique is one of the methods of treating the metal materials nowadays. Smelting casing technique is achieved by melting the material under high temperature to turn into liquid phase and then being poured into the sand mold or crucible for being cooled and solidifying to get ingot, which can be classified to include continuous casting, vacuum induction smelting, and electron beam smelting. Continuous casting is accomplished by continuously solidifying the melt liquid metal to become ingot by continuous cooling of spray water tape, which has the advantages of low cost, high purity, high yield, and can produce complicated shapes of ingots that are not limited by the size. Since continuous casting has the above-mentioned advantages, continuous casting can become the normally used process of producing a large quantity of bulks. However, continuous casting is not suitable for the metals with high melting point such as tungsten, molybdenum, and tantalum. Vacuum induction smelting is accomplished by heating the alloy raw material with inductive coils under vacuum to make the alloy raw material be fused and mixed in the liquid phase and then solidify into shapes. Induction heating is operated at the temperature as high as 1500-1600°C, therefore induction heating can be used for the metals with melting point of 1600°C or high activity as long as appropriate crucibles are used. For example, Ti can be smelted by this method. However, this method cannot be used for the metal materials with higher melting point or for achieving purity≥99.2% (2N) such as tungsten, molybdenum, and tantalum. Besides, the degree of vacuum will seriously influence the smelting purity. Electron beam smelting is accomplished by heating the raw material by electron gun with huge energy to melt and solidify the metals. This process requires higher degree of vacuum and heating with high power of electron beam to melt the metal material with high melting point of 1600-3300°C such as tungsten, molybdenum, and tantalum, and get purity≥4N. However, though the purity of the raw material are high, the disadvantage of this method is that the cost of the manufacturing equipment is expensive. Moreover, the grains of the metal obtained by electron beam smelting are rough and big which cannot be directly used as target and have to be further treated.

[0005] For the above-said smelting processes for preparing the metal material or target, to control the contents of the impure elements in the material, smelting and casting are usually proceeded under vacuum or protective atmosphere. But, in the process of casting, there are some defects such as segregation of the ingredients, porosity, and non-uniform microstructure which appear after slow solidification. Therefore, all these processes need further thermal treatments to lower the porosity.

[0006] Tungsten metal material or tungsten target can be prepared by powder metallurgy. Powder metallurgy is suitable for preparing ceramic compound materials which cannot be solid dissolved due to thermodynamics factors or are easy to result in macroscopic segregation during casting process. Besides, powder metallurgy is suitable for preparing the metals with high activity or the metals with high melting point such as Ti, Ta, Mo, and W, and the ceramic materials such as Al₂O₃ and ZrO₂. Powder metallurgy can be used to get the metal material and target with high purity and high density. However, to prepare sintered body with large area, the specification of the manufacturing equipment has to be enhanced. For example, the capacity in tons of the thermal compression furnace has to be increased, and the chamber of the thermal compression furnace has to be expanded. But, all these costs of investment for the equipment are very expensive, and thus are not advantageous for the industry to carry out mass production.

[0007] Therefore, there is a need in this industry to develop a method for preparing the tungsten metal material and the tungsten target with high purity in order to avoid using expensive manufacturing equipment and to proceed with efficient treatment to get tungsten metal material with high purity. In such way, manufacturing cost and efficiency can be both satisfied for preparing the tungsten metal material and the tungsten target with high purity.

SUMMARY OF THE INVENTION

[0008] In view of the aforesaid drawbacks of the prior art, it is a main objective of the present invention to provide a method of preparing the tungsten metal material with high purity, which includes the steps of a treatment of mixing a tungsten metal powder with a metal nitrate, a ball-grinding
treatment, and a sintering treatment, for increasing the density of the tungsten-based metal and thus obtaining the tungsten metal material with high purity.

[0009] In order to achieve the above objective, the present invention provides a method of preparing the tungsten metal material with high purity, which can prepare the tungsten metal material with purity more than 99.9%, includes the steps of: (A) providing a tungsten metal powder to mix with a metal nitrate to form a mixed powder slurry; (B) ball-grinding the mixed powder slurry to obtain a uniformly mixed powder; (C) sintering the uniformly mixed powder to obtain the tungsten metal material with high purity.

[0010] The tungsten metal material with high purity has the following properties: wherein the purity of the tungsten metal material with high purity is more than 99.9%, and the density thereof is more than 99% of the density of pure tungsten. Therefore, the tungsten metal material with high purity is suitably used to prepare a tungsten metal target. As long as the uniformly mixed powder is further pressed and shaped to a desired shape for the target before the sintering step (C), the tungsten metal material can be used to prepare the tungsten metal target with high purity and high density.

[0011] The tungsten metal powder of the present invention can be prepared by solid state reaction, wherein the initiating material is hexacarbonyl tungsten powder having an average particle diameter of 1-5 μm, and the metal nitrate in step (A) is selected from nickel nitrate, ferric nitrate, and a mixture thereof. In step (A), the tungsten metal powder is mixed with the metal nitrate to form a mixed powder slurry. Then, oleic acid used as a solvent can be further added into the mixed powder slurry to proceed with ball-grinding treatment to obtain the uniformly mixed powder. Therefore, the uniformly mixed powder can be subject to a heating/drying process and a filtering process to make the particle diameter of the mixed powder more uniform.

[0012] The sintering treatment in step (C) can adopt Liquid Phase Sintering (LPS) which is a method that can efficiently facilitate the sintering rate and is usually suitable for the mixture of elementary powders. When the sintering temperature is over the melting point of one of the ingredients or over the eutectic temperature or peritectic temperature of the ingredients, a liquid phase formed. Since the capillary force of the liquid can cohere the powders and the atom diffuses in the liquid faster than in the solid, the sintering rate of liquid sintering is very fast. The sintering treatment of the present invention can include a plurality of stages of heating treatments. For example, the sintering treatment can include four stages of heating treatments (but is not limited thereto), wherein the temperature in the first stage of heating treatments is more than 200°C, and the temperature in the last stage of heating treatments of the sintering treatment is more than 1400°C.

[0013] Both the above summary and the following description and drawings aim to explain the techniques and means required to achieve the predetermined objectives of the present invention as well as the effects thereof. The other objectives and advantages of the present invention are described below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a flow chart of a method of preparing the tungsten metal material with high purity according to the present invention;

[0015] FIG. 2 is a schematic graph showing the temperature-raising curve for the tungsten metal powder during sintering process according to the present invention;

[0016] FIG. 3 shows relative density of the tungsten metal material (having gone through 1400°C sintering temperature) with metal nitrate being added therein to form different proportions of solid phase to liquid phase according to the present invention;

[0017] FIG. 4 is an XRD graph of the tungsten metal material (having gone through 1400°C sintering temperature) at different proportions of solid phase to liquid phase according to the present invention; and

[0018] FIG. 5 is the ingredients analyzing result of the tungsten metal material with purity of 99.93 wt. % which is prepared at the proportion that solid phase to liquid phase is 99.95:0.05 vol. % according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] The following will illustrate the embodiments of the present invention by specific examples. Any persons skilled in the art could easily understand the advantages and the effects of the present invention from the disclosed contents in the present specification.

[0020] The present invention employs powder metallurgy to prepare the material with high density by grain boundary diffusion of the metals with high melting point (such as molybdenum, chromium, tantalum, and tungsten). This process can make the material to have the good properties such as fine grain size, uniform microstructure, and isotropy. In the present invention, the tungsten metal material and the tungsten-based metal target are prepared by powder metallurgy, such as by hot isostatic pressing, hot pressing, and cold isostatic pressing, which can all accomplish the effect of increasing densification. However, the equipments of hot pressing and hot isostatic pressing are limited by the heating temperature and the size of the chamber, and thus they can only be used to prepare the planar target no more than a specific size, and cannot meet the requirement for the target in the semiconductor industry, such as large size, rotary, and custom-made targets. Regarding the present invention in applications, the embodiment employs atmospheric pressure in powder metallurgy which adds sintering aid. Although adding sintering aid can facilitate diffusion under high temperature and is an effective method, it is observed that inappropriate sintering aid, if added, will react with tungsten metal and usually result in non-uniform distribution, much impurities, or not good densification. Therefore, to solve the problems encountered in the process for preparing tungsten alloy with high melting point and to obtain tungsten metal and tungsten-based metal target with good properties, the present invention employs powder metallurgy by adding sintering aid of nitrates in liquid phase (such as ferric nitrate and nickel nitrate), where such method can make metal nitrates and tungsten metal in solid phase to have uniform distribution, so that the quantity of the sintering aid can be lowered and the disadvantage caused by adding sintering aid can be avoided, and finally the tungsten metal material and the tungsten-based metal target with high purity and densification can be prepared.

[0021] Please refer to FIG. 1 which is a flow chart of a method of preparing the tungsten metal material with high purity according to the present invention. As shown, the method of preparing the tungsten metal material with high
purity according to the present invention includes the steps of: (A) providing a tungsten metal powder to mix with a metal nitrate to form a mixed powder slurry (step S101); (B) ball-grinding the mixed powder slurry to obtain a uniformly mixed powder (step S102); (C) sintering the uniformly mixed powder to obtain the tungsten metal material with high purity (step S103); wherein the tungsten metal material with high purity can be used to prepare a tungsten metal target.

EMBODIMENT

The present embodiment mixes \( W(CO)_6 \) (hexacarbonyl tungsten) with \( Ni(NO_3)_2 \) (metal nitrate) to form a mixed powder slurry, and illustrates the influence of different proportions of solid phase to liquid phase on the target (final product). The ingredients are shown in Table 1. According to Table 1, the present embodiment mixes \( W(CO)_6 \) (hexacarbonyl tungsten) with \( Ni(NO_3)_2 \) (metal nitrate) by different proportions of solid phase to liquid phase to form a tungsten-based metal mixed slurry, which is further mixed with oleic acid (solvent) and YSZ grinding balls. After 24-hour ball grinding, the mixed slurry is put into the furnace at 200°C. After being completely dried to become powder, it is filtered through the 325 mesh screen to obtain uniformly mixed powder. The present embodiment further adopts dry pressing to press and shape the powder into green body of circular shaped disk (8 mm in diameter).

**TABLE 1**

<table>
<thead>
<tr>
<th>Proportion of solid phase to liquid phase</th>
<th>W %</th>
<th>Metal nitrate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/L = 88:12</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>S/L = 92:8</td>
<td>92</td>
<td>8</td>
</tr>
<tr>
<td>S/L = 96:4</td>
<td>96</td>
<td>4</td>
</tr>
<tr>
<td>S/L = 98:2</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>S/L = 99:1</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>S/L = 99.95:0.05</td>
<td>99.95</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The present embodiment is just an example, and to prepare tungsten metal target having different properties, the sintering parameters (such as the ingredients, the maintained duration, and the sintering temperature) can be adjusted.

According to the sintering treatment of the present embodiment, there is liquid metal nitrate among the tungsten metal powder particles which is quickly and uniformly distributed among the powders to lower the surface energy, therefore the adjacent powders are pulled towards one another because of capillary force. In normal circumstances, since the capillary force is high, the powder particles are easily be re-arranged, and there is no need to operate with long duration or at extreme high temperature and the material can be densified. Effective control of the temperature-raising curve is mainly to prevent the material from shrinking unduly and thus cracking during the densification process.

Please refer to FIG. 3, which shows relative density of the tungsten metal material (having gone through 1400°C sintering temperature) with metal nitrate being added thereinto to form different proportions of solid phase to liquid phase according to the present invention. Please refer to FIG. 4, which is an XRD graph of the tungsten metal material (having gone through 1400°C sintering temperature) with metal nitrate being added thereinto to form different proportions of solid phase to liquid phase according to the present invention. As shown, since the present embodiment uses \( W(CO)_6 \) (hexacarbonyl tungsten) as the initiating material that is dissolved in metal nitrate, liquid metal nitrate (sintering aid) can be uniformly distributed in gel form among the tungsten metal particles, so as to improve uniform distribution of the sintering aid and remarkably lower the liquid phase percentage which contributed by the added sintering aid. But, once the liquid phase percentage is over 2%, a second phase of NiW is generated, and thus the density of the produced tungsten metal material relative to pure tungsten is lowered.

The example prepared by the present embodiment is analyzed by inductively coupled plasma mass spectrometry (ICP-MS) of the National Science Council Instrument Center of National Cheng Kung University to acquire the ingredients of the tungsten metal material with high purity. FIG. 5 is the analyzing result of the optimized tungsten metal material (tungsten metal target) according to the present embodiment, wherein the parameters conducted on the sample are listed as below: solid phase to liquid phase is 99.95:0.05 vol. %; and the sintering temperature is 1400°C for the duration of four hours. It can be known from the analyzing result that the tungsten metal material (tungsten metal target) with purity of 99.93 wt. % can be obtained.

The above embodiments are just illustrated to explain the characteristics and the effects of the present invention and are not used to limit the scope of the substantial content of the present invention. Any persons skilled in the art can make modifications and changes to the above embodiments without departing from the spirit and scope of the present invention. Accordingly, the scope intended to be protected by the present invention should be defined by the appended claims.
What is claimed is:

1. A method of preparing a tungsten metal material with high purity, comprising the steps of:
   (A) providing a tungsten metal powder to mix with a metal nitrate to form a mixed powder slurry;
   (B) ball-grinding the mixed powder slurry to obtain a uniformly mixed powder;
   (C) sintering the uniformly mixed powder to obtain the tungsten metal material with high purity.

2. The method of preparing a tungsten metal material with high purity as claimed in claim 1, wherein the purity of the tungsten metal material with high purity is more than 99.9%, and the density thereof is more than 99% of the density of pure tungsten.

3. The method of preparing a tungsten metal material with high purity as claimed in claim 2, wherein the tungsten metal material with high purity is used to prepare a tungsten metal target.

4. The method of preparing a tungsten metal material with high purity as claimed in claim 3, wherein before the sintering step (C), the uniformly mixed powder is further pressed and shaped to a desired shape.

5. The method of preparing a tungsten metal material with high purity as claimed in claim 1, wherein the metal nitrate is selected from nickel nitrate, ferric nitrate, and a mixture thereof.

6. The method of preparing a tungsten metal material with high purity as claimed in claim 1, wherein a solvent is added to the mixed powder slurry in the ball-grinding step (B), and the solvent is oleic acid.

7. The method of preparing a tungsten metal material with high purity as claimed in claim 1, wherein the sintering treatment include a plurality of stages of heating treatments.

8. The method of preparing a tungsten metal material with high purity as claimed in claim 7, wherein the temperature in the first stage of heating treatments of the sintering treatment is more than 200°C.

9. The method of preparing a tungsten metal material with high purity as claimed in claim 7, wherein the temperature in the last stage of heating treatments of the sintering treatment is more than 1400°C.

10. The method of preparing a tungsten metal material with high purity as claimed in claim 1, wherein after the ball-grinding step (B), a heating/drying process and a filtering process are further performed.

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