United States Patent [19]

Okagaki et al.

[11] **3,732,454**

[45] **May 8, 1973**

[54] **GLOW DISCHARGE TUBE FOR ATOMIC LIGHT-ABSORPTION ANALYSIS**

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[73] Assignee: **Hitachi, Ltd.,** Tokyo, Japan

[22] Filed: **Nov. 24, 1971**

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[52] **U.S. Cl.** **313/209,** 313/210, 313/218, 313/346

[51] **Int. Cl.**.....**H01j 61/04**

[58] **Field of Search**.....313/209, 210, 213, 313/216, 217, 218, 341, 346, 356

[56] **References Cited**

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Primary Examiner—Roy Lake

Assistant Examiner—Darwin R. Hostetter

Attorney—Craig, Antonelli & Hill

[57] **ABSTRACT**

A glow discharge tube for atomic light-absorption analysis in which a hollow cathode for producing atomic light-absorption lines comprises a molded article of fine powder containing at least one metal element which produces the atomic light-absorption lines, the article being molded without heating it whereby the dislocation of atomic distance remains in the crystalline lattice to improve the sputtering rate of the metal atom so that the density of metal atoms in the hollow of the hollow cathode is increased to enhance the light intensity of the atomic light-absorption lines.

12 Claims, 10 Drawing Figures

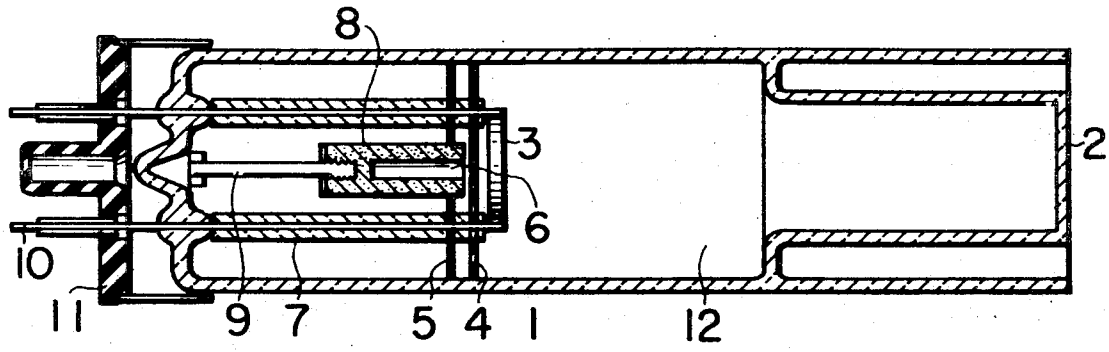


FIG. 1

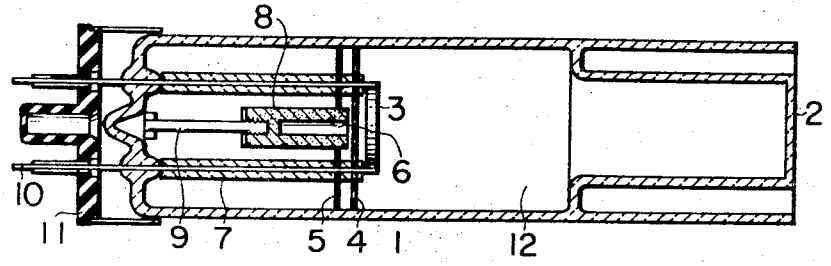


FIG. 2a

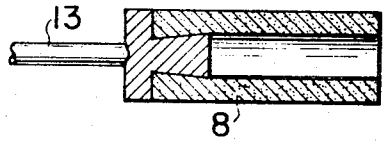


FIG. 2b

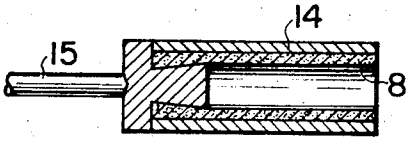


FIG. 2c

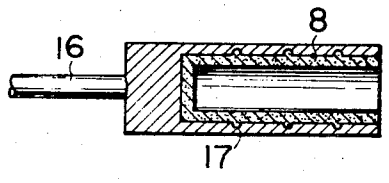


FIG. 3

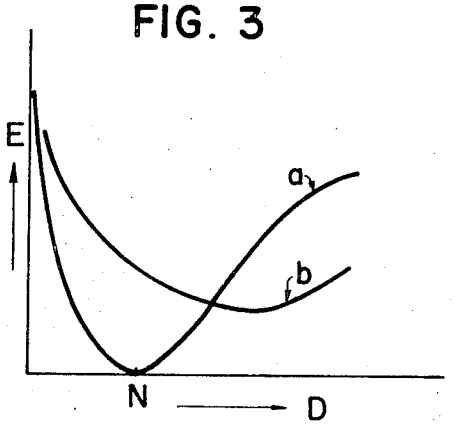


FIG. 4

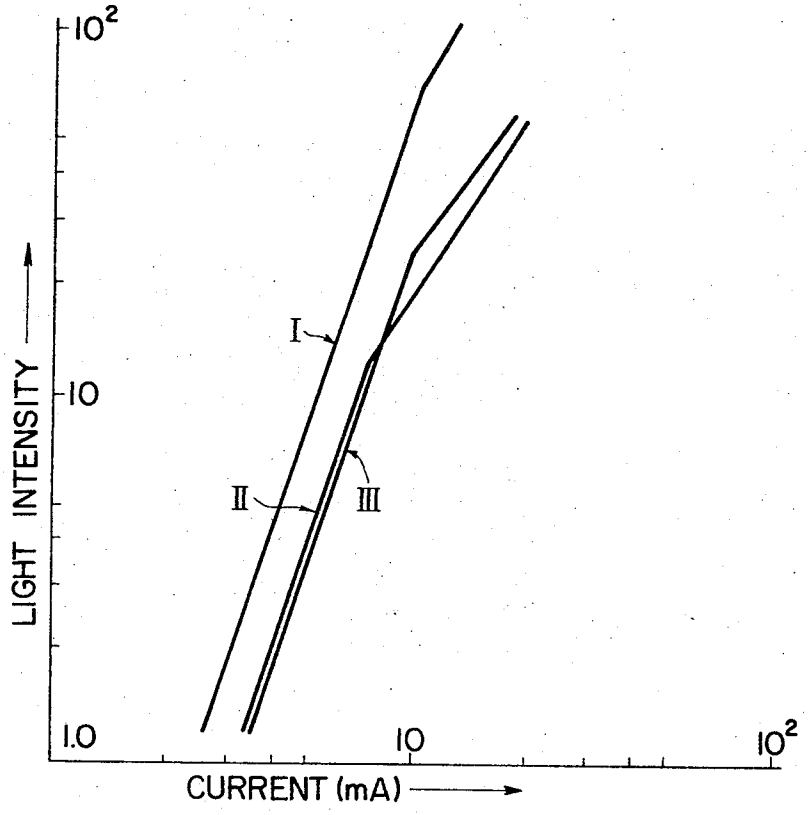

10^2
10
1.0
LIGHT INTENSITY
I
II
III
10
10^2
CURRENT (mA)

FIG. 5

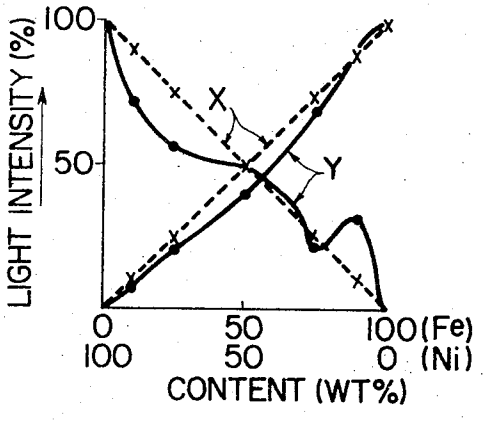

100
50
LIGHT INTENSITY (%)
X
Y
0
50
100 (Fe)
100
50
0 (Ni)
CONTENT (WT%)

FIG. 6a

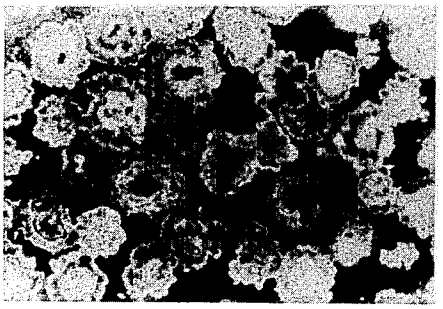


FIG. 6b

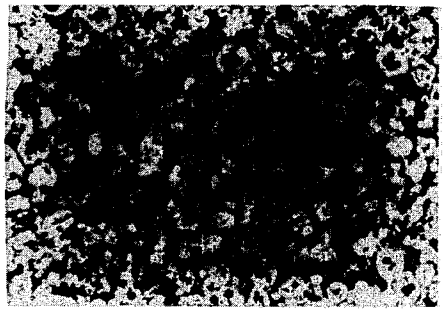
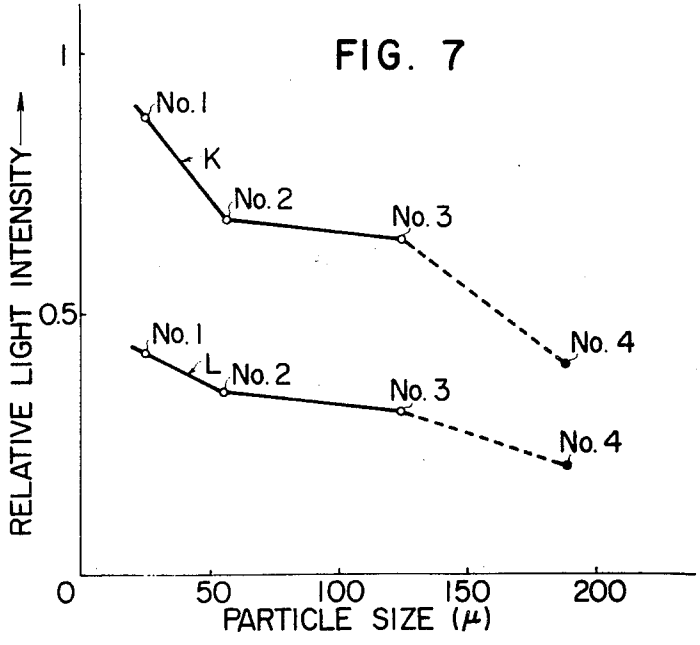


FIG. 7



GLOW DISCHARGE TUBE FOR ATOMIC LIGHT-ABSORPTION ANALYSIS

The present invention relates to a glow discharge tube for atomic light-absorption analysis and more particularly to a glow discharge tube provided with an improved hollow cathode capable of producing a high light intensity of atomic light-absorption lines.

Among methods of quantitatively analyzing a metallic salt contained in a solution sample is the atomic light-absorption analyzing method utilizing the principle of atomic light-absorption.

This method of analysis has recently found extensive use in the fields of medical science, biochemistry, food chemistry, petrochemistry, industrial chemistry and so forth since it is suited to the analysis of a very small quantity of metal in a solution sample.

This atomic light-absorption method of analysis is an optical method in which a metallic salt solution is introduced into a flame to decompose it into atomic vapor by heat energy, and a beam of an atomic resonance line produced by the light source is transmitted through the flame containing the atomic vapor, thereby achieving an analysis of the metal atoms in accordance with the quantity of light absorbed by the atomic vapor. The basic principles of such method are disclosed in United States Patent No. **2,847,899**. In the atomic light absorption analysis method, only the resonance line or atomic light-absorption beam having a desired wavelength is absorbed by atomic vapor, and an analysis is performed by virtue of the fact that there is a particular relationship between the quantity of the absorbed atomic resonance beam and the quantity of atoms to be analyzed. Therefore, irrespective of the coexistence of different atoms in the material of the cathode, there is no problem if their absorption lines do not overlap the absorption line of the cathode material.

Thus, it is possible to make the cathode of a suitable alloy or composite material. In fact, such a cathode is formed by a fusible material of plural kinds of elemental metals melted so as to be alloyed each other, a sintered body consisting of two or more kinds of metals or alloy powders mixed with each other and press-molded and thereafter sintered which is impregnated with a metal of an elemental metal or metal having a lower melting point.

In an attempt to make a cathode of a fusible material, however, a limitation is naturally placed on the selection of metals, because it is necessary that the overlapping of the resonance lines and the lowering of their light intensity be avoided. Furthermore, some metals cannot be alloyed. Disadvantageously, therefore, such a fusible material cannot be utilized in extensive applications. For example, iron (Fe) and copper (Cu) can be alloyed with each other, but by using a cathode formed of such alloy, either a resonance line having a particular wavelength corresponding to the bright line spectrum of iron or copper cannot be obtained or even if it is obtained, its quantity is small. Therefore, such a cathode cannot be put to practical use. It is presumed that the reason is that the bright line spectra of iron and copper are weakened due to the alloying of these metals.

With a cathode consisting of sintered body, it is possible to produce a high light intensity as compared with that made of a melted alloy, since the mixed

metals are bonded without mutual diffusion or alloying diffusion. In the U.S. Reissue Pat. No. Re. 26,855, entitled "Method of cathodes for hollow cathode lamps of spectroscopic analyzers", filed Dec. 13, 1966, assigned to Hitachi, Ltd. (Kabushiki Kaisha Hitachi Seisakusho), there are shown hollow cathodes made of a sintered body containing a plurality of metallic elements.

The inventors of the present invention have, however, found that the light intensity produced by a glow discharge lamp provided with a sintered hollow cathode is not satisfactory. The light intensity is substantially proportional to the quantity of metallic atoms present in the hollow which are sputtered by glow discharge. In the case of a sintered body, the light intensity is not high because of the relatively small sputtering rate.

One of the objects of the present invention is to provide a glow discharge tube provided with an improved hollow cathode.

Another object of the present invention is to provide a glow discharge tube capable of producing atomic light absorption lineswith high intensity.

Still another object of the present invention is to provide a glow discharge tube in which a hollow cathode can be manufactured easily and in low cost.

The present invention provides a glow discharge tube of which a hollow cathode is made of a molded power which is compressed without heating. The present invention is based upon the discovery that the sputtering rate of an element which is subjected to sputtering is increased by the presence of a dislocation of atomic position in the crystalline lattice.

The above mentioned objects and features of the present invention will be understood from the following detailed description taken in conjunction with the drawing in which:

FIG. **1** shows a longitudinal section of a glow discharge tube embodying the present invention;

FIGS. **2***a* to **2***c* show partial section views of hollow cathodes according to the present invention;

FIG. **3** is a graph showing the relationship between atomic distance and atomic bonding energy;

FIG. **4** is a graph showing relations between current and light intensity;

FIG. **5** is a graph showing the relationship between the contents of elements in the cathode and light intensity.

FIGS. **6***a* and **6***b* are photographs showing particle characteristics of a compression molded body and a sintered body, respectively; and

FIG. **7** is a graph showing the relationship between light intensity and the size of particles making up the cathode of the present invention.

In FIG. **1**, reference numeral **1** designates a bulb made of glass or the like, **2***a* window made of a material transparent to atomic resonant lines, which is made of quartz glass or the like. Numeral **3** represents a discharge anode, while **4** and **5** are insulators made of a material such as of mica, which prevent a short-circuit between the anode **3** and a cathode **8** as caused by sputtering. Numeral **7** indicates insulators in the form of a capillary tube, for insulating anode lead wires **10**. The cathode **8**, having a hollow **6**, is connected to a lead wire **9**. The lead wire **9** is connected, together with the

lead wires **10**, to a socket **11** outside the bulb. Represented at **12** is a carrier gas atmosphere of several Torrs of Ne, He or Ar gas.

In FIGS. **2***a* to **2***c*, numeral **8** indicates molded hollow cathodes which are prepared in such a way that a powder consisting of an element or a plurality of elements, e.g. at least one member selected from the group consisting of Cu, Fe, Ni, Cr, Au, Ag, Pd, Zn, Pt, Ta, Ti, Mn, B, Si, etc., is compression-molded into a cylindrical body as it is maintained at the normal temperature.

Shown at **13** is a member which is constructed integrally with the cylinder **8** such that a metal, e.g. Ni, weldable with the lead wire at **9** in FIG. **1** is embedded into the bottom of the compression-molded body **8**, when said mold body is formed, and which has an end weld-connected with the lead wire **9** thereafter.

Referring to FIG. **2***b*, numeral **8** represents a solid cylindrical body and a member or casing **14** serves to mechanically reinforce the cylindrical body **8**. The member **14** is prepared by compression-molding a finely-cut metal piece, e.g. finely-cut copper piece, into the cylindrical form, and is used in superposition on the outer periphery of the cylindrical body **8**.

A member **15** is constructed integrally with the molded cylinder **8** in such a way that a metal weldable with the lead wire **9** is embedded into the bottom of said cylinder.

Referring to FIG. **2***c*, numeral **8** indicates a solid cylindrical body which is prepared by, as in the foregoing, compression-molding a cathode element or elements and which has a porosity of 30 to 50 percent. Shown at **16** is a metal-made cylinder which is used in a manner to be lapped over the outside of the cylindrical body **8**, and which serves to reinforce fragility of the powdery compression-molded body **8**. Grooves **17** are cut in several places of the circumference of the inner opening of the metal-made cylinder **16**, and they are provided in order to improve the close adherence between the cylinder **16** and the molding **8** through ridges therein. There will now be explained the results of comparisons between the glow discharge tube according to the present invention and that having a hollow cathode made by powder-metallurgy and by melted alloy. FIG. **4** shows an example of the comparison of the characteristics of the light intensity versus the current (m A).

The curve I shows the light intensity of the glow discharge tube according to the present invention, II the glow discharge tube having a hollow cathode made by powder-metallurgy, and III the glow discharge tube having a melted alloy hollow cathode.

In the case of the glow discharge tube according to the present invention, the light intensity for identical current values of current is approximately two to four times larger than in the other glow discharge tubes.

This is because, in case of the present invention, the element bonding at the surface of the inner opening of the compression-molded body **8** is in the unstable state, so that the generation of elements **0** due to the sputtering phenomenon is of a large amount under the discharge state, to accordingly strengthen the light intensity.

FIG. **5** shows the characteristics of the light intensity versus the ratio of the elements Ni and Fe.

The curve X shows the light intensity of the glow discharge tube according to the present invention with respect to the mixing ratio of Ni to Fe and Y the light intensity of the glow discharge tube provided with a hollow cathode made by powder-metallurgy.

The relation between the mixing ratio and the light intensity is linear in the glow discharge tube according to the present invention, whereas the relation is non-linear in the conventional glow discharge tube.

There remain some mechanical stresses in the particles of the molded body as shown in FIG. **6***a*, whereas in the sintered body shown in FIG. **6***b* mechanical stresses disappear through sintering. In case a large amount of the mechanical stresses remain in the particles, the atoms in the crystalline lattice are subjected to dislocation such that the atoms become active to sputtering.

Referring to FIG. **3**, the atom bonding energy E, which acts between the atoms in the crystalline lattice, changes with the distance between the atoms. When the atoms are located apart by the distance N in curve (*a*) which shows an energy curve with respect to the metallic bond, the atoms are in the stable state and have a great bonding energy.

Therefore, in the metallic bond a large amount of energy is necessary for separating the atoms. To the contrary, when the atoms are dislocated, the atom bonding energy is changed with the atomic distance as shown by curve (*b*). That is, there is no stable state in which atoms are separated by a large energy. The atoms dislocated by a force of, such as, compression are easily sputtered as compared with the case where the crystalline lattice is in the stable state.

In other words, where particles of powder are bonded by metallurgical connection, the crystalline lattices are bonded by a metallic bond in the sintered body. But, the particles of the molded body which is produced by compression without heating are bonded by sticking so that the atomic dislocation remains in the crystalline lattice to make the metallic atoms active to sputtering.

According to investigations of the inventors, it has been found that the light intensity is normally increased by making fine the particle size of the powder material. There are shown in FIG. **7** the results of investigations in connection with the relationship between the light intensity and particle size (microns). In FIG. **7**, curve L shows light intensity in the case of 20 milliamperes of tube current and curve K in case of 30 milliamperes of tube current. In this figure, specimen No. **1** represents a molded body of powder being 100 to 148 microns in particle size, specimen No. **2** a molded body of powder being 43 to 70 microns in particle size and specimen No. **3** a molded body of powder being 10 to 40 microns in particle size, respectively. It is apparent from these results that the finer the particle size of powder, the larger the light intensity becomes. Therefore, the inventors recommend the use of powder of which the particle size is smaller than about 150 microns, especially powder having a particle size smaller than 70 microns. In specimen No. **4** of a melted alloy, the light intensity is much smaller than other specimens.

By making the particles fine, the degree of dislocation of atomic position becomes large so that the sputtering rate may be increased.

The inventors have thought that the sputtering rate may be increased not only by providing the atoms with dislocation, but also by increasing the surface area of the particles. For this reason, the hollow cathode according to the present invention in which particles of metals or alloys are made as fine as possible has a great sputtering rate because the surfaces of particles to be sputtered become large and the number of energized ions which collide with the surface will be increased.

In the glow discharge lamps in which hollow cathodes contain plural elemental metals for the purpose of producing a plurality of atomic light-absorption lines, the composition of the metals should be chosen in such a manner that each of the atomic light-absorption lines with respect to the metals has the substantially equal intensity. The compositions prepared by the inventors in consideration of the above point of view are as follows:

1. Ni (30% by weight) Fe (45% by weight) —Cu (25% by weight)
2. Fe (50) — Cu (15) — Mn (35)
3. Cr (15) — Cu (10) — Fe (40) — Mn (10) — Ni (25)
4. Cr (16) — Cu (8) — Fe (31) — Mn (8) —Ni (20) — Co (17)
5. Cu (10) — Fe (45) — Mo (45)
6. Cr (20) — Cu (20) — Si (60)
7. Cr (75) — Cu (10) — Mn (15)
8. Cr (40) — Cu (10) — Mn (20) — Sn (40)

At least 5000 kilograms per square centimeter of compression force is preferable when the powder is composed of metals, such as Cu, Fe, Ni, Cr, Au, Ag, Pd, Pt, Ta, Ti, Mn, B, Si or their alloys. When the metals are so hard that the particles do not stick together so as to be strong or tough enough to withstand the mechanical shock imparted to the glow discharge tube during handling or transportation, a suitable soft metal, such as, silver or copper is mixed with the hard metal as a binder. In the above the specimens copper functions not only as an element for producing atomic light-absorption lines but also as a binder.

For metals, such as Bi (m.p. 271°C), Sb (630.5°C), Pb (327.5°C) or the like the glow discharge phenomenon is mainly caused by vaporization of the atoms in the hollow. To the contrary, for metals having a higher melting point of about 660°C, which is lower than the operating temperature of the hollow cathode, the glow discharge phenomenon is supposedly caused by the sputtering of the atoms. The present invention is, therefore, preferably applied to the metals of which glow discharge phenomenon is caused by the sputtering, for example, Al (m.p. 660°C), Ag (960.8°C), Au (1063 °C), Cu (1083°C), Si (1420°C) Co (1489.8°C), Fe (1535°C), Pt (1800°C), Mo (2622°C) or the like.

It was found, however, that the same results can be obtained when the lower melting point metals are combined with the higher melting point metals. In this case, the glow discharge phenomena are caused by both vaporization and sputtering.

In the specification the term "sticking" means a bonding state of particles of a powdery metal in which the particles are bonded together by the action of biting each other. That is, the particles are bonded substantially only by a kind of mechanical force. Therefore, there is substantially no metallic bond and there is dislocation of the atomic distance in the crystalline lattice, while in the sintering the particles are bonded by the metallic bond and there is substantially no dislocation.

Although the powder is subjected to reduction treatment in a reducing atmosphere, such as hydrogen, prior to molding in which the power is heated at a relatively low temperature such as 600° to 800°C the dislocation does not disappear.

We claim:

1. A glow discharge tube for atomic light-absorption analysis which comprises: an envelope confining an inert gas atmosphere and having a window transparent to atomic light-absorption lines; a cathode for glow discharge having a hollow; an anode adjacent to said hollow of said cathode; a cathode lead connected to said cathode; and an anode lead connected to said anode, each of said leads connected to a power source, wherein said cathode is composed of a molded body comprising a powder of at least one metal which serves as an element for producing said atomic light-absorption lines, the particles of said powder being bonded together by sticking.

2. A glow discharge tube according to claim 1, wherein said cathode comprises a cylindrically shaped wall made of said molded body of powder.

3. A glow discharge tube according to claim 2, wherein said cathode further includes an outer reinforcing casing for mechanically reinforcing said cylindrically shaped wall.

4. A glow discharge tube according to claim 3, wherein said casing and said wall each have respective interlocking grooves and ridges for improving the close adhesiveness therebetween.

5. A glow discharge tube for atomic light-absorption analysis which comprises:

an envelope confining an inert gas atmosphere and having a window transparent to atomic light-absorption lines;

a cathode for glow discharge having a hollow;

an anode adjacent to said hollow of said cathode; a cathode lead connected to said cathode; and an anode lead connected to said anode, each of said leads being connected to a power source, in which at least an inner periphery of said cathode is composed of a molded body comprising fine powder of at least one metal having a melting point higher than the operating temperature of said cathode, particles of said powder being bonded together by sticking, whereby atomic dislocation remains in the crystalline lattice of said particles to increase the sputtering efficiency of said metal.

6. A glow discharge tube for atomic light-absorption analysis which comprises:

an envelope confining an inert gas atmosphere and having a window transparent to atomic light-absorption lines, a cathode for glow discharge having a hollow, an anode adjacent to said cathode, a cathode lead connected to said cathode, and

an anode lead connected to said anode, each of said leads being connected to a power source, in which at least an inner periphery of said cathode is composed of a molded body of fine powder containing at least one metal having a melting point higher

than 660 °C, the particles of said metal being connected by sticking, whereby dislocation of atomic distance which is imparted by grinding and compressing said powder remains in the crystalline lattice of said particles.

7. A glow discharge tube according to claim 6, in which said powder comprises at least one higher melting point metal having a melting point higher than that of silver and at least one lower melting point metal having a melting point lower than that of antimony.

8. A glow discharge tube according to claim 6, in which said particles have a particle size smaller than 150 microns.

9. A glow discharge tube according to claim 6, in which said powder comprises at least two metals each having a melting point higher than that of silver, each of said metals being mixed in such a ratio that the light intensity with respect to each of said metals is substantially equal to one another.

10. A glow discharge tube for atomic light-absorption analysis which comprises:

an envelope confining an inert gas atmosphere and having a window transparent to atomic light-absorption lines,

a cathode for generating said atomic light-absorption lines having a hollow in which a glow discharge takes place,

an anode adjacent to said cathode,

a lead connected to said cathode,

a lead connected to said anode, each of leads being connected to a power source, in which at least the inner periphery of said cathode is composed of a molded body of powder having a particle size smaller than about 150 microns and containing at least one elemental metal having a melting point higher than that of aluminum, said body being formed by compression without heating into a desired shape, whereby dislocation of atomic distance remains in a crystalline lattice of said metal to render said atoms active to sputtering.

11. A glow discharge tube according to claim 10, in which said powder comprises at least one metal having a melting point higher than that of silver and at least one metal having a melting point lower than that of antimony, each of said metals being mixed in such a ratio that the intensity of each of the atomic light-absorption lines with respect to said metals is substantially equal to one another.

12. A glow discharge tube according to claim 10, in which said powder comprises at least one hard metal and at least one soft metal which functions as a binder for said hard metal, each of said metals being mixed in such a ratio that the intensity of each of atomic light-absorption lines with respect to each of said metals is substantially equal to one another.

* * * * *