(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 765 012 A2

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
26.03.1997 Bulletin 1997/13

(21) Application number: **95942805.3**

(22) Date of filing: **21.12.1995**

(51) Int. Cl.^{6}: **H01S 3/00**

(86) International application number:
PCT/RU95/00276

(87) International publication number:
WO 96/21958 (18.07.1996 Gazette 1996/33)

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB IE IT LI NL SE

(30) Priority: **29.12.1994 RU 94045576**

(71) Applicant: **TOVARISCHESTVO S OGRANICHENNOI OTVETSTVENNOSTJU "TEKHNOVAK + "**
Moscow, 123479 (RU)

(72) Inventors:
- **REUTOVA, Nina Pavlovna**
  Moscow, 107014 (RU)
- **MANEGIN, Sergei Jurievich**
  Moscow, 109241 (RU)
- **PUSTOVOIT, Jury Mikhailovich**
  Moscow, 123060 (RU)
- **STOLYAROV, Vladimir Leonidovich**
  Moscow, 123479 (RU)

(74) Representative: **Adorno, Silvano et al**
c/o SOCIETA' ITALIANA BREVETTI S.p.A.
Via Carducci, 8
20123 Milano (IT)

(54) NON-VAPORISING GETTER AND METHOD OF OBTAINING THE SAME

(57) The proposed non-vaporising getter contains the following components: vanadium (V) - 20-35 wt.%; calcium (Ca) - 0.1-0.5 wt.%; and titanium (Ti) - the rest. The getter has a porosity of 25-65 % of its total volume. In order to obtain the getter in question, a method is proposed whereby a metal powder containing vanadium (V), calcium (Ca) and titanium (Ti) in the proportions indicated above is fed into a deformation zone at a bulk density of about 0.7-1.5 g/cm^3. In the deformation zone, the powder is shaped by rolling, producing a getter blank in the form of a ribbon. The latter is cut into uniform sections which are then fed into a heating zone, where a pressure below 1 pa is established and maintained and the blank sections are heated to a temperature below 0.6 of the fusion temperature of the titanium-vanadium alloy and subsequently allowed to set. A getter is obtained with a porosity of 25-65 % of its total volume.

Printed by Rank Xerox (UK) Business Services
2.14.1/3.4

Description

FIELD OF TECHNOLOGY

The present invention relates to vacuum techniques, specifically to nonevaporable getter and a process for its production.

The invention may be used as a pump for creating and maintaining high vacuum in electronic vacuum devices, e.g. in a cathode-ray tube, in an optical converter, gyroscope, etc., in elementary particles sources and accelerators, e.g. in a thermonuclear plant of TOKAMAK T-15 type.

Preferably the present invention may be used for creating vacuum in devices reducing heat transfer from environment to thermostated media, e.g. in a vacuum flasks, a liquified gas storage, in pipelines for gas and crude oil transportation from wells, which pipelines are thermally insulated to protect environment in the permafrost zone.

Also the present invention may be successfully used for inert gases purification.

PRIOR ART

Presently intensive development of novel technologies in, e.g. semiconductors production and use, sets stringent requirements to stability of n-type and p-type conduction in p-n-junctions, which conduction is disturbed by detrimental gaseous impurities (i.e. O_2, CO, CO_2, H_2O, N_2 etc.) present in the zone of the treatment of such semiconductors.

Said detrimental impurities are removed by pumping them out from the treatment zone using sorption pumps based on nonevaporable getters, the decrease in the concentration level of detrimental gaseous impurities in said zone depending on the their sorption rate. Therefore the development of getters having improved sorption rate is a matter of great importance. An attempt was made to produce a getter having increased sorption rate (the USSR Inventor's Certificate No. 1715496). The known getter has three layers, one of which being a supporting layer, is made of a plastic material selected from a group comprising, e.g. Fe, Ni or their alloys, and two other surface getter layers each are made of a zirconium-based material, containing, e.g. 16 % by weight of aluminium, the balance being zirconium, or 30 % by weight of vanadium, 20 % by weight of titanium, the balance being zirconium.

Known is the process for producing a getter based on zirconium, comprising the following operations:

- simultaneous feeding into a deformation zone a powder material forming a supporting layer and selected from, e.g. a group comprising Fe, Ni or the alloys thereof, and a zirconium-based powder material comprising 16 % by weight of aluminium (Al), the balance being zirconium (Zr), or 30 % by weight of vanadium (V), 20 % by weight of titanium (Ti), the balance being zirconium (Zr), and forming getter layer, zirconium-based materials being fed to the both sides of the material forming the supporting layer. In said deformation zone said powder materials are formed by rolling, as a result of which a getter blank in the form of a three-layer ribbon is produced. When said ribbon is leaving the deformation zone it is cut into standard sections, e.g. 200 mm. Said standard sections of getter blanks are brought into a heating zone wherein vacuum conditions are created and maintained, and heated up to 950-1.000 Celsius degrees. As a result of this the blank material gets sintered and the final getter is produced in the form of a product having improved mechanical properties, namely, increased tensile strength of getter material, e.g. from 6.3 to 6.8 kg/mm^2 , and increased sorption rate, e.g. reaching 1.9 m^3/m^2 s at room temperature, when sorbed hydrogen quantity is 1.3 m^3. Pa/kg, after getter activation at 900 Celsius degrees.

In spite of increased tensile strength the known getter shows low mechanical strength of the getter layer because getter layers are made of a material based on a Zr-Al or Zr-V-Ti alloy comprising large amount of intermetallic compounds characterized by increased hardness and brittleness. Therefore when such getters are used under alternating loads, they fail, most often as a result of crumbling. Moreover zirconium-based getter containing 16 % by weight of aluminium causes increased power consumption because high temperature (about 900 Celsius degrees) is required to activate such getter.

Furthermore the known getter has low sorptive capacity with respect to such gases as H_2, O_2, CO_2, CO , N_2, etc. because the supporting layer made of, e.g. Fe, Ni and their alloys, is neutral to gas sorption, and because of low porosity of getter layers being about 20%.

The above process for producing nonevaporable getter is hard to realize because it is difficult to reach an optimal correlation between the thickness of the supporting layer and the total thickness of the getter layer; also said process involves high loss in powder material resulting in increased getter costs.

Moreover known is a nonevaporable getter having increased mechanical strength and improved sorption rate (the RF Patent No. 1750256). The known getter contains from 20 to 35 % by weight of vanadium (V), from 0.1 to 0.5 % by weight of calcium (Ca), and the balance being titanium (Ti).

Said getter shows increased mechanical strength when used under alternating loads, due to high plasticity of the material being a solid solution of vanadium in titanium. The presence of elementary calcium in the getter material contributes to an increased rate of gas sorption because calcium showing high chemical activity to oxygen forms calcium oxide (CaO), and calcium oxide particles being uniformly distributed among metal particles, act as antisintering agent contributing to high porosity of the getter.

The above getter is produced as follows.

Metal powder containing from 20 to 35 % by weight of vanadium, from 0.1 to 0.5 % by weight of calcium, the balance being titanium, is fed into a deformation zone, wherein said powder material is formed by rolling to produce a getter blank in the form of a ribbon. When said ribbon is leaving the deformation zone, it is cut into standard sections, said sections being transported into a heating zone.

In said heating zone a pressure of lower than 1 Pa is created and maintained, and the blank is heated to a temperature lower than 0.6 times the melting point of titanium-vanadium alloy, e.g. to 850 Celsius degrees, with further holding. The getter thus produced is a plate having 22% porosity, sorption rate with respect to hydrogen being 1.8 m^3/m^2s at room temperature, when the quantity of sorbed hydrogen is 1.3 m^3Pa/kg. Said getter is activated at 300-350 Celsius degrees.

In view of the foregoing a getter having said composition, may be referred to the getters with low activation temperature, which fact allows to develop pumping means requiring low power consumption. Nevertheless due to reduced sorption rate such getter has restricted applicability, e.g. it cannot be used as a stage in a multistage pumping device used in semiconductors production.

DESCRIPTION OF THE INVENTION

The object of the present invention is to develop a nonevaporable getter having sorptive rate with respect to hydrogen of over 2 m^3/m^2s at room temperature when the quantity of sorbed hydrogen being 1.3 m^3Pa/kg, due to a larger surface. contacting the gas to be pumped out.

The object of the invention is achieved by that nonevaporable getter containing from 20 to 35 % by weight of vanadium, from 0.1 to 0.5 % by weight of calcium and the balance being titanium, according to the invention, has porosity from 25 to 65 % by volume.

Said getter has larger number of pores opening at its surface. As a result larger surface contacts the gas to be pumped out, resulting in increased gas sorption rate, e.g. the sorption rate for hydrogen is over 2 $m^3/m^2 \cdot s$ at room temperature when the quantity of sorbed hydrogen is 1.3 m^3 Pa/kg. A getter having the porosity less than 25%, shows hydrogen sorption rate less than 2 $m^3/m^2 \cdot s$, due to which fact its applicability is restricted. A getter having porosity less than 25% cannot be used, e.g. as a stage in a multistage pumping device used in semiconductors production.

A getter having porosity over 65% has lower mechanical strength, which may result in its crumbling and failing under alternating loads. Such getter cannot be used e.g. in night-vision devices, gyroscopes, etc.

Thus the getter according to the present invention has increased sorption rate (1.5-3 times) after activation at 300-350 Celsius degrees, due to greater open porosity accounted for increased total porosity of the getter.

Also the object of the invention is to develop a process for producing a nonevaporable getter comprising using powder material with branched particles to form porosity in the range from 25 to 65 % in said material.

Said object is achieved by that in the process for producing a nonevaporable getter comprising feeding a metal powder containing from 20 to 35 % by weight of vanadium, from 0.1 to 0.5 % by weight of calcium, the balance being titanium, into a deformation zone wherein said powder material is formed by rolling to produce a getter blank in the form of a ribbon, said ribbon, when leaving the deformation zone, being cut into standard sections, said sections being transported into a heating zone, in said heating zone a pressure of lower than 1 Pa being created and maintained, and the blank being heated to a temperature lower than 0.6 times the melting point of titanium-vanadium alloy, with further holding, producing a getter having the porosity from 22% to 65% by volume, according to the invention, said metal powder has bulk density in the range from about 0.7 to about 1.5 g/cm^3.

Bulk density of a metal powder determines pores quantity and size in formed blank It is generally known that with less values of bulk density the greater values of porosity of the final product are obtained, and vice versa.

Experiments have shown that when bulk density of the metal powder containing from 20 to 35 % by weight of vanadium, from 0.1 to 0.5 % by weight of calcium, the balance being titanium, is approaching the value of 0.7 g/cm^3 , then resulting getter has porosity about 65%, while when bulk density of the above powder is about 1.5 g/cm^3, then the resulting getter has porosity about 25%.

Preferably the metal powder fed into the deformation zone, should contain less than 70 % by weight of fraction having particle size of less than 50 μm. Then the metal powder will have bulk density about 1.5 g/cm^3. In case above metal powder contains less than 20 % by weight of a fraction having particle size of less than 50 μm, bulk density of said powder will be about 0.7 g/cm^3.

Preferably getter blank should be heated within the range from about 750 to about 950 Celsius degrees. Said temperature range is determined by the maximum permissible shrinkage level with which the mechanical strength of resulting getter as well as its porosity (25-65 %) are maintained. In case said blank is heated up to less than 750 Celsius degrees in the heating zone, then weaker bonds are formed among the particles, due to low diffusive mobility of metal atoms, which results in reduced mechanical strength of the getter. In case said blank is heated up to over 950 Celsius degrees, considerable shrinkage occurs which causes reduced porosity of the getter thus resulting in lower sorption rate.

When the porosity of a getter blank is less than 45%, a standard section of said blank may be coiled.

Known is the fact that a ribbon-type blank shows low mechanical strength, which strength reduces when porosity increases. Experiments have shown that when getter blank having porosity over 45% is coiled, said blank fails.

Other objects and advantages of the inventions will be clarified by the following examples of specific embodiments of the present invention.

VARIANTS OF SPECIFIC EMBODIMENTS OF THE INVENTION

A nonevaporable getter according to the invention containing from 20 to 35 % by weight of vanadium, from 0.1 to 0.5 % by weight of calcium, the balance being titanium, has porosity from about 25% to about 65% (by volume).

The getter according to the invention has hydrogen sorption rate over 2 $m^3/m^2 \cdot s$ at room temperature, when the quantity of sorbed hydrogen is 1.3 m^3Pa/kg, the getter being activated at from 300 to 350 Celsius degrees.

Said properties allow to use said getter in sorption pumps used in elementary particles sources and accelerators, e.g. in thermonuclear plants wherein high pumping rate is to be provided in restricted spaces.

To produce a getter having abovementioned properties a process is provided according to the invention, said process comprising the following operations:

Metal powder containing from 20 to 35 % by weight of vanadium, from 0.1 to 0.5 % by weight of calcium, the balance being titanium, and having bulk density within the range from about 0.7 to about 1.5 g/cm^3 is fed into a deformation zone. Said metal powder contains less than 70% (by weight) of fraction having particle size of less than 50 μm. Within said deformation zone a force is exerted, e.g. 1 t/cm^2 , exceeding compression strength of said metal powder, which causes plastic deformation of metal particles.

Further metal powder is rolled to form a ribbon blank having uniform density and higher porosity than the porosity of the final product. Ribbon length is much longer than its width, the ribbon having small thickness and strength sufficient to transport said ribbon into a heating zone. As a result of rolling a ribbon is produced having the width of, e.g. from 15 to 80 mm, and the thickness of, e.g. from 0.4 to 0.8 mm.

During rolling said metal powder undergoes continuous forming, the volume of the powder reducing because the density of particles placement in said powder increases, though the weight remains constant.

When a getter blank is leaving the deformation zone, it is cut into standard sections which sections, e.g. having the length 200, 70 mm, etc., are transported into a heating zone. In said heating zone the pressure below 1 Pa is created and maintained, under which the partial pressure of chemically active gases (excluding hydrogen) should be below 1.10^{-2} Pa in said heating zone, and said getter blank is heated to a temperature lower than 0.6 times the melting point of titanium-vanadium alloy, followed by holding. Said heating temperature is maintained in the range from about 750 to about 950 Celsius degrees. Said temperature range is determined by maximum permissible shrinkage level at which mechanical strength of resulting getter is maintained, namely, tensile strength reaches, e.g. from 1 to 6 kg/mm^2, and the desired porosity is from 25 to 65 %.

In one variant of specific embodiments of the invention a standard section of said getter blank is coiled, provided that getter porosity is below 45%. It is known that a ribbon-type blank shows low mechanical strength, which strength decreases when the porosity increases. Experiments have shown that when a blank having porosity over 45% is coiled, said blank fails.

Example 1.

Metal powder containing 28.45 % by weight of vanadium, 0.31 % by weight of calcium, 71.24 % by weight of titanium, having bulk density γ = 1.17 g/cm^3 is fed into deformation zone, said metal powder containing 57% (by weight) of fraction (q) having particle size of less than 50 μm. Within said deformation zone metal powder is formed by rolling using rollers having the diameter, e.g. ∅ 100 mm and rolling speed (V) 1.5 m/min. As a result a getter blank of uniform density is produced in the form of a ribbon having thickness (h) of 0.5 mm and width of 30 mm, the porosity of said blank being greater than the porosity of the final product. During rolling said metal powder is continuously formed. After leaving said deformation zone said ribbon-type getter blank is cut into standard sections having length 200 mm, and then said sections are transported into the heating zone. Within said heating zone the pressure of 0.025 Pa is created and maintained, and the blank is heated to the temperature (T) of 850 Celsius degrees, followed by holding during 1 hour. After cooling the blank is removed. Porosity (P) of the final product is 43%, and its tensile strength is 2.1 kg/mm^2.

Resulting getter has sorption rate (S) with respect to hydrogen of 4.0 $m^3/m^2.s$ at sorption temperature (t) 20 Celsius degrees when the quantity of sorbed hydrogen (Q) is 1.3 m^3Pa/kg after getter activation at the temperature (T_{aKT}) of 350 Celsius degrees during 15 min.

Example 2.

Metal powder containing 27.20 % by weight of vanadium, 0.21 % by weight of calcium, 72.61 % by weight of titanium, having bulk density γ 0.98 g/cm^3 is fed into a deformation zone, said metal powder containing 48% (by weight) of fraction (q) having particle size of less than 50 μm. Within said deformation zone metal powder is formed by rolling using rollers as described in Example 1. As a result a getter blank of uniform density is produced in the form of a ribbon having thickness (h) of 0.5 mm and width of 30 mm, the porosity of said blank being greater than the porosity of the final product. After leaving said deformation zone said ribbon-type getter blank is cut into standard sections. Said standard sections of getter blank having the porosity (P) below 45% are then coiled into coils with 80 mm inner diameter. The length of said standard section is 2.96 m. Coiled getter blank is transported into the heating zone wherein the pressure of 0.025 Pa is created and maintained, and the blank is heated to the temperature (T) of 850 Celsius degrees, followed by holding during 1 hour. After cooling the coiled blank is removed. Resulting getter is characterized by large sorptive surface which is larger than that of the getter as per Example 1. Porosity (P) of the coiled getter is 38.5%, its sorption rate (S) with respect to hydrogen being 3.3 m^3/m^2.s at sorption temperature (t) being 20 Celsius degrees, when the quantity (Q) of sorbed hydrogen is 1.3 m^{3}Pa/kg after getter activation at the temperature (T_{aKT}) of 350 Celsius degrees during 15 min.

The results of the experiments carried out using metal powder with different bulk densities and applying different sintering temperatures, are provided in the Table.

TABLE

No.	Element content (% by weight)			γ (g/cm^3)	q (%)	T (°C)	P (%)	h mm	S (m^3/m^{2}s at t=20°C Q=1.3m^{3}Pa/kg T_{aKT}=350°C 15 min.
	V	Ca	Ti						
1	28.45	0.31	Balance	1.17	57	850	43	0.5	4.0
2	27.20	0.21	- " -	0.98	48	850	38.5	0.5	3.3
3	27.20	0.21	- " -	1.46	68	780	32	0.65	2.9
4	27.20	0.21	- " -	0.8	26	900	52	0.71	5.2
5	32.2	0.18	- " -	0.77	18	860	54	0.68	7.3

wherein

- γ is bulk density of metal powder;
- q is the quantity of the fraction having particle sizes less than 50 μm;
- T is heating temperature;
- P is getter porosity;
- h is getter thickness;
- S is hydrogen sorption rate;
- t is sorption temperature;
- Q is the quantity of sorbed hydrogen;
- T_{aKT} is getter activation temperature.

INDUSTRIAL APPLICABILITY

Getter according to the invention having porosity of 30%, when used as the first stage formed by forty plates having dimensions 180×30×0.8 mm in a multistage magnetic discharge pump mounted in accelerator used in semiconductors production, has pumping rate with respect to hydrogen from 0.3 to 2 m^3/s.

Claims

1. A nonevaporable getter containing from 20 to 35 % by weight of vanadium, from 0.1 to 0.5 % by weight of calcium, the balance being titanium, characterized by that said getter has porosity from 25 to 65 % by volume.

2. A process for producing nonevaporable getter comprising the following operations:

feeding metal powder containing from 20 to 35 % by weight of vanadium, from 0.1 to 0.5 % by weight of calcium, the balance being titanium, into a deformation zone, wherein said metal powder being formed by rolling, as a result a getter blank being produced in the form a ribbon, said ribbon after leaving said deformation zone being cut into standard sections, said sections being further transported into a heating zone, in said heating zone the pressure below 1 Pa being created and maintained, and heating said getter blank to a temperature lower than 0.6 times the melting point of titanium-vanadium alloy, followed by holding, as a result a getter being produced having porosity from 25 to 65 % by volume, characterized by that said metal powder being fed into said deformation zone, has bulk density in the range from about 0.7 to about 1.5 g/cm^3.

3. A process according to Claim 2, characterized by that said metal powder being fed into said deformation zone contains less than 70% by weight of a fraction having particle size less than 50 μm.

4. A process according to any of Claims 2 and 3, characterized by that said getter blank is heated to a temperature within the range from about 750 Celsius degrees to about 950 Celsius degrees.

5. A process according to any of Claims 2-4, characterized by that when the porosity of said getter blank is below 45%, said standard section is coiled.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 95/00276

A. CLASSIFICATION OF SUBJECT MATTER

IPC[6] : C22C 14/00, B22F 3/11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC[6]: C22C 14/00, B22F 3/11, 3/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR, A1, 2370101 (INCO EUROPE LIMITED), 02 June 1978 (02.06.78); the claims ---	1-5
A	GB, A, 1548581 (MATSUSHITA ELECTRIC INDASTRIAL CO.LTD.), 18 July 1978 (18.07.78), the claims ---	1
A	GB, A, 2161182 (DAIMLER BENZ AKTIENGESELLSCHAFT), 08 January 1986 (08.01.86), the claims ---	1
A	DE, A1, 3031471 (DAIMLER-BENZ AG), 29 September 1983 (29.09.83), the claims --- -----	1

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* 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 document 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

Date of the actual completion of the international search	Date of mailing of the international search report
20 June 1996 (20.06.96)	25 June 1996 (25.06.96)
Name and mailing address of the ISA/ RU	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)