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(54) **New gas sorbents on the basis of intermetallic compounds and a method for producing the same**

Getter auf Grund von intermetallischen Verbindungen sowie Verfahren zu dessen Herstellung

Matériau de dégazage à base de composés intermétalliques et son procédé de production

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WO-A-20/04082873 GB-A- 1 340 015

- **CHUTONOV K A ET AL: "EVAPORATION OF VOLATILE COMPONENT FROM INTERMETALLIC GRANULE WITH NON-VOLATILE COMPONENT SHELL" VACUUM, PERGAMON PRESS, GB, vol. 55, 1999, pages 101-107, XP002328937 ISSN: 0042-207X**
- **PATENT ABSTRACTS OF JAPAN vol. 015, no. 413 (C-0877), 22 October 1991 (1991-10-22) & JP 03 170661 A (KOBELITE LTD), 24 July 1991 (1991-07-24)**

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Description

Background of the Invention

5 Field of the Invention

[0001] The present invention relates to the field of gas sorbents, more precisely of metallic gas sorbents used at room temperature for gas purification and for improvement of vacuum in sealed devices and pumped down chambers.

10 Description of related art

[0002] Modern metallic sorbents, also called getters, can be divided conventionally according to their chemical nature into two groups: getters, containing mainly alkaline-earth metals, and getters based on transition metals. The sorption capacity of the former is in average by three orders of magnitude higher than of the latter [J.J.B. Fransen, H.J.R. Perdijk. Vacuum, 10 (1960)199; B. Ferrario. Vacuum, 47 (1996) 363; P.della Porta. Vacuum, 47(1996)771], but it turned out that it is technically very difficult to achieve high rates of chemical pumping with the help of active metals like calcium, strontium or barium in spite of the fact that the sticking coefficient of these metals for most important gaseous species is by many times higher than that of the transition metals. The reason for this is the following.

[0003] It is known that the sorption rate with which gases are sorbed by solids under otherwise equal conditions is proportional to the specific surface area of the solid. Therefore the developments in the field of getter technologies always followed the path of creating planar materials with high specific surface area, and all commercially realized methods of production of effective getters fit in one and the same scheme: first a starting material is crushed to a high degree of dispersion and then the particles obtained are again bound into an integrated but porous structure with the help of cohesive forces stimulating diffusive "gluing" of the particles in the points of contact.

[0004] Powder compressing and sintering [N.P. Reutova et. al. US 6,322,720], screen printing [A. Corazza et. al. WO 98/03987], spraying [S. Carella et. al. WO 95/23425], electrophoresis [E. Giorgi. US 5,242,559], sputtering [V. Palmieri et. al. US 5,306,406; C. Benvenuti et. al. Vacuum, 60(2001) 57], etc. can be considered as examples for this kind of technologies.

[0005] All these methods showed themselves to be of advantage in the case of transitional metals but they are absolutely inapplicable for alkaline-earth metals due to the extremely high reactivity of these metals in the dispersed state. Among the previous attempts to overcome the problem of chemical reactivity of alkaline-earth metals and to make use of them as gas sorbents, three cost-effective versions were most significant.

[0006] Two of them refer to rather specific cases: to gettering of residual gases in Cathode Ray Tubes by barium films, and to maintaining of negative pressure in Vacuum Insulating Panels with the help of powders of barium-lithium alloys. In the third attempt a general solution of the problem of dispersion of active alloys under conditions of their high purity is claimed [K. Chuntanov. WO 2004/082873].

[0007] Ba-films deposited in a vacuum upon heating a powdered mixture of Al_4Ba and Ni [P. della Porta. US 5,118,988; D. Martelli et. al. US 6,306,314] are in many respects an ideal gas sorbent but they need the support of a large free surface area which contradicts the general trend to miniaturization of electronic devices.

[0008] The second product, called Combogetter™ containing powder pills of the composition BaLi_4 as gas sorbent was apparently developed directly for low-vacuum applications [Manini et. al. US 5,600,957]. Independent of the scale of usage of this product, from the technical view point it is not a breakthrough. Two more patents, US 5,312,606 and US 5,312,607 claiming the usage of barium alloys as getter materials for vacuum vessels are also connected with this topic. In the case of the latter two patents we deal with a purely legal act, which is not supported by technical innovations.

[0009] In fact, the procedure of crushing an ingot with a pestle and a mortar described in these two patents can not be considered a new technology, and the ability of barium-containing alloys to bind many gases including atmospheric air is well-known [see G. Rocktäschel et al. Z. anorg. allg. Chem., 316 (1962) 231; G. Bruzzzone. J. Less-Comm. Met., 25 (1971)361; 7 (1964)368; 11 (1966) 249; M. L. Fornasini et al. Rev. Chim. Miner., 16 (1979)458; W. Klemm u.a. Z. anorg. allg. Chem., 255 (1947) 2; R. Konetzki u.a. Z. Metallkd., 84 (1993) 569]. We also mention that barium itself and even more so its alloys with Pb, Ti, Cd, Hg etc. proposed in US 5,312,606 and US 5,312,607 are rather toxic.

[0010] A possibility to produce high purity powders or cast shot of chemically active materials appeared recently with the development of a new method of quenching melt droplets in liquid inert gas [WO 2004/082873]. The idea of the method looks almost perfect, especially if one takes into account that after the process is over, the quenching liquid, usually argon or a low-molecular alkane, evaporates at room temperature completely and without any residual, after which the product is sealed under vacuum in ampoules or directly in the body of the end device.

[0011] However, experience has shown that the given method has a number of drawbacks:

1. It turned out that alkanes, though weakly, react with the melt droplets. This interaction becomes noticeable at

concentrations of the active component from 45 - 50 at %.

2. Argon as quenching medium is more preferable than alkanes, but liquefaction of gaseous argon under low pressure in quantities sufficient for quenching several tens of grams of melted metal droplets appeared to be a problem difficult to solve.

The temperature interval for the existence of liquid argon under a pressure lower than 1 atm does not exceed three degrees, and taking into consideration the technical limitations of the method, it appeared to be even smaller, about 1.5 degrees. Under such conditions the maximum achievable thickness of a liquid interlayer between solid and gaseous argon comprises only a few millimeters. This allowed producing small quantities of high purity super active powders in a regime of injection of thin jets of melt but did not provide a possibility to obtain cast shot of diameter 2 - 3 mm. Droplets, generated in the drip-off regime due to the lack of liquid argon fused together into one big cake, which then solidified on the solid argon surface.

3. Also the product according to WO 2004/082873 has some drawbacks. Though the properties of the pure powders of alkaline-earth metals obtained by quenching in pure argon are unique, the products are of little use for vacuum applications, and for the time being no methods for their binding into a conglomerate of particles have been developed. At the same time cast shot of diameter 2 - 3 mm obtained by quenching in a liquid alkane have limitations in the concentration of an active component, and their specific surface area is not large.

[0012] So, in spite of extremely high sensitivity of alloys of alkaline-earth metals to air and moisture, up till now no gas sorbent on their basis has been created that would have a structure of today's non-evaporable getters, i.e. which represent by itself a porous body consisting of strongly connected particles the surface of which is easily available for reactions with gases.

Brief summary of the invention

[0013] Thus it is an object of the present invention to provide a new class of gas sorbents with high surface area and a method for producing the same which is free from one or more of the disadvantages of the prior art processes.

[0014] A new approach to the problem of dispersion of chemically active materials, which allows developing gas-permeable intermetallic granules with high concentration of alkaline-earth metal is suggested below.

Brief Description of the Drawings

[0015]

Fig. 1 shows a phase diagram of A - AMe.

Fig. 2 shows the structure of the granules produced according to the method according to the present invention.

Fig. 3 shows a diagram of the vapor pressure of component A above A - Me solid alloys depending on their composition.

Fig. 4 shows an apparatus for producing intermetallic porous granules according to the present invention.

Fig. 5 shows a cryogenic unit.

Fig. 6 shows the vapor pressure p_A above solid mixtures vs. time t (volatilization curves).

Fig. 7 shows sorption characteristics related to 100 mg of getter material according to the present invention.

Summary of the Invention

[0016] The present invention therefore relates to new gas sorbents on the basis of intermetallic compounds with high surface area of the formula A_nMe_m , where A is a chemically active volatile metal and Me is a non-toxic nonvolatile metal, and where $n \geq m$, in the form of an isolated dendrite carcass, separated from a rapidly solidified heterogeneous alloy with the help of sublimation of its volatile fraction, the intermetallic compounds of the alloy being obtainable by a method comprising the following steps:

- mixing and melting of initial metals and homogenization of the melt under negative pressure of inert gas,
- manufacturing of cast shot by quenching of melted droplets under positive pressure,
- obtaining of skeleton-type granules by evaporation of the excess of the component A from cast shot under vacuum.

[0017] Also, the present invention relates to a method for producing high-purity metallic gas sorbents on the basis of intermetallic compounds of the formula



which are in a thermodynamic equilibrium with the component A forming with it an eutectic and in which A is a chemically active volatile metal, Me is a non-toxic non-volatile metal, and $n \geq m$, starting from chemically active metals or alloys, said method comprising the following steps:

- mixing and melting of initial metals and homogenization of the melt under negative pressure of inert gas, preferably argon,
- manufacturing of cast shot by quenching of melted droplets under positive pressure,
- obtaining of skeleton-type granules by evaporation of the excess of the component A from cast shot under vacuum,
- packaging of the product by sealing it off in a container under vacuum or under negative pressure of an inert gas, preferably argon.

[0018] Also, the present invention relates to an apparatus for carrying out the method for producing high purity metallic gas sorbents, said apparatus comprising

- a charging compartment (I) comprising a glove box and a doser (4) for charging and mixing of initial metals or components,
- a melting compartment (II) comprising a crucible (6), wherein the initial metals or components, previously subjected to deep outgassing, are introduced, a flight tube (20),
- a quenching compartment (III), where the droplets solidify in liquid argon,
- a sublimation compartment (IV) comprising a gas collector (13).

[0019] The new product according to the present invention is an intermetallic dendrite carcass, separated from a rapidly solidified heterogeneous material by sublimation of its volatile fraction. Both the product and the method of its production differ in principle from the traditional variants of getter structures and technologies.

[0020] The described method is applicable to intermetallic compounds A_nMe_m , which are in a thermodynamic equilibrium with the component A forming with it eutectics (Fig. 1) and in which A is a chemically active volatile metal, Me is a non-toxic nonvolatile metal, and $n \geq m$. For a case where $A = Ca$ or Sr , these compounds can be specified as Ca_3Ag , Ca_2Cu , $Ca_{28}Ga_{11}$, Ca_3In , Ca_2Si , Ca_2Ge , Ca_2Sn , Sr_3Ag_2 , $SrCu$, Sr_8Al_7 , Sr_8Ga_7 , Sr_3In , Sr_2Si , Sr_2Ge , Sr_2Sn and $SrNi$ [see H.Okamoto. Phase Diagrams for Binary Alloys, ASM International, Materials Park, OH, 2000].

[0021] The essence of the invention is the following. If a molten droplet of concentration c_0 , containing a certain excess of component A over a stoichiometric composition c_s (Fig. 1), is subjected to quenching in a liquid cooling agent, then as a result of crystallization a typical structure will appear (Fig. 2), consisting of a dendritic carcass A_nMe_m and an eutectic c_e , which fills the space between the dendrite arms [see e.g. M. C. Flemings. Solidification processing, McGraw - Hill Book Corp., N.Y., 1974; R. Elliot. Eutectic Solidification Processing, Butterworths, London, 1983; E.J. Lavernia et al., Int. Material Rev. , Vol. 37, No 1, 1992, 1 - 44; B.H. Kear et al., Metal. Trans., Vol.10A, 1979, 191 - 197; S. Annavarapu et al., Int. J. Powd. Met., Vol. 29, No4, 1993, 331 - 343 etc.]. Regarding the alloys A - Me (above), the correlation

$$p_A^0 / p_A (A_nMe_m) \gg 1 ,$$

should hold, where $p_A (A_nMe_m)$ is the partial vapor pressure of the component A above the A_nMe_m phase and p_A^0 is the vapor pressure of pure metal A under the same conditions [see e.g. S. Srikanth et.al. Met. Trans., 22 B (1991) 607 - 616; B.P. Burylev et al., Russ. J. Phys. Chem., Vol.48, No 6, 1974, 809 - 811; F. Sommer u.a., Z. Metallkd., Bd. 74 , 1983 100 - 104; O. Kubaschewski u.a. Z. Elektrochem., Bd. 53 , No 1, 1949 32 - 40; D. Risold et al., Calphad, Vol. 20, No 2, 1996, 151 - 160, etc.].

[0022] Taking into account these two factors (the structural one and the thermodynamic one) let to the idea to generate of accessible voids in a form of micro slits and micro channels in quenched shot of c_0 with the help of the method of evaporation of the volatile component A from the eutectic structural constituent.

[0023] The parameters of the sublimation process are defined by the diagrams T- c (Fig. 1) and p - c (Fig. 3). The first one limits the volatilization temperature T_p to the subsolidus area $T_p < T_c$, to avoid the coursing effect on the dendrite carcass during the appearance of the liquid phase. The second one sets pressure conditions of the process (Fig. 3)

$$p_A^0 > P > p_A(A_nMe_m),$$

where P is the pressure in the volatilization chamber, set by an operator. These conditions provide a sufficient rate of sublimation of A but prevent the decomposition of the A_nMe_m phase. The end product has the form of a ball with a skeleton intermetallic structure (Fig. 2). High chemical activity and high gas permeability of this kind of material make it a very valuable and potent gas sorbent, equally capable of being applied in vacuum devices and gas purifiers.

[0024] Distinctive features and advantages of the new gas sorbent are:

1. High and long-term activity at room temperature towards all gases except noble ones.

2. Fractal structure of the intermetallic carcass formed during droplet crystallization under conditions of rapid heat dissipation during quenching. This kind of structure, imparting high gas permeability to the granules, possesses high specific surface area and due to its intermetallic nature also has higher mechanical stiffness, which by many times exceeds the strength of the elemental components A and Me.

3. Versatility and flexibility of the product:

- binary intermetallic compounds A_nMe_m give a wide choice of material objects of different degree of activity;
- among A_nMe_m phases there are some, in which the second component is also known for high affinity to active gases (e.g. Al, Ni);
- the specific surface area of the granules and their porosity can also be controlled in a wide range by changing the initial concentration c_0 (the porosity is greater the more c_0 differs from c_s and the closer it is to c_e), and the diameter of the droplets (with decreasing diameter the cooling rate increases, which leads to smaller dendrite arm spacing and accordingly to an increase of the specific surface area of the product);
- incomplete volatilization of phase A is also an additional means to increase the fraction of the active component in the granules.

4. Good ventilation properties of the product. A load of porous granules creates a special material medium, which allows two kinds of gas flows: convective flows along the voids between the granules and molecular diffusion along the pores between dendritic arms.

This widens the fields of applications for the product.

5. Damping properties of pores. The external dimension of porous granules does not practically increase during sorption and no breaking stresses are formed in them, unlike in the cast shot of the same composition.

6. Nontoxicity of the granule substance.

[0025] To produce the above described product it is necessary to have equipment allowing performing in a wide temperature range all the necessary operations with the chemically active material without its contamination or unacceptable changes of the composition. An apparatus of this kind is shown in Fig. 4.

[0026] The initial metals, previously subjected to deep outgassing, are introduced into a crucible 6 under argon, active ones from a glove-box, inactive ones from a doser 4. The load is melted, homogenized, and then the resulting melt is pressed through a capillary appendix into a flight tube 20 (Fig. 5), where the droplets solidify in liquid argon, which condensates and is collected in the needed quantities on an argon "stopper" at positive gas pressure. This stopper, formed in the narrowed part of the tube, cooled with liquid nitrogen, closes the cross-section of the flight tube for the duration of the melt drip-off.

[0027] When the dropping process is over the argon stopper is unfrozen and cast shot fall down into a glass collector 13 (Fig. 4), which also serves as a sublimation chamber. From below a furnace 12 is moved onto the collector and vacuum vaporization of the volatile phase of the eutectic is carried out.

[0028] Vapors of component A condensate on the cold curved part of the collector and do not get through into the flight tube. The process is terminated at the moment when vacuum gage 2 (Fig. 4) in a sublimation compartment IV shows an abrupt pressure drop, which indicates the disappearance the last crystals of the A phase (Fig. 6). The furnace is moved down and the lower end of the collector containing the product is sealed off under vacuum to form an ampoule.

[0029] The given method allows producing in one charge of the apparatus several tens of grams of porous granules

A_nMe_m of diameter from ~0.5mm to ~5mm, preferably with the diameter 2-3 mm. This is a result, which was unachievable before and which became possible due to the following technical solutions:

1. Quenching of melt droplets in argon not under negative pressure, like in the method of Pat. WO 2004/082873, but under positive pressure. Increase of pressure up to 5 bar, and preferably to 3 bar, widened the range of the liquid state of argon by more than 10 times and eliminated the problems connected with its condensation in required quantities thus allowing increasing the capacity of the method to ~ 100g of the product during one technological cycle.

2. Additional thermal treatment of the cast shot for adding them a new quality: gas permeability and increase of the specific surface area by many times. This treatment consists of the removal of a volatile constituent of the material by sublimation provided that

$$T_p < T_c, \quad p_A^0 > P > p_A(A_nMe_m),$$

which leads to appearance of a skeleton-type structure.

3. Continuous vapor pressure monitoring in a sublimation chamber as an element of a new technology. A fast drop of vapor pressure above the solid granules under isothermal conditions indicates that the material crossed the phase boundary and signals the necessity to stop the sublimation process (Fig. 6). Essentially, a method of phase analysis of granules in situ is introduced here, and this is the best solution considering the high chemical activity of the treated material. Method justification is given below.

4. A new design of the technological equipment. An apparatus is designed in such a way (Fig. 4), that allows maintaining the processes taking place under the pressure of 5 bar and also periodical evacuation of the inside atmosphere to a level not worse than 10^{-7} mbar. The purity of the product and its isolation from the outside environment are the priorities of the method.

[0030] Other distinctions from the designs known in this field are: uniting a process column with a glove box; a refrigerator with a bypass based on the idea of a solid argon stopper; a sublimation chamber with a zigzag trap for a volatile phase and with a residual gas analyzer.

[0031] The new method radically differs from the traditional methods of production of non-evaporable getters. While the previous methods came down to dispersion of the material and its reassembly into a porous conglomerate of particles, the new method consists of a sequence of actions of the opposite character: first formation of the droplets and their crystallization (analogue of assembly) take place and then removal of one of the structural parts of the material by sublimation (analogue of dispersion) is carried out. At this stage of polyphase crystallization of droplets the morphological contours of the future product are founded.

[0032] In conclusion it should be added that the method developed for producing selected dendritic structures by evaporation of the volatile phase, regularly distributed in the volume of the material, can be applied not only to Ca and Sr alloys and generally not only to binary alloys.

[0033] Equally, this method will also work in case of many other metallic materials containing at least one volatile and at least one non-volatile component. In particular, it is easy to obtain porous metallic materials, in which Li, Na, Mg, Ba, serve as a component A and transitional metals like Fe, Zr, Ni, Ti, Ta, play the role of component Me.

[0034] What concerns applications of skeleton-type metallic materials, it can be expected that they will be used not only as gas sorbents but also as catalysts.

Detailed Description of the Invention

[0035] The given method allows the preparation of an alloy c_0 from corresponding quantities of elements A and Me directly in the melting compartment II of the process column (Fig. 4). Such a solution guarantees a higher purity of the product than it was allowed by the previous technique of the separate synthesis of a semi-ready product in special equipment with the subsequent transfer of the superactive product to the station for granulation (see WO 2004/082873).

[0036] According to the new method high purity dendritic pieces of previously distilled Ca or Sr (e.g., 99.98% metals basis, Alfa Aesar) are taken out from a glass ampoule and thrown down from a glove box into crucible 6 (Fig. 4). Further on metal A is melted in an atmosphere of especially pure argon under a pressure around 10 mbar with the help of

inductive heating (see coil 8 on Fig. 4), maintaining below the crucible excess pressure, which prevents leaking of liquid metal through a capillary into the flight tube. Then pieces of metal Me, thoroughly outgassed before in a process of vacuum remelting under $\sim 10^{-6}$ mbar, are thrown down into melt A from the doser 4.

[0037] To prevent splattering of the metal, foaming of the reacting mass and its moving upwards, continuous observation over the state of the surface of the melt is performed through the window 1. The optimal regime of the process is maintained by varying the gas pressure in the interval from $\sim 10^{-3}$ mbar to ~ 1 mbar, balancing between a state of dead liquid and a slightly boiling state. This allows to keep the melt within the minimum volume and at the same time to achieve its further outgassing.

[0038] After the mixing stage is completed the gate valve 5 is closed, the melt is evacuated for a short time and then the argon pressure in compartments II and III is increased for condensation of liquid argon in a quenching bath (Fig. 5).

[0039] The quenching bath represents by itself a central part of a flight tube with a small narrowed part with a metallic cartridge 1 welded to it, which serves as a reservoir for liquid nitrogen. From outside this cartridge is surrounded with a thermal insulator 90 with a lid 30 (see also 9 on Fig. 4).

[0040] During filling the cartridge with liquid nitrogen up to the level of the lower end of the adiabatic wall 60 (Fig. 5) the narrow part of a thin-walled flight tube quickly freezes to such an extent, that a tight stopper of solid argon with widened ends is formed. This stopper can withstand the weight of a substantial column of liquid argon together with crystallized metallic product. To avoid an impact of parasitic axial forces on the argon stopper which is especially undesirable during unfreezing of the stopper, a bypass line 16 (Fig. 4), which automatically levels the gas pressure above and below the quenching bath, is connected to the flight tube in the refrigerator area.

[0041] For obtaining a liquid argon column of a sufficient height a two-zone model is used with a "cold" zone in the form of a vessel with liquid nitrogen and a "hot" zone in the form of a part of the flight tube with a filament heater 40 (Fig. 5). The height of the liquid argon column $\Delta H = H_{1g} - H_{s1}$ (Fig. 5, b) is controlled by two parameters: the heat power produced by cryoheater 40 and the gas pressure in the flight tube. The first one defines the value of T_n , the second one the range of liquid argon ΔT_L (Ar).

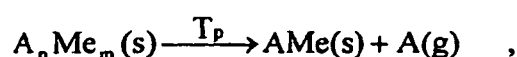
[0042] Formation and adjustment of temperature ranges in the quenching bath is carried out with the help of four thermocouples, two of which are welded at different height to the narrow part of the tube while the other two are welded, also at different height, between the loops of the cryoheater 40 (the thermocouples are not shown in Fig. 5.).

[0043] After stabilization of all the temperature fields inside the refrigerator, the next step is pressing the melt through a capillary into liquid argon. For stimulation of the jet disintegration the surface of the melt is forced with pressure pulses sent along the gas line through a solenoid valve 17 (Fig. 4). For the same purpose low-frequency acoustic vibrations, directed from an outside generator to the area of the capillary, can be used. Characteristic values of this process stage are: the depth of the liquid argon layer is ~ 10 cm, the gas pressure in the column is 1.5 - 2.0 bar, the mass of the quenched particles is 35 - 60 g, the duration of the stage is 10 - 15 minutes, the main fraction of shot with diameter 2 - 3 mm is about 70% of the total product.

[0044] After the quenching stage is completed, maximum pressure, e.g. 3 bar, is set on the safety valve 15, the bypass line 16 is connected with the previously evacuated tank, and unfreezing of the refrigerator 9 (Fig. 4) is started. The argon, collected in the tank, is used again in the next production cycle.

[0045] When the argon stopper melts, particles fall down into collector 13 and compartment IV is isolated from the upper part of the station with the help of the gate valve 10. The collector with cast shot is pumped down to $\sim 10^{-7}$ mbar and heated up to $\sim 250^\circ$ C. Furnace 12 is lifted from below and the pressure is again brought to $\sim 10^{-7}$ mbar. Finally, while the vacuum line is working, a flow regime with argon pressure P is set in the system with the help of the valve rv (Fig. 4) and the temperature of the furnace is raised to T_p . The volatile constituent of eutectic c_e , which fills the space between the dendritic arms of cast shot starts to evaporate and A deposits as a condensate on the cold zigzag part 11 of the particle collector.

[0046] The moment when the last crystals A are evaporated and the entire material becomes single phase of the composition A_nMe_m is critical, because continuation of the process under the same conditions starts the thermal decomposition of the intermetallic carcass A_nMe_m



which leads to deterioration of the product properties (signs s and g mean solid and gaseous states, respectively). That is why the given invention parallel to volatilization of phase A provides for a continuous phase analysis of the material. Diagnostic of phase composition is carried out on the basis of vapor pressure data coming from a vacuum gage and residual gas analyzer (RGA), installed in a vacuum line of compartment IV (Fig. 4). This new method of phase analysis

naturally fits in the process technology and it was only necessary to develop its methodological basis (see Detailed description of the drawings, Fig.1, 3 and 6).

[0047] According to the new method, as long as the vapor pressure above the treated material, recorded in coordinates $p - \tau$ (Fig. 6), can be considered constant, parameters of the sublimation process are maintained unchanged. But as soon as the pressure in the system decreases sufficiently, there is a necessity to refer to indications of a residual gas analyzer in order to define the nature of the registered pressure decay and to distinguish between the effects, which accompany outgassing¹, and the phenomena related to the discussed fundamentals.

¹ All commercially available metals, even the purest of them, contain a large amount of dissolved non-metal impurities, especially gaseous ones. Heating the metal in a vacuum causes a temporary pressure increase followed by a decrease at the end of outgassing. This effect should be recognized and rejected as a false one.

[0048] The experimental dependence $p = p(\tau)$, separated from outgassing effects, has the form of curve 2 in Fig. 6. The time τ_s needed for a material object to reach the homogeneous state can with an adequate for the given case accuracy be found by projection of a point of intersection between an experimental curve 2 and a calculated isobar

$p^* = P + (p_A^0 - P) / 2$ onto axis τ . At $\tau = \tau_s$ when the entire A - constituent of the eutectic is removed from the granules, the sublimation process is stopped by switching the furnace off and moving it down.

[0049] The final product is sealed off under vacuum or inert gas and used further according to the destination. The collector tube must not necessarily be made of glass; it also can be made of metallic materials which can be sealed off under vacuum. The upper part of the collector with a zigzag part and a flange is cleaned from condensate, washed, dried and rebuilt by attaching a new test tube from below.

Detailed description of the drawings

[0050]

Fig. 1. Phase diagram A - AMe:

T_e - eutectic temperature, T_p - sublimation temperature, C_e - eutectic concentration, c_0 - concentration of the initial melt, c_s - concentration of A_nMe_m crystals, c_1 - concentration of AMe crystals, dashed line (---) is a phase trajectory of the material in the process of sublimation.

Here and further under AMe we understand a phase, which is in a thermodynamic equilibrium with A_nMe_m , and which can represent either a compound A_kMe_d , where $n/m > k/d$, or it can be simply a component Me.

Phase composition of A - Me alloys at subsolidus temperatures: in the range (0, c_s) a mechanical mixture of crystals A and A_nMe_m ; at $c = c_s$ a single phase alloy consisting of A_nMe_m crystals; in the range (c_s , c_1) a mechanical mixture of crystals A_nMe_m and AMe; at $c = c_1$ a single phase alloy consisting of AMe crystals; at $c > c_1$ a binary phase area appears again, etc.

The process of vacuum sublimation of a volatile phase A can be described by a motion of a representative point with initial coordinates (c_0 , T_p) along isotherm $T = T_p$ in the direction of increasing Me - concentration (dashed line with an arrow).

Fig. 2. The structure of the granules:

(a) - cast shot after quenching, (b) - skeleton granules after sublimation, I - a small granule with a diameter of $10^{-2} - 10^{-1}$ mm, II - a big granule with a diameter of ~ 1 mm and more, 1 - dendrites of A_nMe_m , 2 - eutectic C_e , 3 - shrinkage void; (e) - skeleton granules, obtained from the shot of concentration $c_0 = c_1$, $c_0 = c_2$ and $c_0 = c_3$, with $c_e < c_1 < c_2 < c_3 < c_s$.

Cast shot c_0 consist of dendrites of primary phase A_nMe_m and eutectic C_e , which is a mixture of phases A and A_nMe_m (a). After sublimation of the volatile phase A granules consist of a dendrite carcass A_nMe_m and remains of eutectic in a form of particles A_nMe_m (not shown in Fig. 2) intercalated between dendritic arms (b).

The dendrite arm spacing is the smaller the larger the droplet cooling rate is, and the cooling rate is the higher the smaller the droplet size is. That is why big granules (II) have rougher structure and smaller specific surface area than small granules. (I). That is, the granule size is a factor defining sorption properties of the product. Another factor of this kind is the initial composition of the alloy c_0 (e): the volume fraction of the pores, i.e. porosity, is the bigger the closer concentration c_0 is to c_e .

Fig. 3. A diagram of the vapor pressure of component A above A - Me solid alloys depending on their composition. The graph shows the property of intensive quantities, to which vapor pressure refers, to retain their value constant in mechanical mixtures of phases independent of the quantitative ratio of those phases.

Fig. 4. An apparatus for producing intermetallic porous granules:

I - a charging compartment; II - a melting compartment, III - a quenching compartment,
IV - a sublimation compartment;

1 - a window, 2 - a vacuum gage, 3 - a valve, 4 - a doser, 5 - an upper gate valve, 6 - a crucible, 7 - a quartz tube, 8 - an inductor, 9 - a refrigerator, 10 - a lower gate valve, 11 - a trap for vapor A, 12 - a furnace, 13 - a collector of granules, 14 - pressure gauge, 15 - a safety valve, 16 - a bypass, 17 - a solenoid valve;
rv - membrane valve, RGA - a residual gas analyzer.

See the detailed comments to this figure in Detailed Description of the Invention.

Fig. 5. A cryogenic unit:

(a) design, 10 - a metallic cartridge, 20 - a flight tube, 30 - a lid of a refrigerator (a thermal insulator), 40 - a heater, 50 - nitrogen vapor, 60 - a part of a tube with a double evacuated wall, 70 - liquid argon, 80 - liquid nitrogen, 90 - a cylindrical body of a refrigerator (a thermal insulator), 100 - solid argon, 110 - liquid argon film, 120 - argon vapor;

(b) vertical temperature distribution in a quenching bath (an idealized scheme), H_{h1} and H_{h2} - coordinates of a "hot zone", H_{1g} - an upper level of liquid argon, H_{s1} - a lower level of liquid argon, H_{N1} and H_{N2} - coordinates of a "cold zone", T_L (N) - temperature of boiling nitrogen, T_{s1} - temperature on the border of solid and liquid argon, T_{1g} - temperature on the border of liquid and gaseous argon, ΔT_L (Ar) - a temperature interval of the liquid state of argon, T_{room} - room temperature.

See the detailed comments to this figure in Detailed Description of the Invention.

Fig. 6. Vapor pressure p_A above solid mixtures vs. time τ (volatilization curves):

τ_s - time for achieving a homogeneous state of A_nMe_m , τ_1 - time for achieving a homogeneous state of AMe, 1 - theory, 2 - experiment.

A stepped configuration of the dependence $p = p(\tau)$ with jumps at $\tau = \tau_s$ and $\tau = \tau_1$ is a consequence of a known law of vapor pressure change with concentration in solid mixtures (see Fig. 3). Pressure jumps at τ_s and τ_1 correspond to the moment of crossing the phase boundaries $c = c_s$ and $c = c_1$ (Fig. 1) by the representative point.

Fig. 7. Sorption characteristics related to 100mg of getter material:

1 - Ba-films [P.della Porta, E.Argano, Vacuum, 10 (1960) 223²; J.J. Maley, J.J.Mascony. J. Vac. Sci. Technol., 6 (1969) 51³];

2 - skeleton like granules of A_nMe_m [see Example and Discussion];

3 - SORB-AC® Cartridge Pumps on the basis of St 707¹ [SAES Getters Group];

4 - pieces of binary Ba-alloys [US 5,412,607²].

² Conversion of data, obtained from the measurements on sorption of hydrogen or nitrogen with coefficients of 0.65 and 4.3, respectively.

³ Direct measurements of sorption of oxygen.

See the detailed comments to this figure in Example and Discussion.

Advantages of the present invention

[0051] Ia. A new product in the form of an isolated dendrite carcass separated from a rapidly solidified heterogeneous alloy with the help of sublimation of the excess of the volatile fraction has been developed. This kind of material with its high surface area and high gas permeability - depending on the composition - can be used as gas sorbents or as catalysts.

[0052] Ib. The new materials form a wide class of substances of different elemental composition, which also differ in dimensional and structural parameters.

[0053] Ic. Novelty and advantages of intermetallic materials based on calcium and strontium:

- specific crystal structure of a loopless tree type with high specific surface area;
- extraordinary reactivity providing high sorption qualities of the material;
- significant mechanical strength;
- controllability of structural characteristics and easy adjustability to different requirements;
- universality with respect to different applications, i.e. equal applicability both to the problems of gas purification and to the problems of vacuum technology.

[0054] IIa. A technology of manufacturing a new product has been developed. It comprises the following four stages:

- mixing and melting of initial metals and homogenization of the melt under negative pressure of argon;
- manufacturing of cast shot by quenching of melted droplets in inert gas, especially in liquid inert gas, under positive pressure;
- obtaining of skeleton-type granules by evaporation of an excess of the volatile component under vacuum;
- packaging of the product by sealing off in glass or metal ampoules under vacuum or under negative argon pressure.

[0055] IIb. New constructional and operational solutions:

- combining of a glove box with charging and melting compartments of a process column (provides cleaner conditions for the process);
- observation of the melt surface through a window during mixing of the components (allows by changing the argon pressure in the melting compartment to avoid blistering and spitting of the reacting mass and its solidification in the upper cold part of the crucible);
- condensation of liquid argon at positive pressure, namely, in the range from 1 to 5 bar, in order to obtain a sufficient quantity of quenching liquid (allows increasing the capacity of the method and quenching of droplets of large diameter, up to 5mm);
- cryorefrigerator based on a two-zone model and the new inventive concept of a solid argon stopper (allows collecting a large amount of liquid argon upon filling with liquid nitrogen and upon unfreezing - to set the cast shot free);
- evaporation of the volatile phase from the cast shot in order to obtain porous granules;
- a sublimation compartment of a reaction and processing column with a particle collector, a furnace, a zigzag trap for A vapor, and tools for analyzing the gas-vapor phase (a vacuum gage and a residual gas analyzer);
- phase analysis of the treated material during the sublimation process according to the results of vapor pressure measurement.

[0056] The invention will now be described by way of examples without limiting the same to them.

Examples (according to the present invention)

[0057] For the preparation of **porous granules of Ca_3In** an *indium* ingot (Puratronic, 99.9999% , Alfa Aesar) is outgassed in an Al_2O_3 boat raising the temperature to 600°C in such a way, that the pressure in the vacuum furnace does not increase higher than 10^{-6} mbar. Then the doser 4 (Fig. 4) is charged, in an argon flow with the gate valve 5 closed, with pieces of the outgassed *indium* (19g), after which compartment I is pumped down and filled again with argon to the pressure of 1 bar.

[0058] The procedure of mixing the components. In the glove box under Ar an ampoule with 25 g of *calcium* metal (crystalline dendritic pieces, 99.98%, Alfa Aesar) is broken, a blank of a feed pipe connecting the glove box with the

process column is opened, pieces of the *calcium* metal are thrown down into a Mo-crucible while the gate valve 5 is open and the connecting feed pipe is closed from inside of the glove box with the blank, and the column is pumped down to $\sim 10^{-7}$ mbar. The *calcium* metal is heated in a vacuum to $\sim 250^{\circ}\text{C}$. extremely pure argon is introduced into the column under the pressure of 10 mbar, the *calcium* is melted and then *indium* pieces one by one are thrown down into this melt from the doser according to the scheme described in Detailed Description of the Invention.

[0059] Quenching of droplets. After the refrigerator is filled with liquid nitrogen, while the gate valves 5 and 10 are closed, the gas pressure in the compartments II and III is increased to 2 bar, in order to start condensation and collecting liquid argon in the quenching bath. After a liquid column of argon $\sim 8\text{cm}$ high is formed, pressing the melt at the temperature of $\sim 800^{\circ}\text{C}$ through a capillary with a diameter of an opening of 0.8 mm under a minimum pressure from above is started, so that the melt jet has a low rate and its disintegration takes place directly at the exit of the capillary.

[0060] During quenching of the melt droplets the compartment IV (Fig. 4) is pumped down and filled with argon to a pressure of 1 bar. When the melt is poured completely, a line which connects the compartment III with the tank is opened for transporting argon into the tank. When the pressure in the column approaches 1 bar, the gate valve 10 is opened, the lid 3 (Fig. 5) is lifted and a flow of warm air is directed from above into the liquid nitrogen for speeding up the unfreezing process.

[0061] The remains of a solid argon stopper fall down into the particle collector 13 (Fig. 4) together with the shot and after the final volatilization of solid argon, first the valve in the line tank - bypass 16 is closed, and then the gate valve 10 is closed, too.

[0062] Sublimation treatment. Following the procedure described in Detailed Description of the Invention, a flow regime is set in the compartment IV under an argon pressure $P = 10^{-6}$ mbar and the temperature of the furnace is slowly raised, not exceeding 450°C , till a film of condensed Ca appears on the zigzag part 11.

[0063] After the gases are removed the process stabilizes and is stopped only at the moment when the pressure in the system rapidly decreases. The product is sealed-off in an ampoule. It consists of porous granules of Ca_3In with a wide particle-size distribution; the main fraction is $\sim 1.8\text{ mm}$ in diameter.

[0064] Porous granules of SnSr_2 are obtained in a similar way. For this purpose, the apparatus is charged with 25 g of pure *strontium* (distilled dendritic pieces, 99.95%, Alfa Aesar) and 10 g of *tin* previously outgassed at 750°C under a vacuum of 10^{-6} mbar (Puratronic, 99.999%, Alfa Aesar). The procedure resembles the one described above for Ca_3In with the following differences: At the stage of mixing the components the argon pressure is varied in the range of 1 - 100 mbar. A Ta-crucible is used for melting, the melt is pressed at the temperature of 1200°C through a capillary with an opening of 0.6 mm in diameter. Sublimation of strontium is carried out at $350 - 400^{\circ}\text{C}$. The porous granules obtained have an average diameter of $\sim 1.4\text{ mm}$.

[0065] For evaluation of sorption properties of the new product a glass tube appendix protruding outside from a high-vacuum chamber was charged with a mixture of porous granules of Ca_3In and SnSr_2 , seven parts of the former and eleven parts of the later one, with the mass ratio being 1:1. Granules of Ca_3In , with a diameter of $\sim 1.8\text{mm}$ had estimated porosity of $\sim 20\%$; granules of SnSr_2 with a diameter of $\sim 1.4\text{mm}$ had estimated porosity of $\sim 30\%$.

[0066] The granules were sealed off under vacuum, weighed together with an ampoule, and introduced into a test chamber containing a mechanism for breaking ampoules. The measurements were carried out by a dynamic flow method using two chambers according to the procedure described in Pat. US 5,312,607. After the ampoule was baked for two hours at 200°C it was opened at room temperature when the pressure in the chamber reached the basic value of 10^{-8}mbar . Oxygen was used as the gas to be sorbed. When the measurements, which were carried out at room temperature, were completed, the glass was collected, rinsed, dried and weighed, to define the mass of the sample from the difference in weight.

[0067] Experimental results are shown in Fig. 7 (curve 2). From them it follows that the new product is an excellent gas sorbent with very high sorption rate and with a sorption capacity close to the theoretical limit. Also in Fig. 7 data concerning other getter materials are presented. These data are averaged with the accuracy of an order of magnitude for the material of each type and reduced to an equal getter mass of 100mg.

[0068] The analysis presented below can not claim completeness and strictness due to the lack of information about the details of the measurements. But differences in the properties of the compared materials are so great that they give grounds for several conclusions.

1. Ba-films (curve 1) till now remain leaders in sorption parameters among all getter materials. Their disadvantages are that they need large free surface, and their toxicity.

2. Granules of A_nMe_m with a skeleton structure (curve 2) are inferior to barium films regarding gettering rates by $\sim 10^3$ times. This correlation coincides with the exposed surfaces of Ba-films which are larger than the exposed surface of the balls of $\sim 1.6\text{mm}$ in diameter taken in an amount equivalent to the mass of the Ba-films.

If the diameter of granules is decreased by one order of multitude, then the sorption rate increases approximately by 50 times due to the increase of the exposed surface of the material and the increase of dispersion of its structure.

3. Getters on the basis of transition metals (curve 3) are characterized by an appreciably lower sorption rate than Ba-films and even lower than A_nMe_m . Partially this can be explained by the lower value of the sticking coefficient of transition metals, and also by the rapid passivation of the surface of the particles of the NEG materials. As a tight film of the products of the reaction with gases is formed on the surface of a transition metal, the sorption process at room temperature is stopped. But the main disadvantage of the modern NEG's getters is the periodical need for heating and very low sorption capacity per getter mass unit, constituting less than one percent of the corresponding specific capacity of Ba-films and of A_nMe_m granules.

4. The sorption properties of high concentration barium alloys (in the form of pieces from ~1 mm to ~5mm in size) shown by curve 4, are obviously unsatisfactory. Regarding size of particles, chemical composition and structure this material is very similar to cast shot c_0 (Fig. 1) before the sublimation treatment. However, sublimation treatment of cast shot c_0 drastically improves the sorption characteristics of the product: the curve 2 (Fig. 7) is by four orders of magnitude higher along the gettering rate axis than the curve 4. Such a large difference in gettering rate is connected, first of all, with the different specific surface area of compact pieces of barium alloy and of porous granules of A_nMe_m . A calculation of the dendrite arm spacing according to [J.F. Seconde, M. Suery. J. Mater. Sci., 19 (1984) 3995] gives for granules of A_nMe_m a specific surface area of about $2.5\text{m}^2/\text{g}$, which is by three orders of magnitude higher than for cast shot of the same size. This clearly shows the advantages of disperse materials not only in the case of transitional metals, but also in the case of chemically highly active substances, which, as it is known, are not inclined to passivation of the surface.

[0069] Thus, Fig. 7 gives a visual picture of the general relation between sorption parameters of getters of different type and serves as a helpful guide for a user in finding the right material for his needs. The new product takes a high position among getter materials and has a potential for development. The most advantageous application fields for the new material are sealed vacuum chambers and gas purification filters.

Claims

1. Gas sorbents on the basis of intermetallic compounds with high surface area of the formula A_nMe_m , which are in a thermodynamic equilibrium with the compound A forming with it an eutectic, where component A is a chemically active and volatile metal selected from the group consisting of alkaline metals, earth alkaline metals, and Me is selected from the group of metals consisting of Ag, Al, Cu, Ga, Ge, In, Ni, Si, Sn, and where $n \geq m$, in the form of an isolated dendrite carcass, separated from a rapidly solidified heterogeneous alloy with the help of sublimation of its volatile fraction, the intermetallic compounds of the alloy being obtainable by a method comprising the following steps:
 - mixing and melting of initial metals and homogenization of the melt under negative pressure of inert gas,
 - manufacturing of cast shot by quenching of melted droplets under positive pressure,
 - obtaining of skeleton-type granules by evaporation of the excess of the component A from cast shot under vacuum.
2. Gas sorbents according to claim 1, wherein the melted droplets containing a certain excess of component A over a stoichiometric composition are subjected to quenching in liquid argon, then as a result of crystallization of a structure occurs consisting of a dendritic carcass A_nMe_m and an eutectic, which fills the space between the dendrite arms.
3. Gas sorbents according to claims 1 or 2, wherein component A in formula A_nMe_m is from the group consisting of Ca, Sr, Li, Mg, Ba.
4. Gas sorbents according to claim 3, wherein component A in formula A_nMe_m is calcium or strontium.
5. Gas sorbents according to claims 1 to 4, wherein the intermetallic compounds are selected from the group consisting of Ca_{23}Ag , Ca_{22}Cu , $\text{Ca}_{28}\text{Ga}_{11}$, Ca_3In , Ca_2Si , Ca_2Ge , Ca_2Sn , Sr_3Ag_2 , SrCu , Sr_8Al_7 , Sr_8Ga_7 , Sr_3In , Sr_2Si , Sr_2Ge , Sr_2Sn and SrNi .
6. A method for producing high-purity metallic gas sorbents on the basis of intermetallic compounds of the formula



which are in a thermodynamic equilibrium with the component A forming with it an eutectic and in which A is selected from the group consisting of alkaline metals, earth alkaline metals, Me is selected from the group of metals consisting of Ag, Al, Cu, Ga, Ge, In, Ni, Si, Sn, and $n \geq m$, starting from chemically active metals or alloys, said method comprising the following steps:

- mixing and melting of initial metals and homogenization of the melt under negative pressure of inert gas,
- manufacturing of cast shot by quenching of melted droplets under positive pressure,
- obtaining of skeleton-type granules by evaporation of the excess of the component A from cast shot under vacuum,
- packaging of the product by sealing it off in a container under vacuum or under negative pressure of an inert gas.

7. The method according to claim 6, wherein the inert gas is argon.

8. The method according to claims 6 or 7, wherein the melted droplets containing a certain excess of component A over a stoichiometric composition are subjected to quenching in liquid argon, then as a result of crystallization of a structure occurs consisting of a dendritic carcass A_nMe_m and an eutectic, which fills the space between the dendrite arms.

9. The method according to anyone of the preceding claims 6 to 8, wherein component A in formula A_nMe_m is from the group consisting of Ca, Sr, Li, Na, Mg, Ba.

10. The method according to claims 6 to 9, wherein the intermetallic compounds are selected from the group containing Ca and Sr as component A in formula A_nMe_m consisting of Ca_3Ag , Ca_2Cu , $Ca_{28}Ga_{11}$, Ca_3In , Ca_2Si , Ca_2Ge , Ca_2Sn , Sr_3Ag_2 , $SrCu$, Sr_9Al_7 , Sr_8Ga_7 , Sr_3In , Sr_2Si , Sr_2Ge , Sr_2Sn , $SrNi$.

11. The method according to anyone of the preceding claims 6 to 10, wherein the metal A is melted in an atmosphere of pure argon under pressure of about 1 to 100 mbar with the help of inductive heating while maintaining below the crucible a slightly excessive pressure.

12. The method according to any of the preceding claims 6 to 11, wherein the parameters of the sublimation process are defined from the phase diagrams and thermodynamic data on A - Me alloys, wherein the volatilization temperature is limited by the subsolidus area and by the pressures at which decomposition of A_nMe_m crystals does not take place.

13. The method according to anyone of the preceding claims 6 to 12, wherein the additional thermal treatment of the cast shot consists of a sublimation for removal of a volatile phase A from the material for obtaining of a skeleton-type structure of isolated intermetallic compounds.

14. The method according to any of the preceding claims 6 to 13, wherein the condensation of liquid argon at positive pressure is in the pressure range from 1 to 5 bar in order to obtain a sufficient volume of quenching liquid.

15. An apparatus for carrying out the method according to one or more of the preceding claims 7 to 14, said apparatus comprising:

- a charging compartment (I) comprising a glove box and a doser (4) for charging and mixing of initial metals or components,
- a melting compartment (II) comprising a heater (8) and a crucible (6), wherein the initial metals or components, previously subjected to deep outgassing, are introduced,
- a quenching compartment (III), where the droplets solidify in liquid argon, a sublimation compartment (IV) comprising a particle collector (13), a vapour tap (11), and a gas analyser.

Patentansprüche

1. Gassorbtionsmittel auf der Basis von intermetallischen Verbindungen mit großer Oberfläche mit der Formel A_nMe_m ,

die sich in einem thermodynamischen Gleichgewicht mit der Verbindung A befinden, die mit ihr ein Eutektikum bilden, wobei Komponente A ein chemisch aktives und flüchtiges Metall ist, ausgewählt aus der Gruppe, bestehend aus Alkalimetallen, Erdalkalimetallen, und wobei Me aus der Gruppe der Metalle ausgewählt ist, bestehend aus Ag, Al, Cu, Ga, Ge, In, Ni, Si, Sn, und wobei $n \geq m$, in Form eines isolierten Dendritgerüsts, das aus einer schnell erstarrten heterogenen Legierung mit Hilfe von Sublimation seiner flüchtigen Fraktion abgeschieden ist, wobei die intermetallischen Verbindungen der Legierung durch ein Verfahren erhältlich sind, das die folgenden Schritte umfasst:

- Mischen und Schmelzen von Ausgangsmetallen und Homogenisierung der Schmelze unter Unterdruck eines Inertgases,
- Herstellen von gegossenem Granulat durch Abschrecken von geschmolzenen Tröpfchen unter Überdruck,
- Darstellen von Granulat vom Skelett-Typ durch Verdampfung des Überschusses der Komponente A aus gegossenem Granulat unter Vakuum.

2. Gassorbptionsmittel gemäß Anspruch 1, wobei die geschmolzenen Tröpfchen, die einen bestimmten Überschuss an Komponente A bezüglich einer stöchiometrischen Zusammensetzung enthalten, einem Abschrecken in flüssigem Argon unterworfen sind, und dann als Ergebnis einer Kristallisation eine Struktur auftritt, die aus einem dendritischen Gerüst A_nMe_m und einem Eutektikum besteht, das den Raum zwischen den Dendritarmen füllt.

3. Gassorbptionsmittel gemäß Anspruchs 1 oder 2, wobei Komponente A in der Formel A_nMe_m aus der Gruppe ist, bestehend aus Ca, Sr, Li, Mg, Ba.

4. Gassorbptionsmittel gemäß Anspruch 3, wobei Komponente A in der Formel A_nMe_m Calcium oder Strontium ist.

5. Gassorbptionsmittel gemäß Anspruchs 1 bis 4, wobei die intermetallischen Verbindungen aus der Gruppe ausgewählt sind, bestehend aus Ca_3Ag , Ca_2Cu , $Ca_{28}Ga_{11}$, Ca_3In , Ca_2Si , Ca_2Ge , Ca_2Sn , Sr_3Ag_2 , $SrCu$, Sr_8Al_7 , Sr_8Ga_7 , Sr_3In , Sr_2Si , Sr_2Ge , Sr_2Sn und $SrNi$.

6. Verfahren zur Herstellung von hochreinen metallischen Gassorbptionsmitteln auf der Basis von intermetallischen Verbindungen der Formel



die sich mit der Komponente A in einem thermodynamischen Gleichgewicht befinden, die mit ihr ein Eutektikum bilden und bei dem A aus der Gruppe ausgewählt ist, bestehend aus Alkalimetallen, Erdalkalimetallen, wobei Me aus der Metallgruppe ausgewählt ist, bestehend aus Ag, Al, Cu, Ga, Ge, In, Ni, Si, Sn, und $n \geq m$, beginnend bei chemisch aktiven Metallen oder Legierungen, wobei das Verfahren die folgenden Schritte umfasst:

- Mischen und Schmelzen von Ausgangsmetallen und Homogenisierung der Schmelze unter Unterdruck eines Inertgases,
- Herstellung von gegossenem Granulat durch Abschrecken von geschmolzenen Tröpfchen unter Überdruck,
- Darstellen von Granulat vom Skelett-Typ durch Verdampfung des Überschusses der Komponente A aus gegossenem Granulat unter Vakuum,
- Abpacken des Produkts durch Versiegeln in einem Behälter unter Vakuum oder unter Unterdruck eines inerten Gases.

7. Verfahren gemäß Anspruch 6, wobei das inerte Gas Argon ist.

8. Verfahren gemäß Ansprüchen 6 oder 7, wobei die geschmolzenen Tröpfchen, die einen bestimmten Überschuss an Komponente A bezüglich einer stöchiometrischen Zusammensetzung enthalten, einem Abschrecken in flüssigem Argon unterworfen werden, und dann als Folge einer Kristallisation eine Struktur auftritt, die aus einem dendritischen Gerüst A_nMe_m und einem Eutektikum besteht, das den Raum zwischen den Dendritarmen füllt.

9. Verfahren gemäß irgendeinem der vorstehenden Ansprüche 6 bis 8, wobei Komponente A in Formel A_nMe_m aus der Gruppe ist, bestehend aus Ca, Sr, Li, Na, Mg, Ba.

10. Verfahren gemäß Ansprüchen 6 bis 9, wobei die intermetallischen Verbindungen aus der Gruppe ausgewählt sind, enthaltend Ca und Sr als Komponente A in Formel A_nMe_m , bestehend aus Ca_3Ag , Ca_2Cu , $Ca_{28}Ga_{11}$, Ca_3In , Ca_2Si , Ca_2Ge , Ca_2Sn , Sr_3Ag_2 , $SrCu$, Sr_8Al_7 , Sr_8Ga_7 , Sr_3In , Sr_2Si , Sr_2Ge , Sr_2Sn , $SrNi$.

11. Verfahren gemäß irgendeinem der vorstehenden Ansprüche 6 bis 10, wobei das Metall A in einer Atmosphäre aus reinem Argon bei einem Druck von ungefähr 1 bis 100 mbar mit Hilfe von induktiver Erwärmung geschmolzen wird, während unter dem Tiegel ein leicht überhöhter Druck beibehalten wird.

12. Verfahren gemäß irgendeinem der vorstehenden Ansprüche 6 bis 11, wobei die Parameter des Sublimationsvorgangs aus Phasendiagrammen und thermodynamischen Daten zu A-Me-Legierungen festgelegt werden, wobei die Verflüchtigungstemperatur durch den Subsolidus-Bereich und durch die Drücke beschränkt wird, bei denen eine Zersetzung von A_nMe_m -Kristallen nicht stattfindet.

13. Verfahren gemäß irgendeinem der vorstehenden Ansprüche 6 bis 12, wobei die zusätzliche thermische Behandlung des gegossenen Granulats aus einer Sublimation zum Entfernen einer flüchtigen Phase A aus dem Material besteht, um eine gerüstartige Struktur von isolierten intermetallischen Verbindungen zu erhalten.

14. Verfahren gemäß irgendeinem der vorstehenden Ansprüche 6 bis 13, wobei die Kondensation von flüssigem Argon bei Überdruck in dem Druckbereich von 1 bis 5 bar liegt, um ein ausreichendes Volumen an Abschreckflüssigkeit zu erhalten.

15. Vorrichtung zur Ausführung des Verfahrens gemäß einem oder mehr der vorstehenden Ansprüche 7 bis 14, wobei die Vorrichtung umfasst:

- einen Beladungsabschnitt (I), umfassend eine Glovebox und eine Dosiereinrichtung (4) zum Beladen und Mischen von Ausgangsmetallen oder Komponenten,
- einen Schmelzabschnitt (II), umfassend einen Heizer (8) und einen Tiegel (6), worin die Ausgangsmetalle oder Komponenten, die vorher einer tiefen Entgasung unterworfen wurden, eingeführt werden,
- einen Abschreckabschnitt (III), wo die Tröpfchen in flüssigem Argon erstarren,
- einen Sublimationsabschnitt (IV), umfassend einen Partikelkollektor (13), eine Dampffalle (11) und eine Gasanalyseeinheit.

Revendications

1. Sorbants de gaz à base de composés intermétalliques ayant une grande surface spécifique de formule A_nMe_m , qui sont en équilibre thermodynamique avec le composé A formant avec lui un eutectique, où le composant A est un métal chimiquement actif et volatil choisi dans le groupe constitué par les métaux alcalins, les métaux alcalino-terreux, et Me est choisi dans le groupe des métaux constitués par Ag, Al, Cu, Ga, Ge, In, Ni, Si, Sn et où $n \geq m$, sous la forme d'une carcasse de dendrite isolée, séparée d'un alliage hétérogène rapidement solidifié à l'aide d'une sublimation de sa fraction volatile, les composés intermétalliques de l'alliage pouvant être obtenus par un procédé comprenant les étapes suivantes consistant à :

- mélanger et faire fondre des métaux initiaux et homogénéiser la matière fondue sous une pression négative de gaz inerte,
- fabriquer une grenaille de coulée en trempant des gouttelettes fondues sous une pression positive,
- obtenir des granules de type squelette par évaporation de l'excès du composant A provenant de la grenaille de coulée sous vide.

2. Sorbants de gaz selon la revendication 1, dans lesquels les gouttelettes fondues contenant un certain excès de composant A par rapport à une composition stoechiométrique sont soumises à une trempe dans de l'argon liquide, puis par suite une cristallisation d'une structure se produit laquelle consiste en une carcasse dendritique A_nMe_m et un eutectique, qui remplit l'espace entre les bras de dendrite.

3. Sorbants de gaz selon la revendication 1 ou 2, dans lesquels le composant A dans la formule A_nMe_m est choisi dans le groupe constitué par Ca, Sr, Li, Mg, Ba.

4. Sorbants de gaz selon la revendication 3, dans lesquels le composant A dans la formule A_nMe_m est le calcium ou

le strontium.

5. Sorbants de gaz selon les revendications 1 à 4, dans lesquels les composés intermétalliques sont choisis dans le groupe constitué par Ca_3Ag , Ca_2Cu , $\text{Ca}_{28}\text{Ga}_{11}$, Ca_3In , Ca_2Si , Ca_2Ge , Ca_2Sn , Sr_3Ag_2 , SrCu , Sr_8Al_7 , Sr_8Ga_7 , Sr_3In , Sr_2Si , Sr_2Ge , Sr_2Sn et SrNi .

6. Procédé de production de sorbants de gaz métalliques de haute pureté à base de composés intermétalliques de formule



qui sont en équilibre thermodynamique avec le composant A formant avec lui un eutectique et dans lequel A est choisi dans le groupe constitué par les métaux alcalins, les métaux alcalino-terreux, Me est choisi dans le groupe des métaux constitués par Ag, Al, Cu, Ga, Ge, In, Ni, Si, Sn et où $n \geq m$, en démarrant à partir de métaux ou alliages chimiquement actifs, ledit procédé comprenant les étapes suivantes consistant à :

- mélanger et faire fondre des métaux initiaux et homogénéiser la matière fondue sous une pression négative de gaz inerte,
- fabriquer une grenaille de coulée en trempant des gouttelettes fondues sous une pression positive,
- obtenir des granules de type squelette par évaporation de l'excès du composant A provenant de la grenaille de coulée sous vide,
- emballer le produit en le scellant dans un conteneur sous vide ou sous une pression négative d'un gaz inerte.

7. Procédé selon la revendication 6, dans lequel le gaz inerte est l'argon.

8. Procédé selon la revendication 6 ou 7, dans lequel les gouttelettes fondues contenant un certain excès de composant A par rapport à une composition stoechiométrique sont soumises à une trempe dans de l'argon liquide, puis par suite une cristallisation d'une structure se produit laquelle consiste en une carcasse dendritique A_nMe_m et un eutectique, qui remplit l'espace entre les bras de dendrite.

9. Procédé selon l'une quelconque des revendications 6 à 8 précédentes, dans lequel le composant A dans la formule A_nMe_m est choisi dans le groupe constitué par Ca, Sr, Li, Mg, Ba.

10. Procédé selon les revendications 6 à 9, dans lequel les composés intermétalliques sont choisis dans le groupe contenant Ca et Sr en tant que composant A dans la formule A_nMe_m constitué par Ca_3Ag , Ca_2Cu , $\text{Ca}_{28}\text{Ga}_{11}$, Ca_3In , Ca_2Si , Ca_2Ge , Ca_2Sn , Sr_3Ag_2 , SrCu , Sr_8Al_7 , Sr_8Ga_7 , Sr_3In , Sr_2Si , Sr_2Ge , Sr_2Sn et SrNi .

11. Procédé selon l'une quelconque des revendications 6 à 10 précédentes, dans lequel le métal A est fondu dans une atmosphère d'argon pur sous une pression d'environ 1 à 100 mbar à l'aide d'un chauffage inductif tout en maintenant sous le creuset une pression légèrement en excès.

12. Procédé selon l'une quelconque des revendications 6 à 11 précédentes, dans lequel les paramètres du procédé de sublimation sont définis à partir des diagrammes de phase et des données thermodynamiques sur les alliages A - Me, dans lequel la température de volatilisation est limitée par l'aire de sous-solides et par les pressions auxquelles une décomposition de cristaux de A_nMe_m n'a pas lieu.

13. Procédé selon l'une quelconque des revendications 6 à 12 précédentes, dans lequel le traitement thermique additionnel de la grenaille de coulée consiste en une sublimation destinée à éliminer une phase volatile A du matériau pour obtenir une structure de type squelette de composés intermétalliques isolés.

14. Procédé selon l'une quelconque des revendications 6 à 13 précédentes, dans lequel la condensation de l'argon liquide à une pression positive se fait dans la gamme de pression de 1 à 5 bar afin d'obtenir un volume suffisant de liquide de trempe.

15. Appareil destiné à réaliser le procédé selon une ou plusieurs des revendications 7 à 14 précédentes, ledit appareil

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comprenant :

- un compartiment de charge (I) comprenant une boîte à gants et un doseur (4) destinés à charger et mélanger des métaux ou composants initiaux,
- un compartiment de fusion (11) comprenant un dispositif de chauffage (8) et un creuset (6), dans lequel les métaux ou composants initiaux, précédemment soumis à un dégazage profond, sont introduits,
- un compartiment de trempe (III), où les gouttelettes se solidifient dans de l'argon liquide,
- un compartiment de sublimation (IV) comprenant un collecteur de particule (13), un robinet de vapeur (11) et un analyseur de gaz.

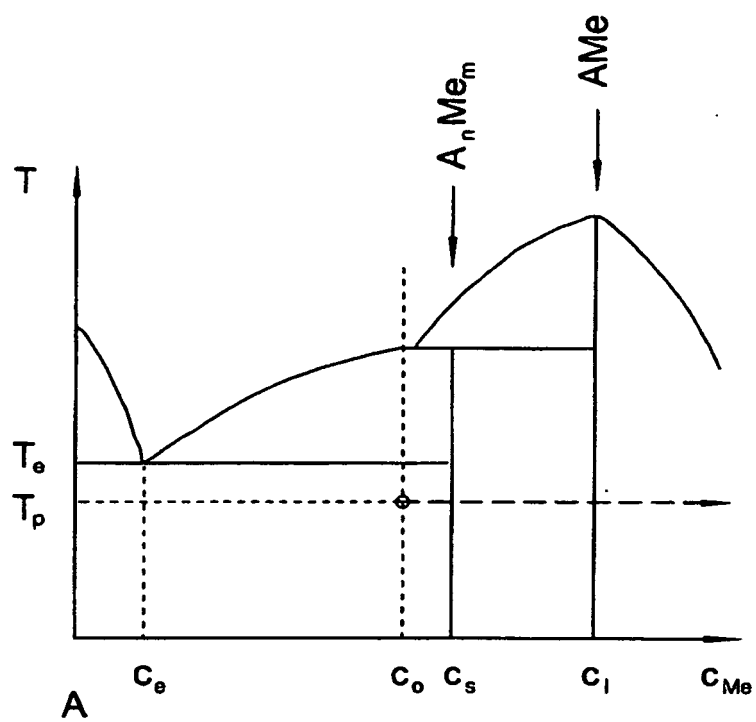


Fig.1

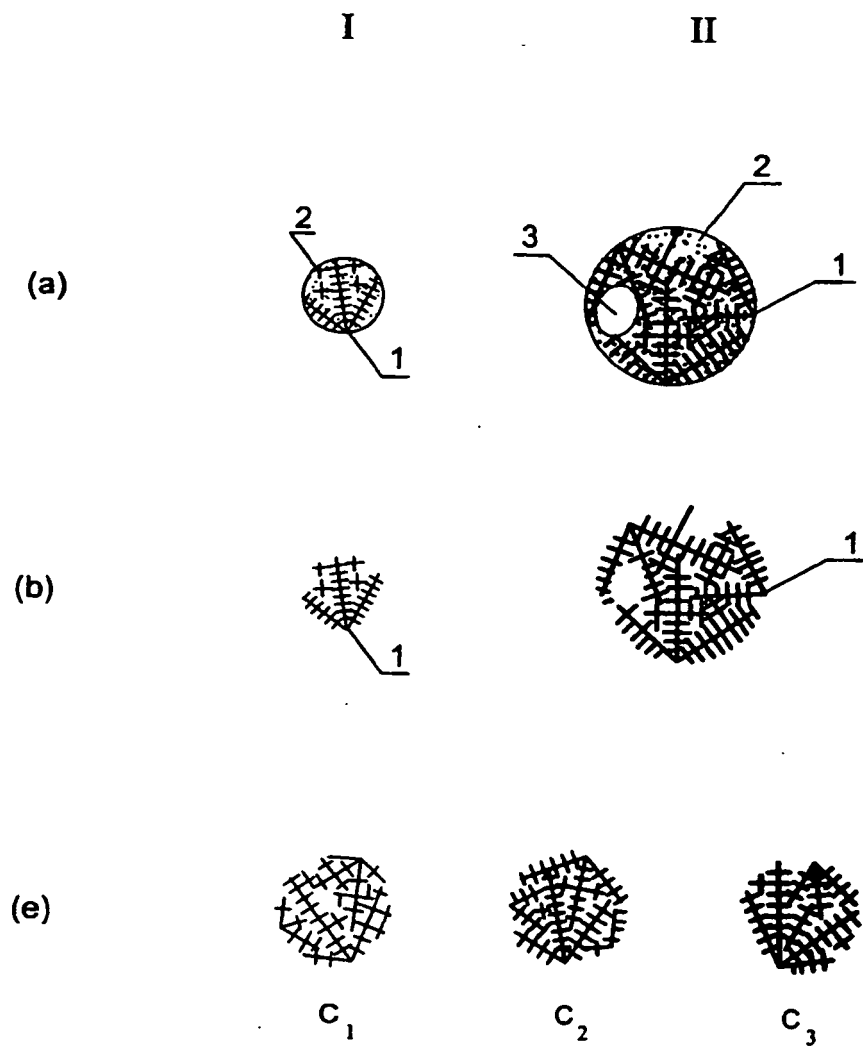


Fig.2

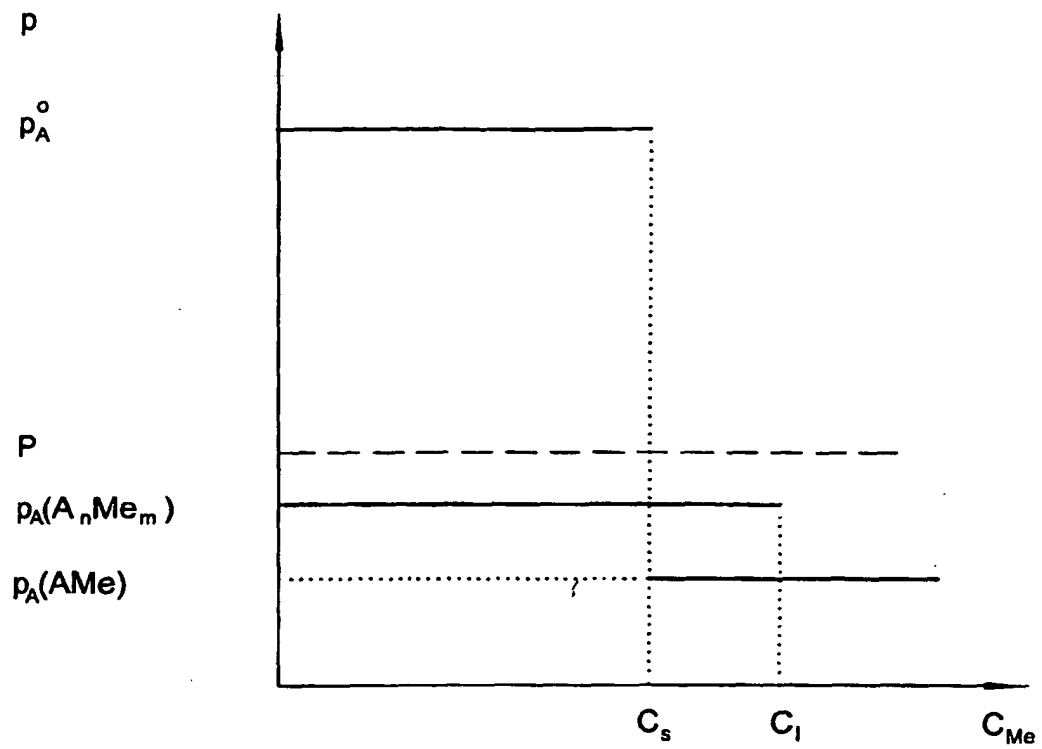


Fig.3.

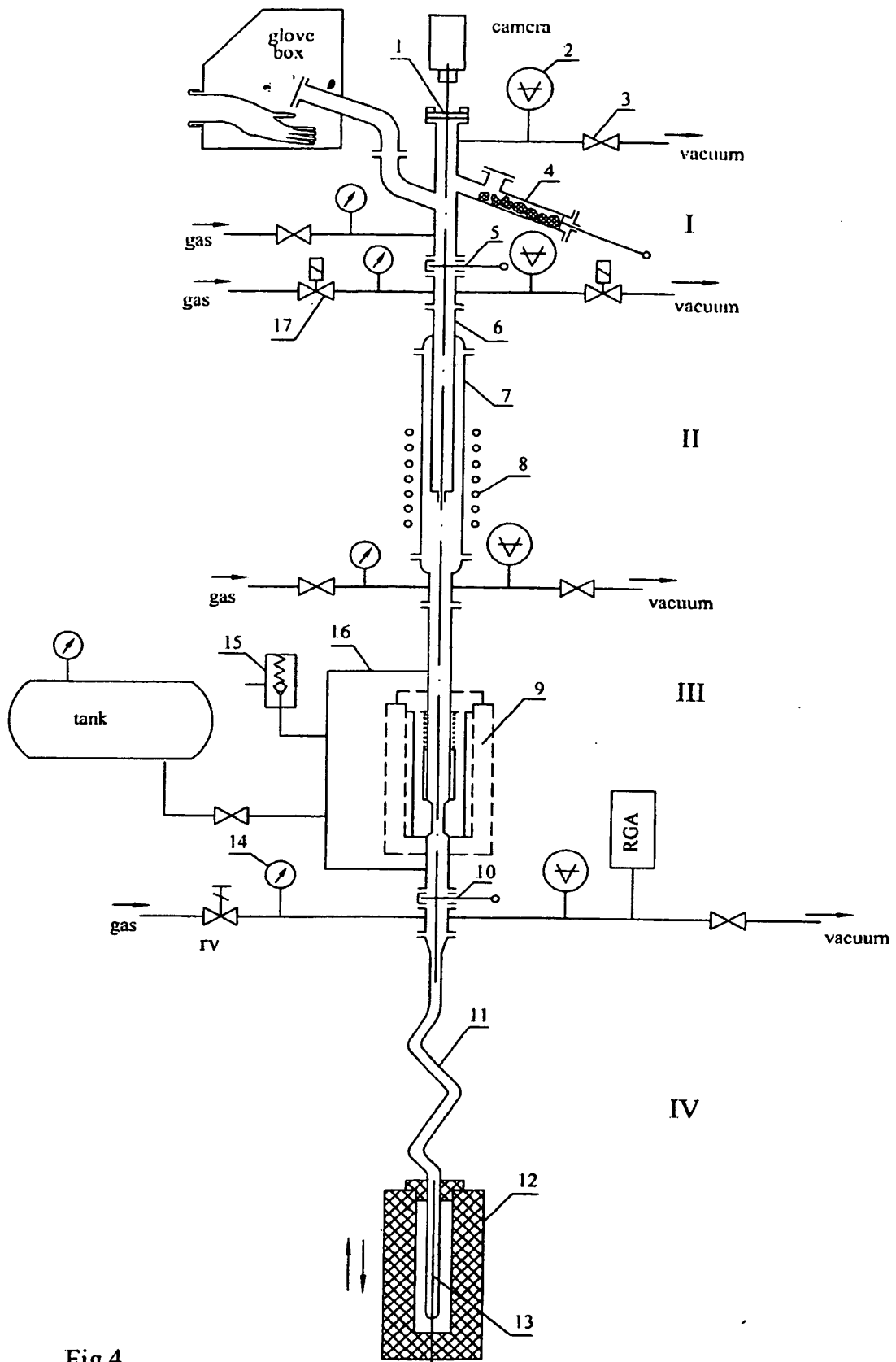


Fig.4

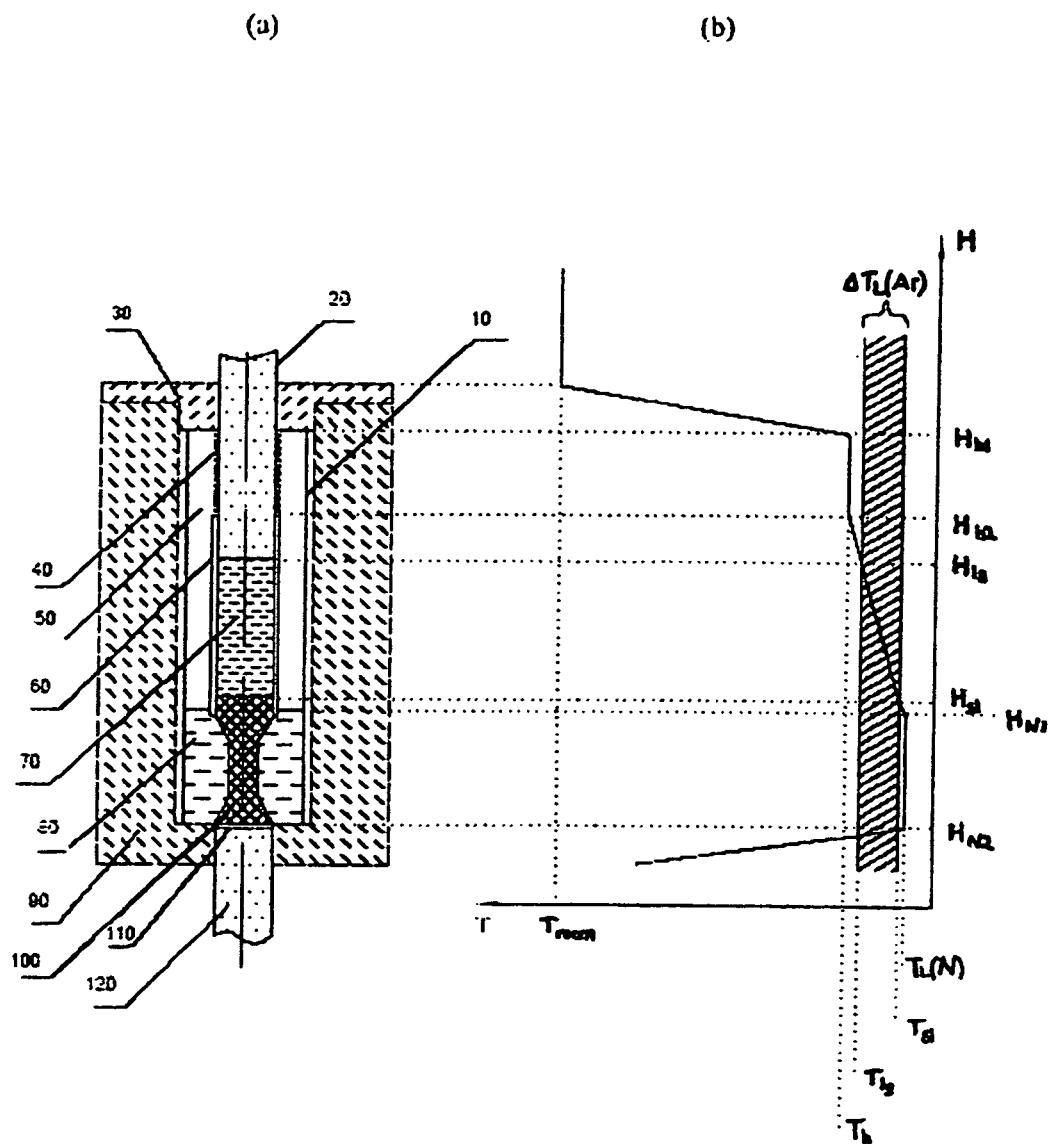


Fig.5

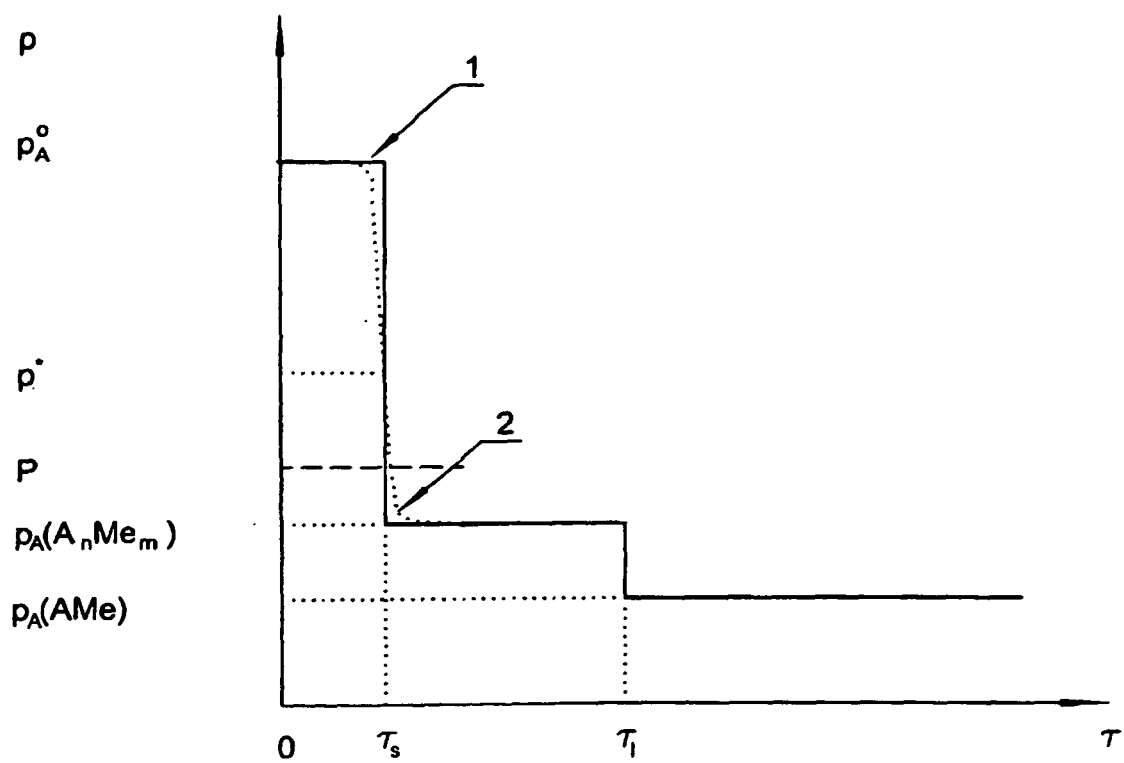


Fig.6

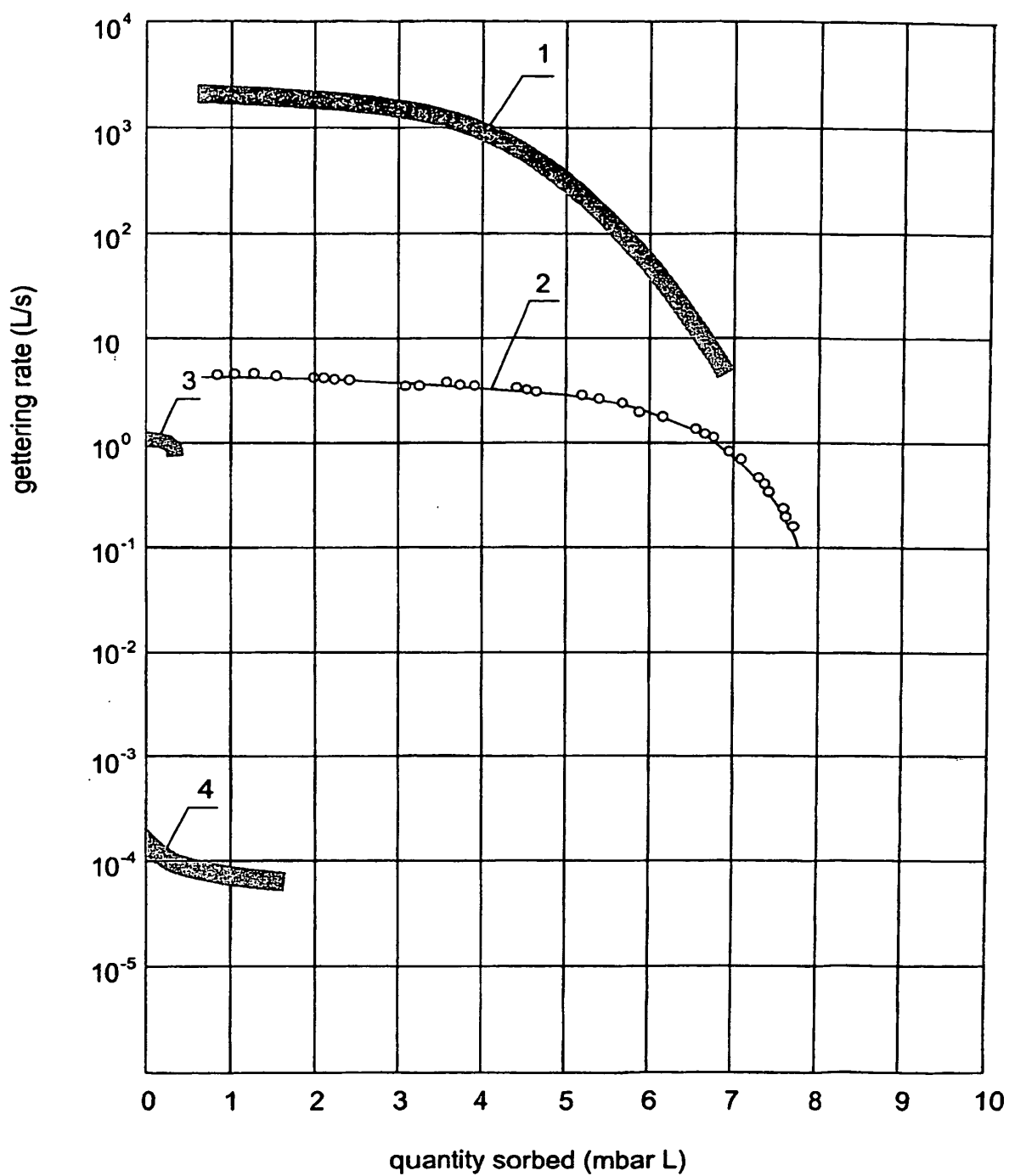


Fig.7