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Getters Reactants. I. Thermo-Sedimentational Activation

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Abstract

A new method for chemical pumping of gases has been developed using reactive alloys of Li with IIA metals in the liquid state. It is an answer to the need for ultra-high and extremely high vacuum without loose solid particles. Another application of this development is the production of high- and ultra-pure noble gases in a one-step process. Both of these solutions are unprecedented; they are based on a new gas/melt sorption interface that raises the overall bar of technical advances in the field to a higher level, simplifying sorption equipment and leading to cost savings.

Keywords

Interface Gas/Melt, Vacuum Pump, Gas Sorption, Getters Reactants, Sedimentation, Noble Gases

1. Introduction

The present work is devoted to getters reactants, a new class of sorbent materials, which are based on Li with IIA metals alloys and are many times superior to all the conventional absorbents, adsorbents and chemisorbents in terms of sorption characteristics [1]-[4]. This superiority is explained by the special chemical nature of these alloys, which behave in the gas environment according to other laws than those known to us from the experience of traditional sorbents.

The position of getters reactants is equally strong from the point of view of sorption equipment, which in this case stands out for its structural simplicity and drastic reduction in the number of production operations [5] [6]. All this, the record sorption performance of reactive alloys and more efficient equipment, demonstrate an unconditional progress in the field of sorption technologies, increasing in times and even by orders of magnitude the level of their working characteristics.

The goal of this sorption direction is to solve a number of problems that have accumulated in the field of gas and vacuum applications, and which are directly related to the pressing problems of our time. These are tasks such as energy saving, climate protection, waste-free production, as well as the production of ultra-pure materials that are critical for microelectronics, the semiconductor industry, mobile communications, space technology, nuclear energy, science, medicine, etc.

2. Chemisorbents and Getters Reactants

To understand the current situation in the sorption field, let us compare getters reactants with chemisorbents, otherwise just getters [7], which still occupy leading positions among sorption materials. The sorption advantages of chemisorbents appear due to the chemical nature of the forces of their interaction with gases, but getters reactants also have the same quality. Therefore, let us briefly consider the processes of gas sorption by these two products and evaluate in the most general form their sorption advantages as well as production costs.

Chemisorbents of NEGs (non-evaporable getters) type have transition metals such as Ti, V, Zr and others as their material base [8]-[11]. When in contact with gases, they are covered with a stable thin film of products, which stops the sorption process. This film is removed by thermal activation, temporarily converting the chemisorbent into an absorbent that dissolves the gases of this film in its volume by diffusion. However, such renewal of the chemisorbent surface leads to significant costs and creates inconvenience.

The working characteristics of a chemisorbent, sorption kinetics and sorption capacity depend on the value of specific surface area of the material and increase with it. Therefore, the interest from applications in chemisorbents is higher, the more developed their surface is, but this is precisely what creates problems. Indeed, the production of NEGs or such a popular product as getter inks [12] is a multi-stage complex process, but further growth of the specific surface area of this product leads to an even greater increase in production costs and to additional loss of the sorbent material itself during its thermal activation [4] [13].

On the contrary, getters reactants are ready to capture gases even in the form of macrobodies with a monolithic structure, *i.e.*, ingots. At the initial stage of the sorption process, these ingots react with gases like ingots of IIA metals [14] or monolithic Li samples [15], forming a loose and slowly growing layer of chemical compounds of gas with metal on their surface. However, a bit later, the behavior of the getters reactants changes dramatically: unlike ingots of elemental metal ingots of the reactive alloys containing an intermetallic brittle constituent demonstrate rapid destruction of their body into many individual particles [4] [5].

From the standpoint of sorption applications, it is important to see that this corrosion decomposition of the cast structure of the alloy feeds the reaction of the metal with gas with more and more new areas of fresh surface, becoming the main driving force of the sorption process. As a result, such interaction of gas with the reactive ingot ends with the consumption of its entire mass, exceeding by ~10 times or more the specific sorption capacity of getters of the inks or NEGs type and exceeding by the same amount the sorption kinetics of pure reactive metal ingots [4] [14] [15].

The above does not exhaust all the strengths of getters reactants. Thus, their sorption efficiency increases even more with the use of activation methods, mechanical activation [5] [6] or thermal-sedimentational activation [16], which are most appropriate and useful in the case of Li alloys with IIA metals. Let us also note the high adaptability of these alloys to changes in their operating conditions, the lack of need for catalytic support and other properties important for practice. We will demonstrate this using the example of applications where getters reactants create a new sorbent product by their transition to a liquid-phase state.

3. Melts of Getters Reactants

The use of low-melting reactive alloys as a chemical pump is a long overdue step in getter technology, especially given the rapidly growing need for technologically advanced and cost-effective gas pumping methods, as well as for the production of high- and ultra-pure gases. This step became possible after we realized that there is a direct connection between the kinetics of gas capture by reactive melts and sedimentation mass transfer in gas/melt systems [16].

3.1. Getter Pump and Sedimentation

Getters as a tool for capturing gases have two clear advantages over other means of creating vacuum: they are silent and compact. But they have a generic disadvantage: in the process of gas sorption, they generate free solid particles, which consist of chemical compounds of gas with metal and which are undesirable, interfering with the working system. One of the goals of developing a new pump is to get rid of these particles.

Another goal is to overcome the barrier formed at the traditional for getters gas/solid interphase boundary, which consists of the products of the reaction of gas with metal and which either slows down sorption, as is the case with getters reactants, or stops it altogether, as is the case with chemisorbents. However, the situation changes fundamentally if the said solid is a low-melting getter reactant and if it is converted into a liquid state by heating.

Here we are already dealing with the gas/melt sorption boundary, where the melt of the reactive alloy captures gases faster than in the solid state, but at the same time, as many years of experience in working with reactive melts show [16], the above-mentioned barrier does not appear at the specified interphase boundary (see **Appendix**). Although upon contact with gases, solid particles of products of reaction are formed on the surface of the melt, they immediately sink into the volume of the melt and go to the bottom under the influence of gravity. That is, the mechanism of sedimentation transfer of these solid particles is switched on, which protects the surface of the melt from the appearance of a barrier interfering with the sorption process. This process is shown schematically in **Figure 1**.

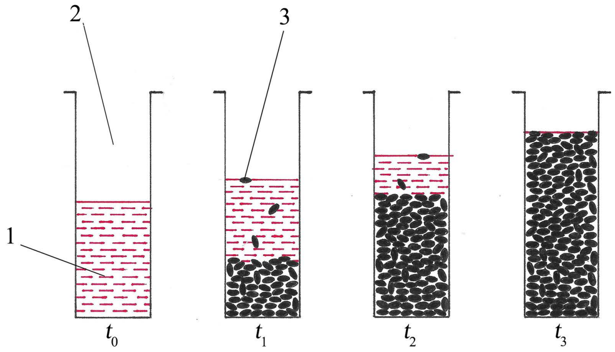


Figure 1. Mechanism of thermo-sedimentation activation. 1—melt, 2—gas, 3—solid particles, *t*—time; under the influence of gravity particles 3 sink, releasing the surface of the melt 1, but a sediment layer grows on the bottom (see t_1 and t_2). This regime does not change until the moment of time t_3, when the sediment reaches the surface of the melt.

The sedimentation rate V according to the Stokes formula [17] is expressed as $V = 2\Delta\rho g r^2/9\eta$, where $\Delta\rho$ is the difference in density of the solid particle and the melt, r is the particle radius, g is the gravitational acceleration and η is the viscosity of the melt. In the case that is interesting for us everything is in favor of extremely fast cleaning of the melt surface from solid products of reaction. Indeed, the growth kinetics of these particles is high, which leads to large r values, the melt viscosity η at a high Li concentration is small [18], and the density of solid particles compared with the density of the melt is high, since chemical compounds of Li and IIA metals with gases are characterized by high volume contraction, about 30% - 40% [19].

The proposed new pump is extremely simple in its design (**Figure 2**): it consists of a stainless steel cylinder with a reactive melt inside and a heater outside, and at this, it is capable of reducing the ultimate pressure in the pumped chamber to 10^{-10} - 10^{-14} mbar [16], which belongs to the field of ultra- and extremely high vacuum. Naturally, such a pump needs support from a fore-vacuum pump to reach the starting level of ~10^{-1} mbar and periodic connection of a cryo pump to remove inert gases when the need arises.

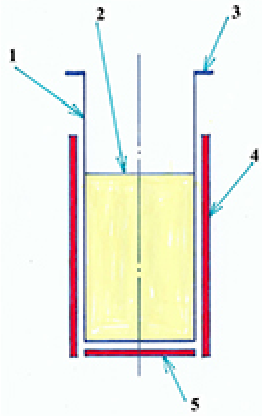


Figure 2. Pump design. 1—cylindrical stainless steel container; 2—getter reactant melt; 3—flange; 4—side heater; 5—lower heater.

This pump uses new solutions that change the established practice of handling getters. Thus, the gas/solid sorption boundary is here supplemented by a gas/melt boundary; liquid eutectic lithium-based alloys are used to capture gases instead of highly porous solid bodies; periodic thermal activation with diffusion transfer of gas into the volume of the crystalline body is now replaced by continuous heating of the reactive alloy, which triggers sedimentation purification of the gas/melt boundary.

The material basis for the above innovations are low-melting Li alloys and this choice is dictated by the very nature of the application under consideration, which requires a solution that does not create free solid particles in the vacuum chamber. The answer to this requirement is a melt of a reactive alloy with a self-cleaning surface and a low melting point T_f, which guarantees low metal vapor pressure above the melt.

The solution sought is provided by Li alloys with Ca, Sr and/or Ba, in which, in the concentration range $0.8 \leq x \leq 0.9$, the liquidus temperature T_f satisfies the conditions $T_e \leq T_f \leq 200^\circ\text{C}$, where x is the atomic fraction of Li in the alloy, and T_e is the temperature of Li-based eutectics [20]. At temperatures $T = T_f + \Delta T$, where $20^\circ\text{C} \leq \Delta T \leq 30^\circ\text{C}$, these alloys have a metal vapor pressure above the melt not higher than 10^{-10} - 10^{-11} mbar [21] [22], which is what is required of them in the role of a chemical pump for ultra-high vacuum chambers.

These alloys now serve as a consumable getter material, which is used in both of its phase states, liquid with a gas/melt sorption boundary at temperatures $T = T_f + \Delta T$ and solid with a gas/solid sorption boundary at T_{room}. The first of these boundaries provides ultimate pressure of the order of 10^{-10} - 10^{-11} mbar in the evacuated chamber, after which the second one creates in it extremely high vacuum of the order of ~10^{-14} mbar in full agreement with the intrinsic vapor pressure of the reactive alloy components at T_{room} [21] [22].

3.2. Pumping Mode

The first operating stage of this pump begins when the sorption process runs at the gas/melt boundary in the temperature range from ~150˚C to ~220˚C leading to the formation of solid phase particles on the surface of the melt. However, the cleaning of the sorption boundary runs according to the sedimentation mechanism at an unprecedentedly high speed when compared with the processes of thermal activation of chemisorbents, where the kinetics is limited by the diffusion of gas in a solid.

The vacuum level, with timely support by a forevacuum and cryo pump, quickly stabilizes within the range of 10^{-10} - 10^{-11} mbar, being limited only by the vapor pressure of the melt itself, which gives a chance to move to the second stage of pumping. Now the gas/solid boundary starts working, which brings the vacuum chamber to the highest pumping level, about 10^{-14} mbar, also without contamination of the vacuum chamber with solid particles due to the participation of the second pump.

The second stage of pumping is the operation of a system of two identical pumps that alternately replace each other, connected by a single chain of actions. It looks like this: when a pressure of 10^{-11} mbar is reached in a vacuum chamber with two pumps operating simultaneously, the valve of one of them (let's call it the first, **Figure 3**) is closed and its heating is turned off. After the melt solidifies and the ingot temperature approaches T_{room}, the valve of the first pump with the gas/solid boundary formed in it is opened, and the valve of the second pump, which was still in operation, is closed and its heater is turned off.

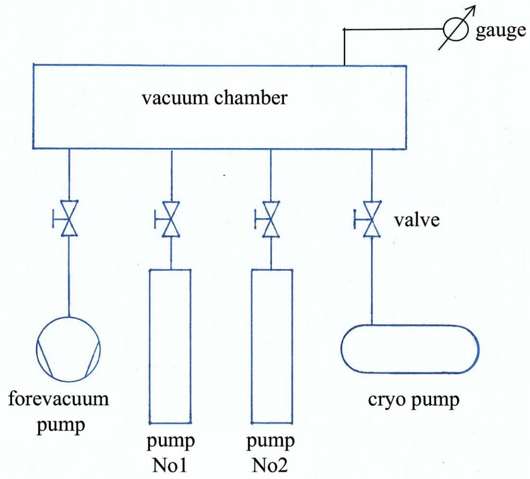


Figure 3. General scheme of the pumping system.

From this point on, only the solid surface of the reactive alloy is directly involved in the pumping process. As the layer of reaction products grows on this surface, the sorption rate decreases, but it is restored by reactivating the ingot, for which the second pump is turned on. This pump, after the melt → solid phase transition has taken place in it, is in reserve and awaits its turn. When such a time comes, the valve of the second pump, which takes over the pumping process, is opened and the first pump is simultaneously disconnected from the vacuum chamber.

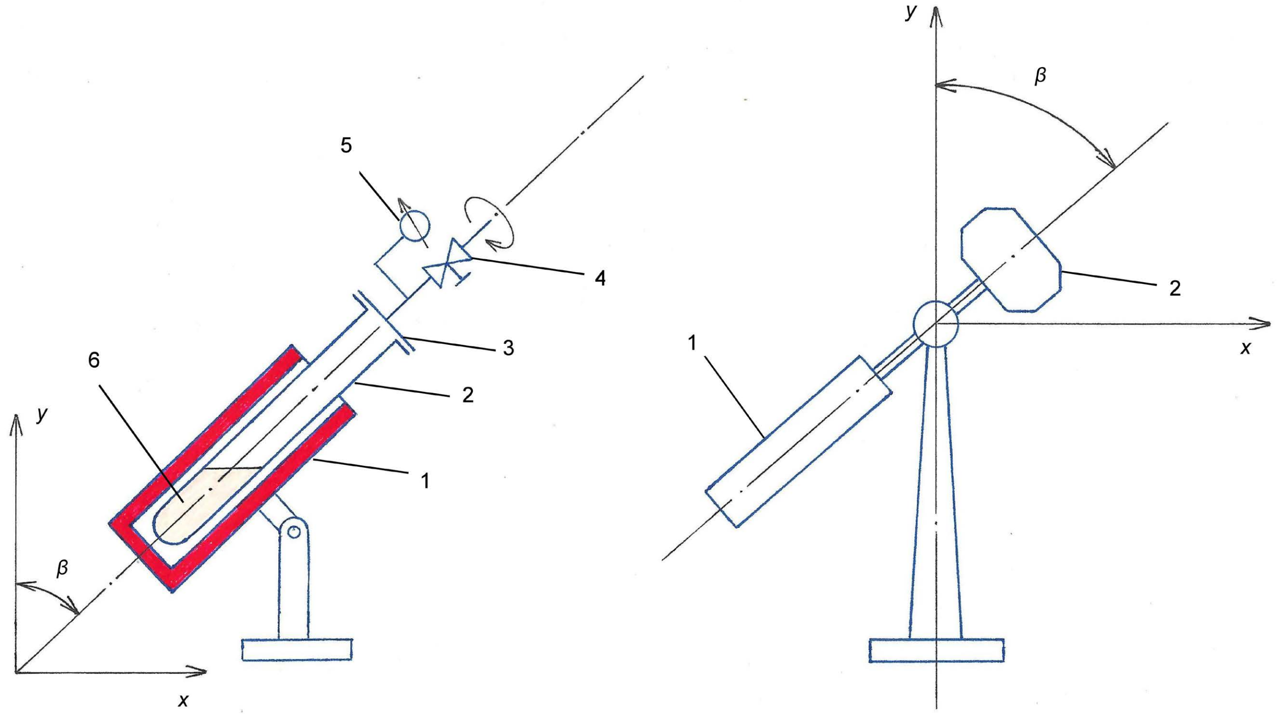
Now the task of the first pump (in its isolated state) is to heat the ingot to melt and renew its surface using sedimentation mass transfer. After these actions, the heating of this pump is turned off, returning the sorption boundary to the gas/solid state, and the pump goes into standby mode, characterized by a gradual decrease in pressure inside the cylinder. This exchange of roles between the two pumps continues in the future until their sorption resource, which is very large here, is completely depleted.

In general, covering the whole picture of pumping gases with a getter melt, we can predict the emergence of many vacuum applications on this basis. However, two types of new vacuum equipment are beyond doubt, these are single pumps as a competitor to diffusion and turbo vacuum pumps in the vacuum range up to 10^{-10} - 10^{-11} mbar, and a pumping system of two pumps as an obvious competitor to all known getter pumps in the vacuum range up to 10^{-12} mbar.

3.3. Purification of Noble Gases

Essentially the same solutions that are used in the getter pump described above are also included in the new technology for removing active and low-active gas impurities from noble gases. Here, too, everything is built on the chemical capturing of gases by the surface of the reactive melt, the composition of which corresponds to the same eutectic alloys with a high Li content. We will briefly describe three options for complete purification of inert gases: two in vessels with gas under high pressure (up to several tens of bars) and one in a flow system with a slight excess of pressure over atmospheric, eliminating leakage from the outside.

Gas purification in a high-pressure cylinder is shown in **Figure 4**.



(a) (b)

Figure 4. Gas purification in an isolated vessel. (a) inclined rotation of the cylinder with gas; 1—furnace, 2—cylinder, 3—flange with valve 4 and pressure gauge 5, 6—getter melt and β—angle of inclination of the cylinder axis; (b) cylinder swinging; 1—general housing containing a cylinder inside, 2—counterweight, β—swinging amplitude.

Inside a tube furnace, which is inclined at an angle β relative to the vertical, a metal cylinder with the reactive melt and processed gas rotates around its axis (**Figure 4(a)**). Let the cylinder with the inner radius r be hermetically sealed with a flange, which is equipped with a pressure gauge and valve. By changing the value of the angle β, the size of the surface area s of the melt can be regulated according to the formula $s = \pi r^2/\cos\beta$, and with it, the sorption rate, while the pressure gauge gives approximate information about the purity degree of the gas product if the initial impurity concentration is high [5] [16].

One more variant for purifying compressed gas is shown in **Figure 4(b)**, where the method of swinging a cylinder performing oscillatory movements with a swing angle β relative to the y axis is implemented. Both of these solutions use dynamic action on the melt as a measure to prevent the formation of a hard crust of reaction products of the gas with the metal on the surface of the melt. Such a course of events is probable at the initial stage of the purification procedure for the reason that in this technology there are no restrictions on the impurity concentration and the mass of the melt is calculated for many portions of the gas to be purified.

Figure 5 schematically shows still another purification variant, using a flow-through bath, which is isolated from the atmosphere with a lid that has two openings, one for the inlet of the gas being purified and the other for its outlet. The bath is made of stainless steel or other metal material that is chemically resistant to the melts of Li-IIA metals. This design is simple and convenient, and its purpose is to force the flow of the processed gas into contact with the melt surface until all molecules of the gas impurity hit the required number of times against the reactive melt.

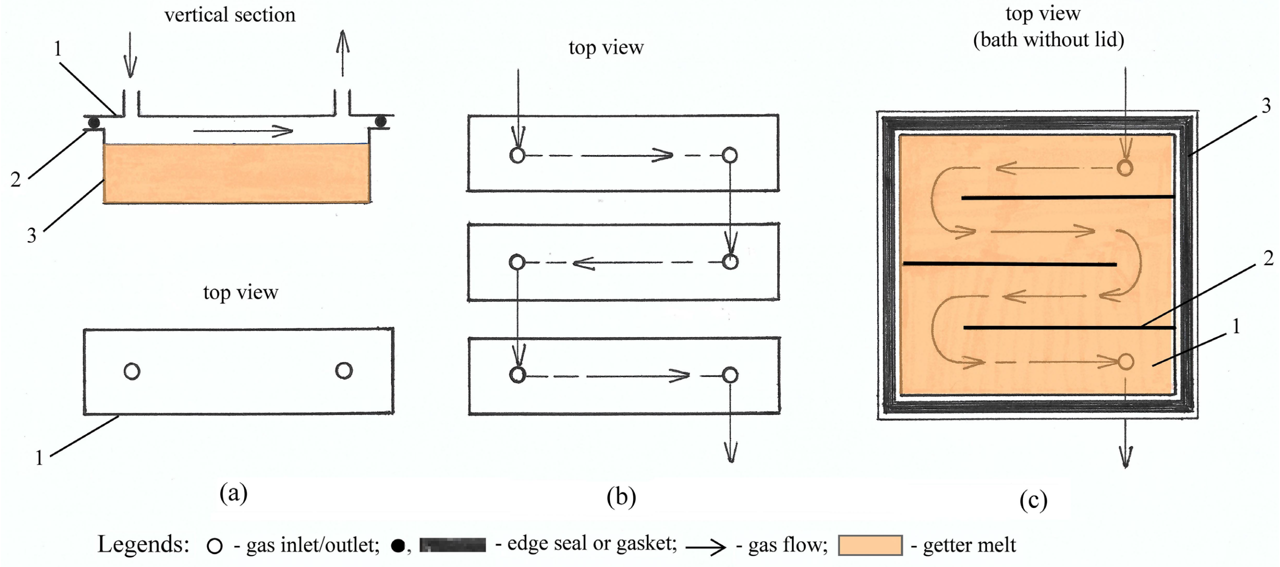


Figure 5. Gas purification in a flow bath. (a) single bath; 1—lid with gas inlet/outlet hole, 2—flange for edge seal or gasket, 3—bath with melt; (b) system consisting of several baths; (c) “labyrinth” type bath (lid not shown); bath 1 is divided by partitions 2 into several sections having a common flange 3 for edge seal or gasket.

To implement this condition, the length of the corridor along which the gas moves must be sufficiently large, protrusions and irregularities must be provided on the side walls and on the lid on their inner side in order to give the gas flow the required degree of turbulence. If necessary, such baths can be combined into a larger system, as shown in Figure 5(b) or rearranged as shown in Figure 5(c).

Thus, as follows from the above, low-melting reactive melts open the way to a new technology for the efficient purification of noble gases, covering all cases of purification, from recycling of exhaust gases to the production of ultra-pure gas using for this a chemical reaction of the impurity with the melt for this purpose.

The advantage of this solution is that, unlike the existing complex and multi-stage gas purification processes [23] [24], it is now a single-stage and controllable process. It should also be noted that new methods for the production of ultra-pure noble gases have clear advantages over Gas Purifiers [25] [26] both in terms of the purity of the final product and in terms of the overall costs of the process itself.

4. Conclusions

This work reveals new effective solutions in the field of getter technologies, based on the sorption interface of the gas/melt type, where melt is a melt of eutectic alloys of Li with Ca, Sr and Ba. Comparison of gas sorption by these low-melting alloys with gas sorption by traditional getters leads to the conclusion that the chemical reaction of gas with metal at the gas/melt boundary and the continuous entrainment of solid products of this reaction into the melt volume according to the sedimentation mechanism guarantee multiple sorption superiority of the new technology over the current ones.

For vacuum applications, the transition to melts of getters reactants provides the following benefits: it reduces the costs of manufacturing and operating the pump by many times, ensures the purity of the vacuum chamber from solid particles, and increases the ultimate vacuum to 10^{-14} mbar.

Another application of reactive melts with a low solid → melt transition temperature is a new technology for purifying noble gases to the level of absolute purity with respect to active and low-active gas impurities. This type of sorption process takes place in one stage with minimal expenditure of consumable material and time.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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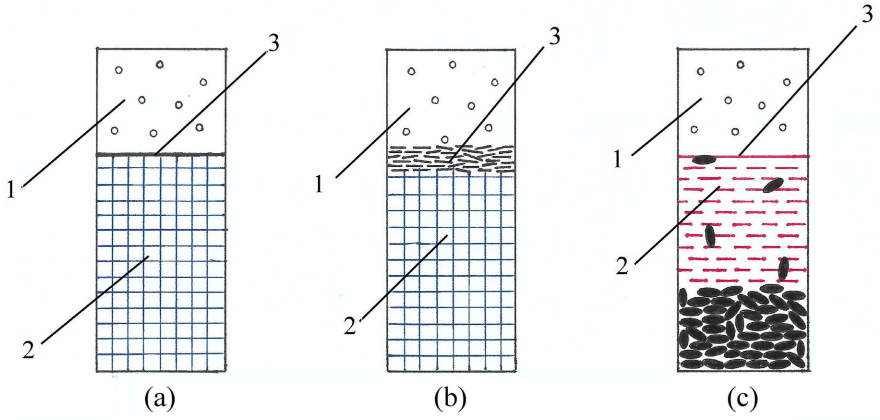
Appendix

The gas/sorbent interface influences both our practical steps and the overall sorption result. Figure A1 shows three types of such an interface, when the sorbent is a getter.



(a) (b) (c)

Figure A1. Gas/chemisorbent and gas/getter reactant interphase boundaries. (a) 1—gas, 2—chemisorbent, 3—thin dense film of products in saturation state; (b) 1—gas, 2—getter reactant, 3—loose slowly growing layer of products; (c) 1—gas, 2—reactive melt, 3—practically clean surface.

In the case of chemisorbents (Figure A1(a)), with the appearance of a continuous thin film 3 that completely isolates the getter material from the gas, thermal activation is usually used to restore the performance of the sorbent material. This is achieved by heating the chemisorbent in a vacuum to 350˚C - 500˚C for diffusion dissolution of the film 3 into the body of the chemisorbent.

Unlike chemisorbents, getters reactants (Figure A1(b)) are quickly covered with a loose and slowly growing layer of products 3 when in contact with gases. Over time, sorption accelerates due to the corrosive decomposition of the getter body [4].

Finally, clearly favorable in terms of sorption is the melt of getters reactants (Figure A1(c)) with its practically clean surface 3, which guarantees the stability of sorption kinetics at the highest possible level. The heating temperature here is three times lower than during thermal activation of chemisorbents.