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## New lithium gas sorbents I. The evaporable variant

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## Abstract

Solid solutions of lithium in Ag and Cu in the form of balls, wires, or strips are convenient sources for depositing lithium films as getters on the walls of vacuum vessels.

Measurement of the  $O_2$ , CO and  $CO_2$  sorption characteristics have shown that these films – e.g. those generated electrothermally from Ag/Li solid solutions – excel the best getters of the Ba-film type or the high porosity getters based on Ti, V and Zr alloys. It has been found that tight lithium films passivate as a sorption depth of approximately 100 Å is reached. Methods for further improvement of the sorption behavior of lithium coatings are discussed.

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## 1. Introduction

Getter technologies currently experience a rapid upsurge. Within less than a decade a large number of metallic gas sorbents of new types have been developed. It is enough to mention here as examples multilayer film coatings in which at least one of the layers serves as a barrier for gases entering the vacuum chamber through its walls [1,2] or protects the getter layer itself from gas poisoning at the stage of the device assembly [3], or gas sorbents with the structure of an isolated dendritic carcass [4] as well as high selectivity getters [5,6].

Here we describe new lithium gas sorbents on the basis of solid solutions of Li in Ag, Al, Au, Co, or Cu [7], which not only work – depending on the temperature – either as evaporable (EGs) or non-evaporable getters (NEGs), but are also the first representatives of passivating getters with a chemically highly active component.

In many applications, where according to the operating conditions temporary contacts between the getter material and the atmosphere are inevitable, passivation is not just useful, but also

0925-8388/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2007.01.158 necessary, because it provides safety and preserves functional material. Together with the activation operation it is an instrument for the sorption process control. Therefore, the availability of a passivating gas sorbent with lithium as the active component could mean an important progress in pertinent technology.

The favorable mechanical properties of solid solutions, which allow comparatively easy shaping of the material into any desirable form, make the new gas sorbents even more attractive. The material can be manufactured in the form of balls, wires, strips, and foils with a dense compact structure, formed by pressing, rolling or drawing the initial homogeneous ingots, which are readily produced by vacuum metallurgy methods [7].

As evaporation of Li from its solid solutions and also sorption of gases by lithium and lithium alloys have their peculiarities, in the present and in the following publications we describe the behavior of lithium alloys in both getter applications, evaporable and non-evaporable, hoping that this will serve for a more effective usage of the new material.

#### 2. Experimental methods

The parent components, Ag (Alfa Aesar, 99.999%), Cu (Alfa Aesar, 99.999%), and Li (Chemetal, 99.9%), were remelted in vacuum to remove volatile impurities and charged in the appropriate atomic ratio under argon into thin walled steel tubes (12.7 mm in diameter), which were sealed off under

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vacuum on both ends. To generate the solid solution, the metallic ampoule with the components was heated in a vertical vacuum furnace to a temperature higher then the melting point of the more refractory component and after an exposure for about half an hour was turned around its vertical axis by 180° several times for homogenization of the melt.

Without being taken out of the ampoules, the ingots were rolled with a press in a hot state in order to obtain strips 2.5–3.0 mm thick. Subsequently, the outside steel envelope was removed. The released semi-ready substrate was either rolled into foil, or cut longwise to produce wires with a square cross-section, which were finally brought to the required diameter by drawing.

Thin films of Li were evaporated from the new alloys onto a borosilicate glass substrate in ultrahigh vacuum to evaluate their gettering properties. Evaporation was done in situ in a getter testing apparatus, which was an all-metal vacuum system. During initial evacuation and evaporation it was pumped with a turbomolecular pump.

A wire with a diameter of 0.5 mm was made from the alloy. It was placed coaxially in a glass cylinder with an inner diameter of 27 mm. The ends of the wire were connected to a power supply for resistive heating to the evaporation temperature. The whole system was evacuated over night (without baking) to a residual pressure below  $1 \times 10^{-6}$  Pa. During evaporation, which typically lasted 10–15 min, the pressure in the system increased into the  $10^{-4}$  Pa region. This pressure increase was partly due to outgassing of the vapor source itself and mainly due to thermal outgassing of power leads and surrounding parts, which were indirectly heated. After switch-off of the heating power the pressure dropped below  $1 \times 10^{-6}$  Pa within few minutes. Sorption tests were started approximately half an hour after evaporation. This time interval was estimated to be enough to cool down the glass substrate with the film to room temperature. In ultrahigh vacuum, thermal energy can be exchanged by radiation only and this is quite a slow process.

The area of the evaporated getter films on the inner surface of the glass cylinder was from 30 to  $45 \text{ cm}^2$ , depending on the length of the vapor source.

The area had to be kept small enough so that the initial getter pumping speed was not larger than molecular conductance for a test gas to the film inside the glass cylinder. Gas transport was limited mainly by the dimensions of the substrate cylinder. In all cases where the gas transport was influencing the measurements the appropriate corrections for the gas pressure above the Li film were made.

The total amount of Li in the film was measured after the sorption test. The glass cylinder was removed from the vacuum system and the film was simply washed from the surface with pure water. The lithium concentration in the aqueous solution was determined with a Flame Atomic Absorption Spectrometer (FAAS—Perkin-Elmer 2380). Lithium compounds contained in the reacted film are non-volatile at room temperature and are readily soluble in water, and therefore the calculated mass of Li dissolved in the water solution is equal to the mass of Li previously condensed as a film onto the support. Concerning the procedure of sorption measurements see Appendix A.

## 3. Physicochemical basics

Among the chemically most active metals, mainly the alkali and alkaline-earth metals, lithium shows the highest capability to interfuse with the metals of other groups in the Periodic Table, and only lithium forms solid solutions in a wide concentration range with some of the metals which themselves are stable in the atmosphere at room temperature. Alloys of this kind, containing the active metal in an inert matrix of a metal solvent appear to be gas sorbents which are more convenient to handle than true intermetallic compounds of the same active components [8] or the so-called supported metals (referring to alkali metal films on solid carriers, e.g., of K/Al<sub>2</sub>O<sub>3</sub> [9]), as well as silicon- or graphite-alkali metal clathrates or intercalates [10]. We consider here the properties of solid solutions using the most studied Ag–Li alloys as an example, but the conclusions are also valid in the case of analogous systems.



Fig. 1. Phase diagram of Ag-Li.

According to the phase diagram Ag–Li (Fig. 1), maximum solubility of Li in solid Ag can reach 61 at.%, but at room temperature the homogeneity boundary of solid solutions is close to 46.5 at.% Li [11]. In the annealed state these alloys are very ductile and are easily treated mechanically at room temperature with the help of standard tools and techniques.

In the subsolidus range, and at average concentrations of Li in the alloys, the partial vapor pressures of the components have a ratio  $P_{\text{Li}}/P_{\text{Ag}} \simeq 10^6$ . At this the value of  $P_{\text{Li}}$  can vary with the temperature from a negligibly small value up to  $10^{-1}$  mbar, satisfying any needs which can appear in practice concerning the deposition rate. More precisely, the vapor pressure of Li over the Ag–Li solid solution with an fcc crystal lattice is described by a formula:

$$\ln(P_{\rm Li}, \, \text{bar}) = \ln(P_{\rm Li}^0) + A + B(1-x)^2 + \ln(x),$$

where

$$\ln(P_{\text{Li}}^{0}, \text{ bar}) = 11.8019 + 0.7530 \left(\frac{T}{100}\right)$$
$$-\frac{19.4268}{T/1000} - 2.0532 \ln\left(\frac{T}{1000}\right)$$

is the vapor pressure of pure Li at  $453.67 \le T$  (K)  $\le 3000$  according to [12], A = 374.5/T - 0.9533, and  $B = -0.5075.46/T + 0.34 \ln(T) - 1.94$  (*T* is the temperature in K, *x* is the mole fraction of Li in the solid solution).

Fig. 2 shows in a graph form the temperature dependence of the lithium vapor pressure for some Ag–Li solid alloys.

In the system Cu–Li the solid solution range according to [13] is limited to the interval 0–22 at.% Li. The vapor pressure of Cu under the temperatures lower than 1300 K is by two orders of magnitude lower than of Ag while the vapor pressure of Li in binary alloys with these metals is approximately the same at equal concentrations. Thus, the lithium vapor pressure above the solid solution of Cu–15 at.% Li in the temperature range from



Fig. 2. Dependence of the vapor pressure of Li above solid solutions of Ag–Li on temperature.

200 to 846 K is equal to

$$\ln(P_{\rm Li}, \, \rm bar) = \frac{-18731.3}{T} + 12.068.$$

It follows from these data, taking into account the high activity of metallic lithium, that solid Ag–Li alloys in the concentration range 0–50 at.% Li as well as solid Cu–Li alloys in the concentration range 0–22 at.% Li, can be used as evaporable getters (EG) with lithium film condensates as the active sorbent phase. Basically, lithium, as well as barium, is able to sorb any gases except noble gases. Lithium compounds with the elements of all common residual gases or their components are known, and these compounds are stable in vacuum at room temperature as well as at higher temperatures [14,15].

Table 1 shows selected results of calculations using FACTSAGE program [16] for the equilibria in the systems Li–O–H–N–C, which give an idea about the affinity of the corresponding gaseous species towards lithium.

The same correlations are shown – in a more convenient form for analyzing vacuum problems – in Fig. 3. On the whole it follows from the thermodynamic estimations that in the temperature range from room temperature to  $\sim 240 \,^{\circ}\text{C}$  lithium can be considered as a potential gas sorbent for a particularly broad application spectrum.



Fig. 3. Partial pressure of some gases in equilibrium with solid Li.

## 4. The gettering model

It is useful to generalize the known facts and ideas about getter materials in the form of a simple sorption model. Usually sorption is understood as a two stage process, in which first the getter surface is saturated with gas molecules and then the volume of the material becomes involved in the process (Fig. 4).

The sorption rate of the first stage is proportional to the number of available sorption sites

$$V^{\mathrm{I}} = V_0^{\mathrm{I}} \left( 1 - \frac{n}{n*} \right),\tag{1}$$

where  $V_0^{\rm I} \sim \varepsilon p$ ;  $\varepsilon$  is a sticking coefficient, which for getters is always smaller than 1, p is the pressure of the gaseous medium, n = n(t) is the current density of adatoms, t is the time, and  $n^*$ is the surface gas density at saturation. The value of  $V^{\rm I} = V^{\rm I}(t)$ changes with time from the maximum value of  $V_0^{\rm I}$  at n = 0, to zero at  $n = n^*$ .

For the second stage, the sorption rate  $V^{\text{II}} = V^{\text{II}}(t)$  is determined by the rate of gas diffusion into solid bodies, and usually  $Q \sim t^{1/2}$  for the mass throughput of the sorbed gas, while the mechanism of the volume sorption depends on the nature of a getter. Chemically active metals (Fig. 4b), which form no solid solutions with gases, bind gases in the form of compounds like

Table 1

Change of the Gibbs energy for reactions of Li metal with some gases in vacuum at the temperatures of 300, 400, and  $500 \, \mathrm{K}$ 

Reaction	$\Delta G_{\rm r}$ (kJ/mol)		
	300 K	400 K	500 K
$\overline{\text{Li}(s) + (1/4)\text{O}_2(g)} = (1/2)\text{Li}_2\text{O}(s)$	-280.945	-274.744	-268.459
$Li(s) + (1/2)H_2(g) = LiH(s)$	-68.325	-60.739	-52.962
$Li(s) + (1/6)N_2(g) = (1/3)Li_3N(s)$	-42.811	-38.737	-34.575
$Li(s) + (1/3)CO(g) = (1/3)Li_2O(s) + (1/6)Li_2C_2(s)$	-150.874	-143.574	-136.230
$Li(s) + (1/5)CH_4(g) = (4/5)LiH(s) + (1/10)Li_2C_2(s)$	-50.140	-45.680	-41.240

(s) and (g)—solid and gaseous state, respectively; the value  $\Delta G_r$  is calculated for 1 mol Li.



Fig. 4. Two types of metallic gas sorbents: (a) the stage of adsorption of gases; (b) alkali, alkaline-earth and rare-earth metals; for simplification only gas diffusion through the layer of reaction products is shown (absorption at room temperature); (c) transition metals, characterized by high solubility of gases (absorption at elevated temperatures).

oxides, nitrides, hydrides, etc., formed on the surface of the metal. Even at room temperature, the layer of products grows fast enough due to diffusion of the reagents through this layer.

On the contrary, another group of getter materials like Hf, Ti, V, and Zr forms with most of the gases solid solutions in a wide concentration range (Fig. 4c). At room temperature, after saturating the surface of the metal with gases, the surface is passivated, but on heating, with activation of diffusion processes, the gases start to dissolve in the crystal lattice, and thereby sorption acquires a volume character.

These two types of behavior of getter materials predetermine the corresponding form of the sorption curves for the case of a smooth atomic surface: continuously descending curves of the form  $(V^{I} + V^{II})$  for active metals, and more abruptly descending curves of the form  $V^{I}$  for transition metals (Fig. 5).

In order to single out the contribution of the *structure* of the sorbent in gas sorption, let us complicate our model (Fig. 4) by replacing the continuous phase boundary vacuum/sorbent by a plane equal in area but perforated (*S*, Fig. 6). Let the new boundary consist of a system of holes with the total area  $S_1$  distributed in a certain way, and a remaining part of the surface  $S_2 = S - S_1$ , which has the properties of transition metals, i.e.  $\varepsilon < 1$ . The density of adatoms at saturation is  $n^*$ , and at room temperature there is no diffusion into the volume. For holes  $\varepsilon = 1$  (which is correct till the equilibrium reaction sets in) and the equivalent surface density of gases at saturation is equal to  $n^*k (1 + \alpha)/\alpha$ , where  $k = S_p/S$ .  $S_p$  is the total area of all the internal voids available to gases, which are situated below the holes ( $\alpha = S_1/S_2$  and  $k \gg 1$ ).

The specific sorption capacity of such a surface, imitating the surface of a porous body, is equal to

$$C_{\rm p} = \frac{C_0 [1 + k(1 + \alpha)]}{1 + \alpha},\tag{2}$$

where  $C_p$  has dimensionality mol/cm<sup>2</sup>, and  $C_0 = n^*$ .

It can be seen that the quantity of sorbed gases is directly proportional to k and thus does not depend on  $\alpha$ , namely,  $C_p \simeq n^*k$ .



Fig. 5. Typical forms of sorption curves as a function of time.



Fig. 6. Structural aspects of adsorption: (a) continuous surface; (b) surface of a porous body: (I) A granule type; (II) "brush" type.

Unlike the capacity, the gettering rate depends on  $\alpha$ , and the more this applies the smaller is  $\varepsilon$ . Thus, for the initial gettering rate we have

$$\frac{V_{\rm p}^{\rm I}}{V_{\rm 0}^{\rm I}} = \frac{\alpha + \varepsilon}{\varepsilon (1 + \alpha)},\tag{3}$$

where  $V_0^{\rm I}$  is the initial sorption rate of the smooth continuous surface. The influence of  $\alpha$  on the value of  $V_p^{\rm I}$  is shown in Fig. 7 demonstrating the obvious fact that with the increase of the fraction of the holes on the surface its pumping action grows as a result of the increase of the averaged sticking coefficient  $\bar{\varepsilon} = (\alpha + \varepsilon)/(1 + \alpha)$ .

The present model takes into account only the surface sorption but even with this limitation it leads to important conclusions:

- 1. According to (2) the capacity of the porous is higher than the capacity of a continuous body with the same surface *S* by approximately *k* times.
- 2. The sorption rate increases with the part of the surface accounting for the holes (Eq. (3)). In cases of larger values for  $\alpha$  and k, immediately after the filling of the area  $S_2$  (Fig. 6) with gas particles, the process is stabilized, because for holes  $\varepsilon = 1$ , and thus their capacity is high. This explains



Fig. 7. Dependence of  $\alpha$  on rate V at different values of  $\varepsilon$ .

the presence of a horizontal region, common for the sorption curves of high porosity materials, in the graph  $V_p-t$  (Fig. 5). It should be pointed out that the given sorption effect is based on purely geometric reasons and does not depend on the nature of the material, i.e. the result for a given material structure will be the same for metals, ceramics or polymers.

- 3. Unlike *k* and  $\alpha$ , porosity, the parameter which is often mentioned in getter certifications [17–19], cannot strictly be correlated with the values *V* and *C*, i.e. it is not informative.
- 4. The values of the coefficients  $\alpha$  and k can be maximized, if the same getter mass is distributed in an ordered way as shown in Fig. 6b(II). This is a structure of a "brush" [20] type consisting of a set of parallel isolated needles or rods of the same diameter, the bases of which stand on the substrate with the tops forming the apparent (virtual) boundary with vacuum. The voids are united into a connected system of slits, reaching towards the vacuum boundary of the voids, which makes the transportation of gas molecules inside the voids easier. The coefficient of the material utilization and accordingly its lifetime increase by many times compared to the getter films produced from powder particles (Fig. 6b(I)).

#### 5. Experimental results and discussion

Oxygen and oxygen containing gases (CO, CO<sub>2</sub>), known for their high affinity to lithium, were selected for the first sorption tests. Dense lithium films from 180 to 350 Å thick, which correspond to 70-140 atomic layers, were studied.

A wire of the composition Ag–25 at.% Li with a diameter of 0.5 mm was suspended along the axis of a glass or metal tube and served as a source of the lithium film deposited on the inner surface of this tube. The wire was directly heated with electric current in vacuum of about  $10^{-6}$  mbar and lithium was evaporated at the temperate of 450–600 °C.

The results of the measurements are given in Figs. 8–12. As expected from the general properties of lithium [21], thin lithium condensates show high sorption activity at room temperature. If we assume, that sorption of  $O_2$ , CO, and  $CO_2$  takes place according to the reactions

$$4Li + O_2 = 2Li_2O$$
  
 $5Li + 2CO = Li_2C_2 + 2Li_2O$ 

AT ' O

$$10\mathrm{Li} + 2\mathrm{CO}_2 = \mathrm{Li}_2\mathrm{C}_2 + 4\mathrm{Li}_2\mathrm{O}$$



Fig. 8. Sorption of  $O_2$  by a Li film at room temperature (the mass of the film is 0.040 mg, the area of the film is  $30 \text{ cm}^2$ ).



Fig. 9. Sorption of CO<sub>2</sub> by a Li film at room temperature (the mass of the film is 0.029 mg, the area of the film is  $30 \text{ cm}^2$ ).

and taking into account the total amount of sorbed gases Q, it is not difficult to define the mass of lithium, which has reacted in each concrete case (Figs. 8–10). The calculations show that about one third of the total amount of lithium atoms in the film took part in sorption, which corresponds approximately to a layer not more than 120 Å thick.

With its sorption activity exhausted, observed from the outside of the glass, the lithium film looked like the initial "mirror" and maintained its color and metallic lustre for several days even after atmospheric air was admitted. In a dry



Fig. 10. Sorption of CO by a Li film at room temperature (the mass of the film is 0.055 mg, the area of the film is  $30 \text{ cm}^2$ ).



Fig. 11. Dependence of the sorption of O<sub>2</sub> by a Li film on time.

atmosphere this state is conserved for an indefinite time. Any further erosion occurring is due to the moisture contained in the air.

This effect represents a case of passivation of the lithium surface in contact with oxygen containing gases at room temperatures. The density of the passivated layer increases approximately by a factor of four compared with the native state of the film. The thickness of the reacted part of the film decreases from 120 Å to approximately 60-70 Å. Since the growth of the product layer takes place at a very small rate, which is smaller than required for the growth of a compact monocrystalline layer, the formed passivated coating is structurally almost defectless.

Since it took at least 30 min from the end of the film deposition period to the beginning of the sorption measurements, at a vacuum of  $10^{-7}$  mbar, the surface of the condensate had enough time to become covered with a monomolecular layer of the residual gases. Therefore all the sorption curves given in Figs. 8–12 refer to absorption and not to adsorption. However, in the given context the form of the curves for the lithium films is surprising: curves V - Q in Figs. 8–10 clearly show an extended horizontal region, while the curves Q-t in Figs. 11 and 12 evidently do not follow a parabolic but a linear sorption law. These phenomena and also the high pumping rate require an explanation which can be based on the following chemical arguments.

All the products of the sorption reactions between lithium and reactive gases can be considered as ionic compounds [22]. The Li<sup>+</sup> cations are small, feature a big Coulomb potential and therefore have a strong polarizing effect on the gas molecules, facilitating their dissociation into atoms and with this preparing them for diffusion into the film. In addition there are favorable transport conditions. It is reasonable to suppose, that besides the usual diffusion of cations, considered for the oxidation of metals [23,24], in the given case a counter flow of atoms of the reacting gases also takes place and this diffusion of gases through the layer of the takes place according to an interstitial mechanism. The O–O distance in



Fig. 12. Dependence of the sorption of CO<sub>2</sub> by a Li film on time.

Table 2
CO sorption by planar getters of different composition

Sorption characteristic	Ba–film	Li–film (this work)	HPTF strips
Gettering rate, $G_A$ (mbar L/s cm <sup>2</sup> )	0.035 [26]	0.28	0.30 [18]
Sorption capacity, $C_m$ (mbar L/mg)	4.2 × 10 <sup>-2</sup> [26]	$1.8 \times 10^{-1}$	7.5 × 10 <sup>-6</sup> [18]

the structure of a monoxide Li<sub>2</sub>O, which is the basis of the growing layer of the products, is 3.27 Å [21], from where we can derive that the volume of octahedral voids ideally corresponds to the size of an oxygen atom (the radius of the latter is 0.66 Å, whereas the radius of the inscribable sphere for the mentioned voids is 0.67 Å).

This hypothesis still needs experimental confirmation.

Normalized sorption characteristics of lithium films are compared regarding CO sorption as an example in Table 2 with the corresponding values for barium films and for the so-called HPTF films based on Ti, V, Zr and other transition metals [18,25].

The data show that according to the sum of the sorption parameters lithium obviously performs best as a getter, having only a slightly lower sorption rate than HPTF. However, this advantage of HPTF materials is only due to their structure rather than to their chemical nature: high porosity layers of transition metals are compared to dense lithium films.

The analysis of scanning electron microscopy photos of HPTF–materials [18] allow defining  $\alpha = 1$ , and taking into consideration the data [27–29] it is possible to use  $\varepsilon = 0.1$  as an averaged sticking coefficient for the main residual gases on a smooth surface of transition metals. Then according to (3) we get  $V_p^I/V_0^I \simeq 6$ . This means that the value of 0.30 mbar L/s cm<sup>2</sup> mentioned in column 4 of Table 2 is practically determined by purely geometrical parameters: by the presence of holes on the surface with  $\varepsilon = 1$  and with high sorption capacity (dense films of the same alloys would have a gettering rate 0.30:6 = 0.05 mbar L/s cm<sup>2</sup>). This also means that in the case of lithium there is also a substantial reserve for enhancement of the sorption properties of film coatings by varying their structure. Given the practical importance of this issue, let us discuss it in more details.

There are three ways of increasing the effectiveness of film getters by means of the structural factor. They are the usage of porous films of a granule type (a), of ordered structures of a "brush" type (b), and of periodically renewed thin layers (c).

(a) HPTF materials (Fig. 6b(I)) and getter films of group IIA metals have this kind of structure in the form of a conglomerate of powder particles connected by diffusion bridges. Diffuse deposits of group IIA metals are obtained by evaporation of the metal in dilute gas atmosphere, usually Ar or N<sub>2</sub> [17,30,31].

A weak point of these films which is shortening their lifetime are diffusion bridges, where saturation of the volume with gases, and, consequently, embrittlement of the material with its further destruction take place long before the theoretical limit of the sorption capacity is reached. Besides, for active metals with their high values of  $\varepsilon$ , disintegration of the structure does not produce such a strong effect as for transition metals with small  $\varepsilon$ , because the increase of the sorption rate is determined by the ratio  $\overline{\varepsilon}/\varepsilon$  and it is not large for large  $\varepsilon$  (Fig. 7). In fact, in accordance with (3) diffusive films of barium compared with dense films show the increase of the initial sorption rate for CO only by two times [31].

(b) "Brush" structures in short represent a considerable step forward compared to granule type structures. Besides the improvement of the sorption properties, these structures due to their dimensional uniformity defer the time boundary for the appearance of loose particles and for the pealing off of the material to such an extent, that this phenomenon is no more a problem.

Film structures of a "brush" type can be grown by crystallization from a vapor or from a melt under a controlled heat dissipation from the substrate through vacuum evaporation of a more volatile impurity [4,20], which during solidification is pushed to the intercellular or interdendritic space.

(c) Continuous or periodical deposition of thin lithium layers on the walls of a vacuum vessel is a further development of the idea of a titanium vacuum

pump, but with a more active gas sorbent. The thickness of the deposited layers can be set in the range from a monoatomic layer to  $\sim 120$  Å, which is the limit of gas permeability according to our measurements.

The low temperatures of lithium evaporation, from 450 to 600 °C, and also the high specific resistance of solid solutions of metals (for the 75 at.% Ag/25 at.% Li alloy, the value of  $\rho$  is 31  $\mu$ Ω cm) make expensive heavy-current power supply units unnecessary. Further, if needed, lithium condensates and products of their reactions with gases can be removed completely and without any consequences for the metallic or other substrate by rinsing with water or alcohol. And, finally, another advantage of lithium is the easy ionization of its vapors accompanied by a strong increase of the reactivity of the gaseous species. This is an aspect, which may be important for further developments of lithium vacuum pumps.

## 6. Conclusions

- 1. Sorption of dilute oxygen or oxygen containing gases (like CO, CO<sub>2</sub>) by lithium has a volume character and involves layers of a thickness of about 100 Å, beyond which passivation of the film takes place.
- 2. The sorption rate is unusually high even at the internal absorption stage which can be ascribed to the catalytic activity of Li<sup>+</sup> cations and favorable diffusion characteristics of the sorption products.
- 3. The factors which are limiting the depth of the passivated layer are not clear and require further studies.
- 4. One of the most promising mode of practical application of lithium getter films is the periodical deposition of the metal in the form of dense layers not more than 120 Å thick.
- 5. The analysis of the sorption process based on the simple gettering model shows that the optimal getter film structure is the "brush" type structure.

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# Appendix A. Measurement of sorption properties of getter films

The sorption properties of evaporated Li films were measured in a getter test apparatus, which was constructed according to ASTM Recommendations [32]. This document has been written for non-evaporable getters (NEGs), but can be also applied to evaporated getter films. According to the Recommendation a getter is exposed to a well-known mass throughput Q of pure test gas, measured in mbar L s<sup>-1</sup> at 23 ± 2 °C. Equilibrium pressure *p* above the getter surface is established according to the instantaneous getter pumping speed *G*, measured in  $L s^{-1}$ 

$$G = \frac{Q}{p}.$$

The gas sorption capacity *C* is a cumulative quantity of gas sorbed by the getter while at operating temperature until the pumping speed drops to 5% of the initial value (terminal pumping speed  $G_{\rm T}$ ). It can be calculated by integrating the mass throughput:

$$C = \int_0^\tau Q \,\mathrm{d}t,$$

where  $\tau$  denotes the time required until the terminal pumping speed is reached. If the mass throughput is constant during the test, then *C* is simply given by:

$$C = Q\tau$$
.

It is convenient to normalize the getter pumping speed by dividing *G* by the geometric area *A* of the film:

$$G_A = \frac{G}{A}.$$

Similarly, the sorption capacity *C* of the film can be normalized by the mass of active material *m*:

$$C_m=\frac{C}{m}.$$

Such normalization of pumping speed and sorption capacity allows comparison of sorption properties of various films having different areas and different thicknesses.

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