GETTERS

Function: Permanent removal of gases by formation of stable compounds.

(1) Remove gases
(2) Maintain vacuum
(3) Sorption of bursts (at switch on and during life).

Active element in most getters is barium which getters most gases. (Argon and Methane are not gettered and constitute most of gases left in tubes after gettering.)

The barium forms oxides, carbides.

Two types of getters:

1. Evaporable	2. Non-Evaporable
Calcium	Zirconium
Strontium	Titanium
Barium	Thorium

What is wanted in a getter:

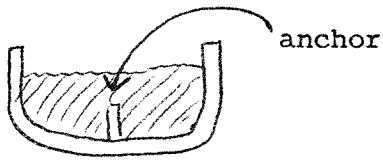
Chemical stability
Mechanical stability
Absence of particles
Easy and uniform activation
Low gas emission
Uniformity
Easy and safe handling
High sorption rate and capacity
Low vapor pressure
Low equilibrium pressures
No peeling or flaking

Getter fabrication:

Use $BaAl_4$ in powder form which is pressed into a stainless steel container (normally a ring configuration for most CRTs.)

Getter can be either endothermic or exothermic. They are normally endothermic but can be made exothermic by the addition of nickel powder (50%).

Some construction techniques to avoid particles:

(a) 

Use of anchor in channel helps retain any remaining material after flashing in the channel.

(b) 

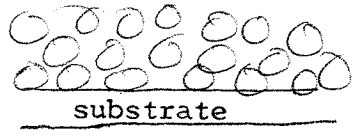
Use of reflector allows better heat uniformity.

Getters can be gas doped (nitrogen, argon) to prevent heavy evaporation in center of tube and to provide a more porous type of flash.

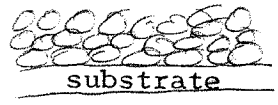
Normally in evaporation of gas doped getter, the initial evaporation will form a gas which will then tend to disperse the getter material as it is then evaporated.

Temperature of substrate onto which the getter is being evaporatedd will determine type of getter surface formed.

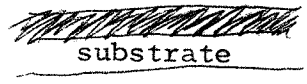
at 25°C: Porous surface, good gettering



At 100°C: Partially sintered surface, poor gettering action



Higher temperatures: Completely sintered surface, very little gettering action



When to use non-evaporable (bulk) getter:

1. Low volume
2. Absence of surface
3. Barium pressure too high
4. Low quality of getter material

Normally used in wires, strip or powder form.

saes getters

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A Non-evaporable Getter for Low Temperatures

BY

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TECHNICAL REPORT TR 25

TP 93

A Non-evaporable Getter for Low Temperatures

1. - Introduction.

The object of the getter in any vacuum device is to permanently remove from the gaseous phase any gas released from its constituents during life. By so doing the getter maintains the necessary low pressure or gas environment essential for good functioning of the device. In general, when space is available and device characteristics permit, the best overall getter is a barium film. Even in numerous special tubes such as travelling wave tubes, phototubes, vacuum switches or interrupters, ceramic tubes, magnetrons, klystrons, X-ray tubes, gas or vapour tubes, etc., it is often desirable to employ flash getters due to their good room temperature activity. However, this is not always possible due to the low volume available, the absence of a suitable surface on which to deposit the film, the high vapour pressure of barium which through sublimation and migration may cause inter-electrode leakages or stray capacitance effects, the low quantity of getter material which may not ensure sufficient tube life, etc.

To overcome these difficulties non-evaporable getters are therefore employed, they are usually called bulk getters. These getters are normally based on alloys from metals of the IV A group and thorium or even on the elements themselves (1-17). The reactions of the various gases with these metals are such as to produce solid solutions for hydrogen and interstitial compounds for the other gases. Efficient bulk getters should possess a high sorption capacity and a high gettering rate. The gettering rate should remain high throughout the life of the getter and should be independent of the condition and temperature of the ambient in which the getter is located. In fact the ideal getter should always function both during short or long term room temperature storage as well as during continuous or intermittent operation at high temperatures. In all the bulk getters used up to now the whole of the volume of the material has been involved in the gettering process when the temperature of the getter was sufficiently high (in excess of 300-400°C). At these high temperatures the rate limiting step is the bulk diffusion or the grain boundary diffusion depending on the conditions prevailing. However, since at lower temperatures surface reactions alone are responsible for the gettering process, it is necessary that these surface reactions be promoted to improve the gettering rate. This can be achieved by increasing the surface of the getter without, however, increasing its physical dimensions. A first significant practical step in this direction has been made with the coated getters (18) developed by Kindl and Rabusin and in a more scientific but less practical way by the porous type getters of Hansen (9, 10). In the present contribution we wish to report some preliminary data which characterizes a high surface area low temperature getter now being produced by SAES Getters under license from Siemens AG.

2. - The St 171 Getter Material.

This new bulk getter material, designated St 171™, makes use of zirconium powder as

the active element. The zirconium powder is sintered at high temperatures in the presence of graphite. The getter mass obtained, as a result of the proprietory techniques employed in the sintering process, has a large surface area and a high porosity though presenting good mechanical strength.

The porosity of the St 171 getter material is clearly observed, for example, on Scanning Electron Microscope photomicrographs (Fig. 1)

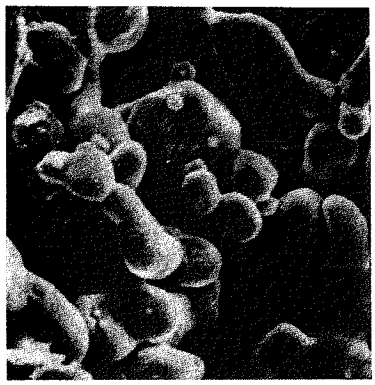

FIG. 1. — Photomicrograph (x 1500) of St 171 getter surface.

which show the presence of channels departing from the surface toward the interior of the getter. A more precise study of the porosity of the getter material has been made using a Hg porosity meter *. This study has shown that the porous structure accounts for 50 % of the volume of the getter mass and that the pore size distribution is as shown in Fig. 2. It will be noted that the pore size present in the

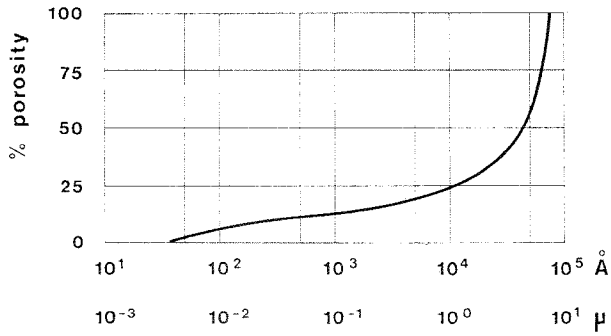

FIG. 2. — Pore size distribution of St 171 getter material as obtained with a Hg porosity meter.

(*) Carlo Erba Porosimeter Mod. 70.

getter mass covers the whole practical measuring range of the instruments employed, i.e. from 7.5×10^4 to 40 Å. As a result of this very high porosity most of the bulk of the getter material is available for surface gas reactions. The actual surface area available for these reactions has been measured using the BET technique with Kr (19). The results obtained show that the surface area of the zirconium present in the sintered mass is practically the same as that of the original zirconium powder before sintering.

To investigate if the porosity and the surface area observed for the St 171 getter material are in fact available for gettering a series of tests have been conducted. These tests employed samples in which, while maintaining a constant geometric surface area, different quantities of getter material were used. These samples were made by sintering different quantities of getter material within metallic cylinders open only at the top. In Fig. 3 the gettering rate for CO at room temperature is plotted as a function of the quantity of gas sorbed on equal density * (1,9 g/cm^2) samples of « porous » St 171 and pure « non-porous » Zr sintered materials. These gettering rate measurements have been carried out using the dynamic technique (20) at constant CO pressure

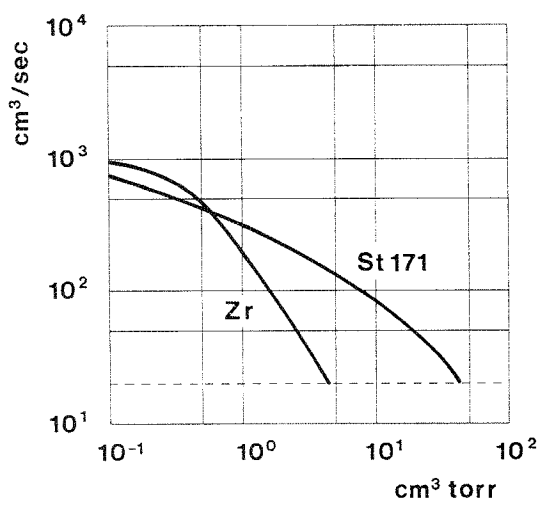

FIG. 3. — Room temperature CO gettering characteristics for high « density » samples.

(*) Mass of getter material/geometric free surface of getter material.

(3×10^{-6} torr N_2 equivalent)* on the surface of the getter material, which had been previously activated as described later. The curves reported in Fig. 3 clearly show the porosity of the St 171 material as referred to pure Zr. If it is assumed that the quantity of CO sorbed when the gettering rate has fallen to 20 cm^3 sec^{-1} is a meaningful parameter to consider in order to characterize these getter materials, the plots of Fig. 4 may be constructed in which

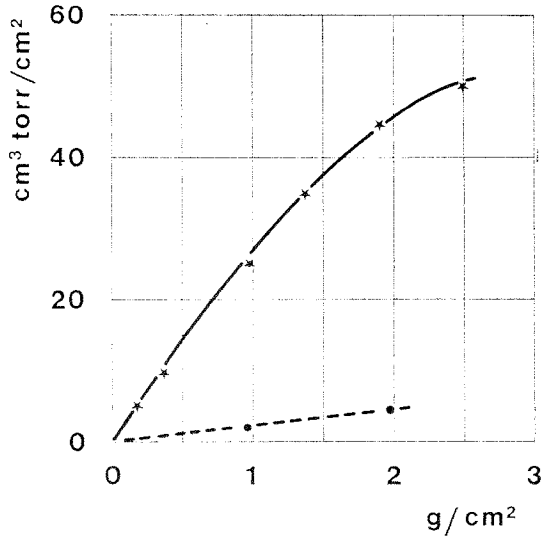

FIG. 4. — Characteristic quantity sorbed as a function of getter material density.

the « characteristic quantity sorbed », as defined above, is plotted as a function of the « density » of getter material.

These results indicate that, with the St 171 getter material, there is a large continuous increase in characteristic capacity with increase in material density. For pure Zr the bulk of the sintered material takes very little part in the gettering action. The quantity of CO chemisorbed, if compared with the possible number of Zr atoms on the exposed surface of the St 171 getter material, indicates that each CO molecule seems to be associated with four Zr atoms, as may be calculated from the data found by Hansen for his porous getters (9, 10, 21).

(*) All experiments reported have been carried out under these conditions.

3. - The practical use of the St 171 getter material.

The St 171 getter material may be used in a variety of practical getter devices. Two of these are shown in Fig. 5. Fig. 5a shows a cross-section through a traditional ring type getter, filled with St 171 getter material,

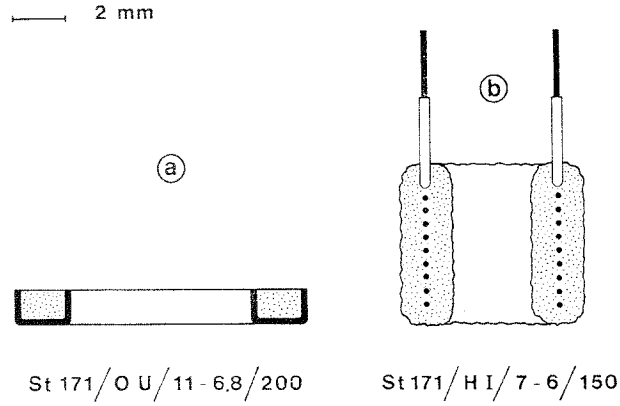

FIG. 5. — Cross-section through practical devices using St 171 getter material.

suitable for induced radio frequency heating. The ring container must be of a high melting point refractory material. Fig. 5b shows a cross-section through St 171 getter material mounted on a tungsten heater which, besides giving mechanical support and strength to the getter material, is also used to heat it whenever required.

In the present work, having previously shown that over wide « density » limits there is practically no difference in the sorption characteristics of the St 171 getter material, due to its high porosity, we have chosen to characterize this low temperature bulk getter in the form of the device of the type shown in Fig. 5b. This device has a density which falls at about 0.15 g/cm^2 in Fig. 4. The standard getter device chosen has overall dimensions of 7 mm diameter and 6 mm height. The geometric surface area is 2 cm^2 while the BET surface is 3300 cm^2 for 350 mg of St 171 getter material.

4. - Study of activation conditions.

Using the well known dynamic sorption technique at constant pressure on the getter (22) the gettering characteristics for CO, N_2 and H_2 have been studied at room temperature and at 400°C after various activation treatments. The sorption curves obtained, which show the gettering rate as a function of the sorbed quantity, are of the type illustrated for CO in Fig. 6. The characteristic quantity sorbed, to

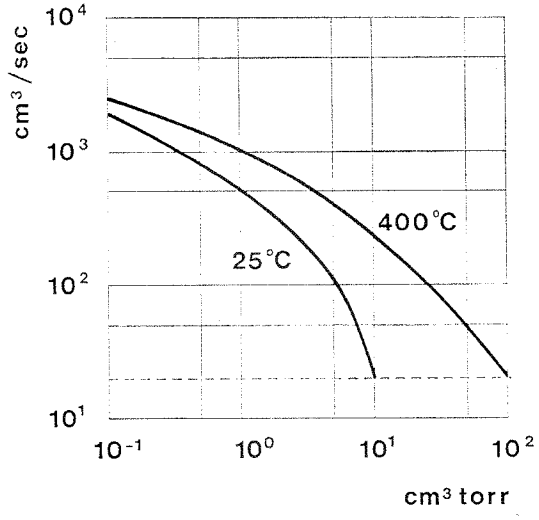

FIG. 6. — Typical CO sorption curves for standard St 171 getter.

which reference will often be made, is that corresponding to a gettering rate of 20 cm^3/sec.

The St 171 getter material, like all other non-evaporable getter materials, must be activated to enable it to function as a getter. The activation process must be carried out by heating under vacuum at a temperature, and for a time, such that from the surface of the getter material the thin protective layer, formed at room temperature during air exposure after the sintering process, is removed. To determine these conditions of activation various standard getters have been tested using different combinations of time and temperature. The results obtained for the characteristic quantities of CO sorbed at room temperature and at 400°C are shown respectively in Fig.s 7 and 8. It can be observed that appreciable clean up of the surface begins to manifest itself from about 600°C and increases continuously with temperature. The best activation conditions are reached at about 900-1000°C. The influence of the activation time is seen to decrease at increasing temperatures. The results of this behaviour is observed when using the getter at room tempera-

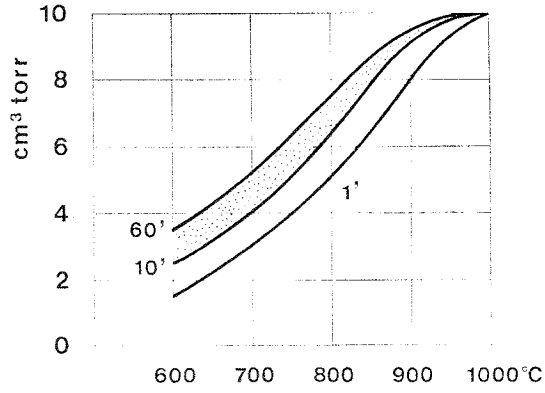

FIG. 7. — Characteristic quantity of CO sorbed at room temperature as a function of the activation temperature for different activation times.

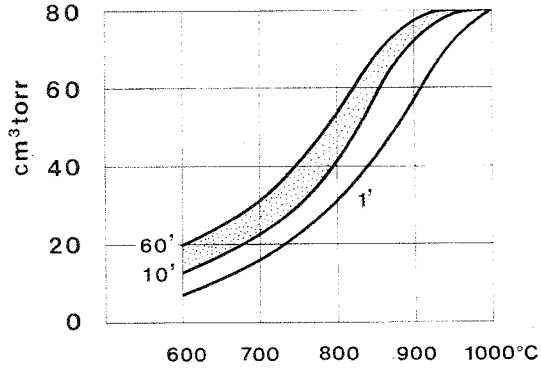

FIG. 8. — Characteristic quantity of CO sorbed at 400°C as a function of the activation temperature for different activation times.

ture or at 400°C. The activation behaviour has also been studied for N_2 and H_2 and it has been observed that it is parallel to that shown for CO.

All these data have been obtained by activating at pressures which were never in excess of 10^{-6} torr. Using activation conditions of 900°C for 10 minutes a study has been made on the influence of the CO pressure during the activation process. The results obtained in this case

are illustrated in Fig. 9 which shows the room temperature CO sorption characteristics of the standard St 171 getter device activated in the presence of CO pressures from 10^{-5} to 10^{-3} torr. Such pressures were maintained throughout activation. It will be observed that, even in the worst of these conditions, while there is an appreciable reduction in speed, the capacity is not influenced to the same degree.

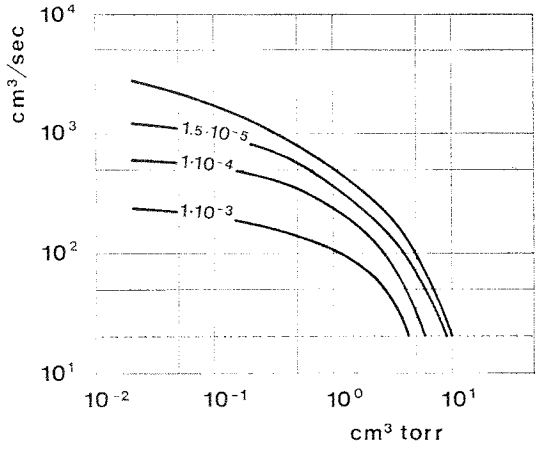

FIG. 9. — Room temperature CO gettering characteristics of the standard St 171 getter device activated at 900°C for 10 minutes in the presence of different pressures of CO.

In practice these limiting conditions should never present themselves during device processing except in the case of leaky devices! Hence, even if the pressure during activation may initially reach the values studied, the pressure will decrease during processing. The getter therefore reaches the end of the activation at such low values of pressure that the full gettering characteristics are restored.

The case may, however, arise in which this type of getter is mounted in a device which, as a final assembly step before pumping, requires a temperature treatment under forming gas. To investigate the effect of such a treatment some getters have been heated in forming gas (80 % N_2 + 20 % H_2: dew point — 50°C) with the following temperature cycle: 10 minutes to reach 800°C, 800°C maintained for 60 seconds, 10 minutes from 800°C to room temperature. Getters which have been treated in this way show a certain residual activity if, during subsequent vacuum processing, they are taken up to at least 600°C for 20 minutes. It is possible that good sorption characteristics can be re-established if the successive vacuum treatment occurs at higher temperatures for longer times. In fact, the low activity measured is essentially due to saturation with hydrogen which, being reversibly sorbed, can be totally removed under suitable conditions. It may be that such a release of hydrogen during device processing could have beneficial effects on the final product obtained.

In many of the activation processes carried out simultaneous mass spectrometric analyses were run. These have shown hydrogen to be the predominant gaseous species emitted by this type of getter.

5. - Room and high temperature gettering characteristics.

The gettering characteristics of these getters for different gases at room temperature and at higher temperatures are shown in Fig.s 10 and 11 respectively. The getters used in these

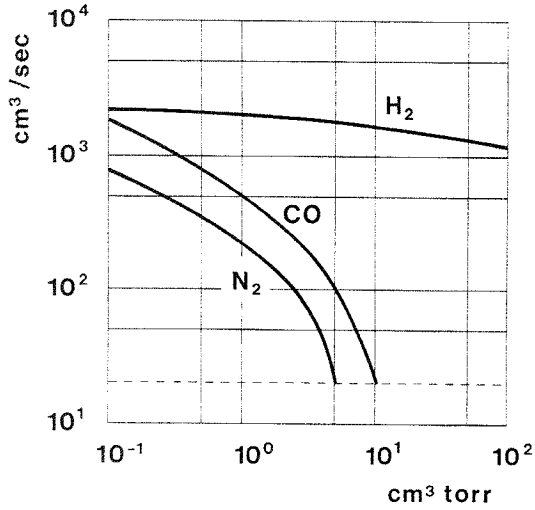

FIG. 10. — Room temperature gettering characteristics for different gases on St 171 standard getters.

tests are still of the type shown in Fig. 5b and were activated at 900°C for 10 minutes under a pressure lower than 10^{-6} torr. From these figures it will be appreciated that the sorption

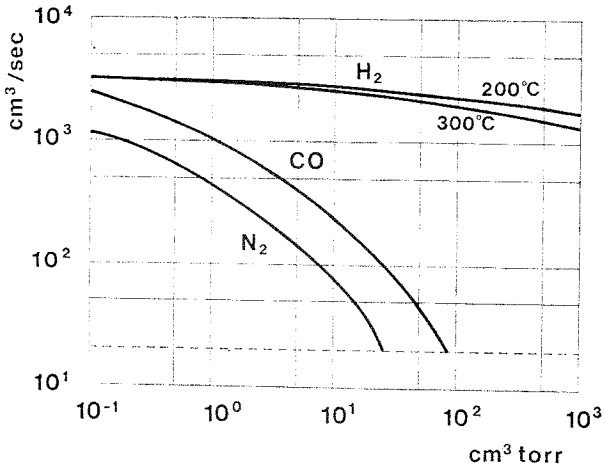

FIG. 11. — High temperature gettering characteristics for different gases on St 171 standard getters.

temperature has practically little influence on the gettering rates while it introduces appreciable variations on the sorption capacity. For these gases, which form interstitial compounds, this is due to diffusion processes becoming important at these higher temperatures. While for hydrogen, which forms a solid solution, extremely large capacities are already available at low temperatures. However, on increasing the temperature from 200 to 300°C the increasing equilibrium pressures, at the concentrations and pressures considered, begin to influence negatively the sorption capacity. For hydrogen it has been impossible, in practice, to reach saturation quantities (at 20 cm^3/sec).

6. - Discussion.

The characteristics just illustrated for St 171, the new getter material particularly useful for room temperature operation, may now be usefully compared with those of the St 101® nonevaporable getter which, for years now, has been recognized as one of the best nonevaporable getter materials commercially available.

This comparison has been carried out using the getter devices show in Fig. 5a so as to avoid interference from other parameters. The filling with getter material is such that the same « density » is present of St 171 material as of St 101 alloy. The room temperature gettering characteristic for CO are illustrated in Fig. 12. It will be observed that the gettering rates are initially the same while the sorption capacity for St 171 getter material is about a factor of 4 greater, at the terminal velocity considered, due to the greater porosity and real surface area of the St 171 getter material. In this same figure are also reported the gettering characteristics of one square centimeter of coated St 101 getter where the « density » is implicitly lower by a factor of about 4 with respect to that of the St 101 alloy

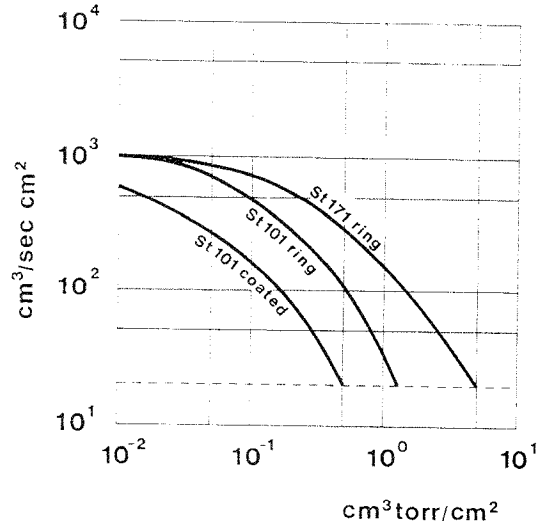

FIG. 12. — Room temperature CO gettering characteristics on different getter devices.

mounted in a ring. This may be easily overcome by pleating as realized in SORB-AC® cartridges. A comparison between these three curves underlines the importance and necessity of having a high surface area and high porosity for good gettering characteristics at room temperature.

If these factors are of paramount importance at low temperature they become less decisive at higher temperatures where diffusion processes begin to become appreciable (1). In these conditions the St 101 alloy overcomes its lack of porosity as shown clearly by the data

reported in Fig. 13, where the gettering characteristics for CO at 400°C are depicted for the same getter devices previously considered in Fig. 12.

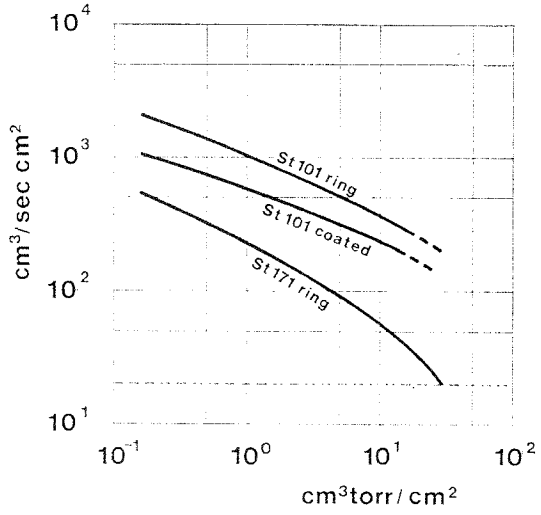

FIG. 13. — CO gettering characteristics on different getter devices at 400°C.

The same type of comparison has also been carried out using N_2 and H_2. The results obtained, in terms of the characteristic capacity, are reported in Tables I and II for room temperature and high temperature operation respectively.

In Table I the data relative to a compact barium film of 0.02 mg « density » is also reported. The superior behaviour of the St 171 getter material at room temperature, even with respect to a barium film, is apparent. For H_2, due to the high sorption capacities available with these bulk getters it has not been possible, at the moment, to establish « characteristic capacity values ». The values reported in parenthesis have been extrapolated from other data available in our laboratories and are to be considered as indicative. Nevertheless it can be observed that these bulk getters are in all case very competitive even with barium films.

TABLE I.

Comparison of room temperature capacity for various getters.

getter type	capacity at 25°C (cm^3torr/cm^2)		
	CO	N_2	H_2
St101 coated	0.5	0.15	20
St101 ring	1.3	0.5	> 20 (100)
St171 ring	5	2	> 20 (100)
Ba film	0.5	0.1	2.5

At 400°C, as show in Table II, the situation for CO and N_2 is now in favour of the St 101 getters as referred to the St 171 getter. For hydrogen, the even greater sorption capacities now available make a quantitative comparison at present impossible. For all gases the values given in parenthesis have been extrapolated from data available in our laboratories and again the must be considered as indicative.

TABLE II.

Comparison of high temperature capacity for various getters.

getter type	capacity (cm^3torr/cm^2)		
	CO	N_2	H_2
	400°C	400°C	200°C
St101 coated	> 30 (70)	> 15 (30)	> 100 (200)
St101 ring	> 30 (120)	> 15 (50)	> 100 (500)
St171 ring	30	12	> 100 (500)

7. - Conclusions

Comparing the gettering rate and sorption capacity of the various getters studied, the room temperature superiority of the getters using St 171 getter material is evident when reference is made to the same unit geometric surface area exposed. A comparison, from the point of view of the volume occupied by the different getters, will show equivalence between coated St 101 alloy and St 171 material. At

higher temperatures the superior characteristics of the St 101 alloy are obvious also when considering equivalent geometric surface areas.

The getters produced using St 171 material are rather expensive due to complex production procedures and the especially selected materials employed in their manufacture. Their use is therefore suggested particularly in those special tube applications when a very clean getter with high gettering characteristics at room temperature during shelf life or during functioning is required to achieve and maintain the necessary ultrahigh vacuum ambient.

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