High-Porosity Thick-Film Getters

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Abstract—**The difficulties in finding a suitable unoccupied volume to accommodate a nonevaporable getter (NEG) in the restricted spaces of certain devices may sometimes limit their use. Moreover, the getter porosity often has to be maximized to provide the best gas sorption performance. A new getter family is presented based on highly porous getter coatings having a thickness range of 50-150 μm. They are obtainable on almost any metallic surface (even device parts) and are suitable as a solution to fit special geometry and high sorption speed requirements. As is known, to become active, getters need to be heated in vacuum for times and temperatures that are to be specifically selected to be compatible with the various application constraints. The materials of this getter family can be of different natures to cope with this need. Practical use considerations are given. The sorption performance of this new getter family, for various gases (CO, H_2, CH_4), are reported and discussed together with other characteristics such as porosity and mechanical stability.**

I. Introduction

IN vacuum devices there are often problems for getter material accommodation due to limited available space. Restricted spaces may not allow the use of evaporable getters [1], which require large surfaces on which they can be deposited as a film. At the same time, nonevaporable getters, which are usually prepared in limited configurations (by pressing or mechanically coating powders of getter materials), are quite compact and not always compatible with small and specific geometries. A proprietary technique is used to manufacture this new family of getters and provides getter coatings in a large variety of configurations and with highly porous structures. These coatings, with a range of thickness typically from 50 to 150 μm, can be deposited on almost any metallic substrate including device parts. The porous structure of this getter family ensures a large available surface for the sorption process. As a result of this high porosity, these materials have very good gettering performance even at room temperature.

In order to become active, the getter material must be heated in vacuum for a suitable temperature and time that can be selected to be compatible with the various application constraints. Two different getter compositions are presented: one activatable at relatively high temperatures and another useful for those applications where activation can only be performed at relatively low temperatures. Practical use considerations are given.

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The pumping performance of these getters for various gases (CO, H_2, CH_4) in different working temperatures (25 and 150°C) has been studied.

Considerations of the influence of coating thickness on the getter sorption characteristics is also given. The good mechanical stability of this family of getters, mainly due to the sintering process they undergo, is also discussed.

II. Structural Configuration

The new getter family material is based on a powder mixture of Ti and Zr_{84}–Al_{16} (St 101) or Zr_{70}–$V_{24.6}$–$Fe_{5.4}$ (St 707) getter alloys in the weight ratio typically of about 7:3. These mixtures, named St 121 and St 122, respectively, are deposited onto a metallic substrate in the shape of strips, discs, cylinders, etc., by means of a proprietary coating process. This produces coatings with a thickness in the range of about 50–150 μm. The precise control of the coating deposition process was used to prepare samples of different thickness (50, 75, and 100 μm) for the tests reported below. Other thickness values can be obtained depending on the application. The getter coating is then heated for controlled sintering in a high-vacuum system in the temperature range of 800–900°C. The presence of the Zr alloys acts not only as a getter but, at the same time, suitably controls the sintering rate of the Ti powder. This results in a getter coating with a very porous structure (50–60 percent) combined with good mechanical stability [2].

Coatings have been successfully applied to substrates made of Ni, nickel-chrome, SS, Mo, Ti, and Zr. On each of these substrates the getter coating exhibits strong adhesion due to the production of a diffusion layer at the interface during the high-temperature sintering [2].

III. Materials

The intrinsic gettering characteristics of these new getters depend not only on the titanium powder but, to a larger extent, on the nonevaporable getter alloys used in the getter mixture [3], [4]. The mixtures (St 121 and St 122 getter) were tested to study the influence of the two Zr-based alloys.

The St 101 gettering alloy has been used as a "general purpose" nonevaporable getter material for years in various applications [5], [6]. This getter can be considered a relatively "high activation temperature getter." The activation temperature can range, for example, between 700 and 900°C for times of a few minutes to tens of minutes. The activation is performed using a suitable combination of temperature and time to remove the layer of surface

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oxides, nitrides, and carbides by diffusion into the bulk and provides a "clean" metallic surface ready to react with the impinging gaseous molecules. Depending on the diffusion constants of the getter materials, for the elements mentioned, we can have a more or less effective "cleaning" of the surface during the activation process. The diffusion rate increases thus raising the temperatures. The activation of the getter must be done when it is used for the first time or whenever exposed to air.

The St 707 getter alloy has been developed more recently [4] and can be considered to be a relatively "low-temperature-activable getter," inasmuch as the activation process can be performed at 200–500°C for a few minutes or hours. It is often used as a getter for *in situ* pumping during vacuum device processing [7].

IV. Sorption Characteristics

A. Tests

In vacuum devices, the main gases present in the residual atmosphere are usually H_2 and CO when metallic components are particularly used [8]. Also, CH_4 becomes important after baking. The sorption characteristics of the getter types under investigation therefore have been studied particularly for the above mentioned active gases; they are either permanently sorbed by the getter material or reversibly sorbed (H_2). Also, hydrocarbons (especially CH_4) are present in vacuum devices in small amounts. These are not normally considered to be "active" gases from the getter point of view; however, by heating it is possible to crack their molecules on the getter surface (or on heating elements) and therefore some pumping is obtained [9]–[12]. The gettering effect on CH_4 has been studied for the present getter family.

The following tests have been performed on getter samples having a coating thickness of 100 μm:

1) sorption of H_2 and CO at 25°C at different activation temperatures,
2) sorption of H_2 and CO at 150°C, and
3) sorption of CH_4 as a function of temperature.

Further tests have also been made to study the effect of the getter coating thickness (50–75 and 100 μm) on the sorption performance (test gases: CO and H_2 at 25°C). Some tests have also been carried out to see how St 121 getters can withstand heat treatment in air without drastic damage.

B. Experimental Results

The results of tests on the sorption of H_2 and CO at 25°C at different activation temperatures performed on St 121 and St 122 getters (thickness of 100 μm) at 4×10^{-4} Pa are shown in Figs. 1 and 2. The pumping speeds for H_2 and CO for the getter samples as a function of the sorbed quantity have been measured by means of the "dynamic flow method" [11]. While the performances of both the getter materials are practically the same if activated at 500°C for 10 min, the St 121 getter is more efficient than the St 122 getter when activated at 750°C for 10 min. The opposite results hold if the getters are activated at 350°C for 3 h (as could be the case, for example, where the getter is used as an *in situ* pump during the vacuum device baking process [7]).

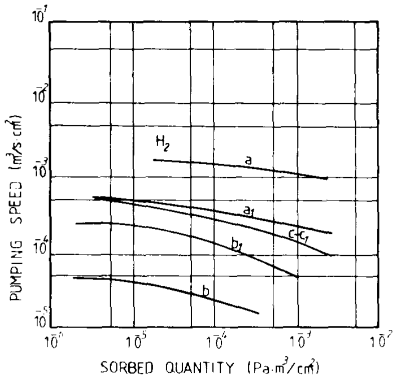

Fig. 1. Hydrogen sorption characteristics at room temperature for St 121 and St 122 getters after different activation conditions. Curve *a*: St 121 getter activated at 750°C for 10 min. Curve *b*: St 121 getter activated at 350°C for 3 h. Curve *c*: St 121 getter activated at 500°C for 10 min. Curve a_1: St 122 getter activated at 750°C for 10 min. Curve b_1: St 122 getter activated at 350°C for 3 h. Curve c_1: St 122 getter activated at 500°C for 10 min.

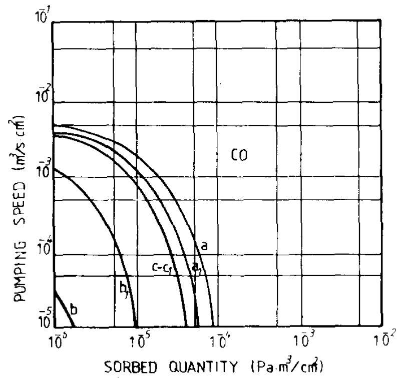

Fig. 2. CO sorption characteristics at room temperature for St 121 and St 122 getters after different activation conditions. Curve *a*: St 121 getter activated at 750°C for 10 min. Curve *b*: St 121 getter activated at 350°C for 3 h. Curve *c*: St 121 getter activated at 500°C for 10 min. Curve a_1: St 122 getter activated at 750°C for 10 min. Curve b_1: St 122 getter activated at 350°C for 3 h. Curve c_1: St 122 getter activated at 500°C for 10 min.

Concerning the sorption of H_2 and CO at 150°C as the getter working temperature, the tests have been performed on St 122 getters with the "dynamic flow method." The results are shown in Figs. 3 and 4 where it is possible to see how the getter material performance is improved if the working temperature is increased from 25 to 150°C.

CH_4 sorption has been carried out on an St 121 getter, and the curves obtained at different temperatures (from 200 to 700°C) at constant volume [12] are reported in Fig. 5. These tests show that CH_4 can be sorbed in a

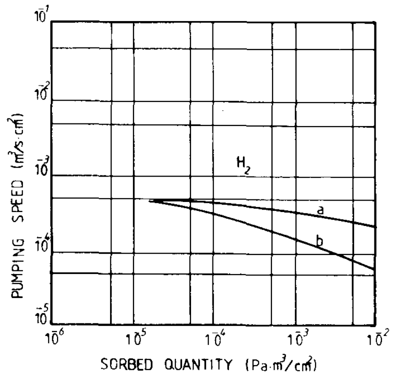

Fig. 3. Hydrogen sorption characteristics for St 122 getters at different working temperatures after activation at 500°C for 10 min. Curve *a*: 150°C. Curve *b*: 25°C.

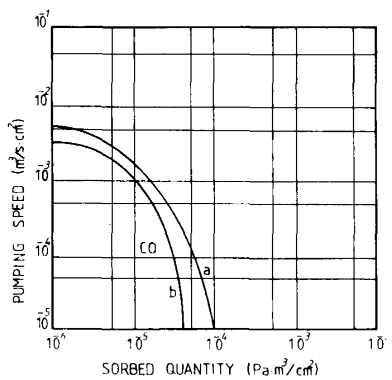

Fig. 4. CO sorption characteristics for St 122 getters at different working temperatures after activation at 500°C for 10 min. Curve *a*: 150°C. Curve *b*: 25°C.

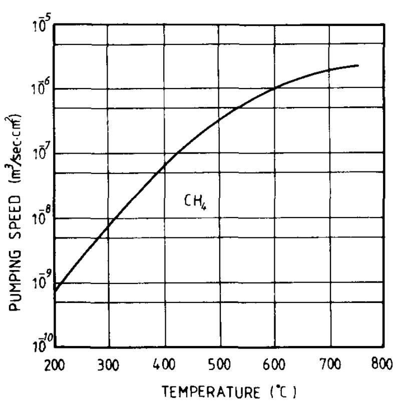

Fig. 5. CH_4 pumping speed for St 121 getters as a function of temperature.

measurable way by these getters at temperatures of about 200°C or above.

The tests performed to determine the influence of the thickness on getter sorption characteristics for H_2 and CO are reported in Figs. 6 and 7. The data show that, in going from 50- to 100-μm films, the St 121 getter capacity in-

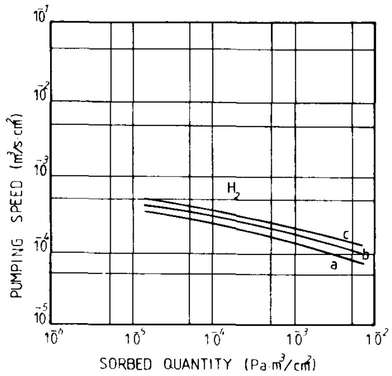

Fig. 6. H_2 sorption characteristics at room temperature of St 121 getters after activation at 500°C for 10 min to show the effect of film thickness. Curve a = 50 μm thick. Curve b = 75 μm thick. Curve c = 100 μm thick.

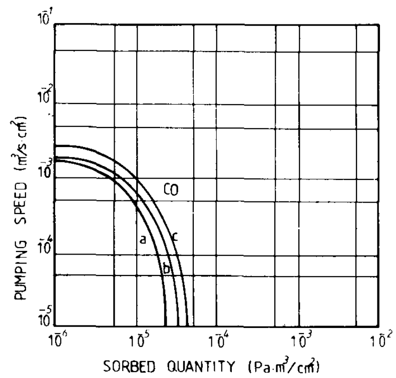

Fig. 7. CO sorption characteritics at room temperature of St 121 getters after activation at 500°C for 10 min to show the effect of film thickness. Curve a = 50 μm thick. Curve b = 75 μm thick. Curve c = 100 μm thick.

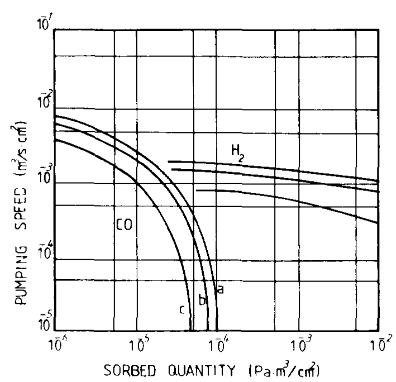

Fig. 8. H_2 and CO sorption characteristics of St 121 getters after air baking at 400°C for 1 h and then activated under different conditions compared with a new (nonbaked) getter. Curve *a*: new getter activated at 750°C for 10 min. Curve *b*: air baked, activated at 500°C for 10 min. Curve *c*: air baked, activated at 750°C for 10 min.

creases proportionally with the thickness, indicating, in the considered range, the maintenance of the porosity with increased thickness.

TABLE I
H_2 EQUILIBRIUM ISOTHERM LAWS FOR St 121 AND St 122 GETTER MATERIALS
(Units: P, torr; C, torr · 1/g; T, degrees Kelvin; ΔH, kcal/g at.H. Range of validity: P 10^{-4}–1 torr; C = 0.1–5 torr · 1/g; T = 500–900°C.)

MATERIAL	SIEVERTS' LAW	ΔH
Ti/Zr - Al	$\log P = 4.87 - \log C^2 - 6710/T$	15.3
Ti/Zr - Fe - V	$\log P = 4.10 - \log C^2 - 5540/T$	12.6

Considering that St 121 getters seem to be more impervious to gas diffusion than St 122 getters (higher activation temperatures), further tests on St 121 coatings have been carried out by heating the getter material in air at 400°C for 1 h (to reproduce the effects of special processing conditions used for some vacuum devices). The getter was then activated and its sorption performance was checked (Fig. 8). The resulting gettering characteristics are quite similar to those of a fresh getter, especially if the activation is performed at 900°C instead of 750°C, thus indicating good resistance to air baking.

V. Other Characteristics

Getter materials, sorbing H_2 after reaching certain concentration limits, exhibit embrittlement phenomena. It has previously been shown [2] that the present getter materials have a very good resistance to high H_2 loads and to thermal fatigue. The embrittlement limit for St 121 coatings has been found to be as high as 90 l · torr/g.

As H_2 is sorbed in a reversible way, the H_2 equilibrium pressure of both the St 121 and St 122 getters has been studied and the resulting equilibrium isotherm laws are reported in Table I. Also, the resistance to thermal fatigue has been tested using a previously described vacuum apparatus [13] that allowed the getter coatings to be submitted repeatedly to the following cycle: from 25 to 700°C in 5 min, 40 min at 700°C, and cool down in 15 min to 25°C. The tests were stopped after 400 cycles without observing any peel-off phenomena, thus confirming the good adhesion of the getter layer to the substrate.

VI. Conclusions

By studying the coatings of St 121 and St 122 getters, we have determined the influence on their gettering performance of:

1) the activation temperature, determining that the St 121 material could be considered a "high activation temperature getter";
2) the coating thickness, determining that gettering performance increased proportionally with thickness in the considered range (50–100 μm) because of maintained porosity;
3) baking in air treatment, determining that the sorption properties of St 121 getters can be almost completely recovered with a suitable activation process.

We have also studied the St 121 getter sorption performance for CH_4, which becomes appreciable for temperatures above 200°C.

The main characteristics of these materials are a highly porous structure, the ability to be deposited on almost any support, good mechanical stability, and interesting gettering performance.

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E. Giorgi, photograph and biography not available at the time of publication.

B. Ferrario, photograph and biography not available at the time of publication.