NON-EVAPORABLE GETTERS

Non-evaporable getters are essential for those tubes, special devices and lamps in which the use of evaporable getters is not possible for technical reasons.

Traditional non-evaporable getters such as sheets or wires of zirconium or titanium are able to sorb gases efficiently only at temperatures in excess of about 600-700°C and this considerably limits their field of application. But by alloying zirconium with a specific amount of aluminium, a getter material is obtained which is active at more moderate temperatures (300-400°C).

This Zr-Al alloy, produced and marketed by SAES GETTERS S.p.A. under the trade name of St 101, has greatly enhanced the range of application of non-evaporable getters.

St 101 ALLOY

Alloys of zirconium with aluminium show substantial improvements of the gettering performance when compared with elemental zirconium.

The optimum is for an alloy of composition Zr 84%-Al 16% which is the nominal composition of the St 101 getter alloy.

It consists essentially of a mixture of two intermetallic compounds: Zr₅Al₃ (the most abundant) and Zr₅Al₆₅. Both are able to sorb active gases, but their coexistence considerably increases the gettering characteristics of the alloy over the sum of the individual activities. This could be related to the fact that these intermetallic compounds have different lattice parameters. Because of this, some stress is present in the boundary area between two components and this makes the area particularly active. Consequently bulk diffusion of the gaseous molecules sorbed on the surface takes place at a much lower temperature than that required by the elemental zirconium.
Fig. 1 compares the gettering performance of 1 cm² of activated St 101 coated strip with 1 cm² of activated zirconium sheet for both H₂ and CO at 400°C and at 25°C. The mass of active material is around 30 mg in both cases.

ACTIVATION OF St 101 GETTERS

A common characteristic of any non-evaporable getter is that its surface is immediately covered with a thin oxide film when exposed to air.

This film is very stable and "airtight". It prevents the atmospheric gases from reacting with the bulk of the alloy which remains uncontaminated.

During getter manufacture the surface oxide film allows the alloy to be reduced to a fine powder without the subsequent gettering performance being affected. The powder may be safely handled also in the open air, without danger of spontaneous ignition, unlike zirconium powder.

It is then compressed into different containers or coated onto metallic strips for introduction into the device to be gettered. (*)

(*) During processing in air, the temperature of the devices within which the getter is introduced should not exceed 300-350°C for more than 10 - 15 minutes. When the device is processed under vacuum or an inert gas atmosphere, both the indicated maximum temperature and time may be increased.
Once the device has been processed and prior to being sealed off, it is necessary to remove the surface oxide film from the getter material, so that the St 101 alloy can exert its gettering characteristics.

The removal of the film is carried out by dissolving it into the bulk of the grains. This is accomplished by heating the getter under vacuum or inert gas at a sufficiently high temperature and for a suitable time.

This treatment is called "ACTIVATION" of the getter. Various levels of activation are possible, according to the conditions under which the treatment is carried out (i.e. temperature vs. time) as indicated in Fig. 2.

![Graph showing temperature vs. time for activation of St 101 getter alloy](image)

**Fig. 2**
Efficiency of ACTIVATION for St 101 getter alloy as a function of the temperature and of the heating time.

Full getter activation may be achieved at about 900°C for 20-30 seconds, at 800-850°C for 4-5 minutes or at about 750°C for 1/2 hour. A heating at 750°C for 3 minutes activates the getter to 60% whereas about 600°C for 1/2 hour activates the getter about to 30%.

It is important to point out that the degree of activation is a parameter related to the extent of diffusion of the surface oxide film into the getter bulk and therefore it influences mainly the magnitude of the gettering speed. The total gettering capacity is only marginally affected.

Activation can also be achieved by an intermittent heating of the getter. In this way localized overheating of nearby tube parts can be avoided.

In some cases the degassing process used during tube processing or the operating temperature of the device may be sufficient for partial activation.
SORPTION OF ACTIVE GASES BY St 101 GETTER ALLOY

After activation, the St 101 getter is able to sorb active gaseous impurities such as \( \text{O}_{2} \), \( \text{CO} \), \( \text{CO}_2 \), \( \text{H}_2\text{O} \), \( \text{H}_2 \), which may be present within the device as a residue of the exhaust and/or as a result of the outgassing of the components.

These impurities are sorbed first on the getter surface where they dissociate. The products of dissociation react chemically with the St 101 alloy to form oxides, nitrides and carbides. Providing the temperature is sufficiently high, these surface reaction products diffuse towards the bulk of the getter, continuously regenerating the surface so that it is able to sorb further gaseous impurities.

When the getter operation temperature is below about 250°C, the mobility of the surface products towards the bulk is slow (with the exception of hydrogen). In this situation, especially when the number of oxygen containing molecules striking the getter surface is large, another more or less compact passivating film builds up with time. This causes a considerable decrease in the gettering performance of the alloy.

Above 300 °C the mobility of the surface products increases and these diffuse more quickly towards the bulk of the getter. This allows some of the surface to remain clean and to continue the process of removing further gaseous impurities.

SORPTION OF HYDROGEN BY St. 101 GETTER ALLOY

Hydrogen, as opposed to all other active gases, does not react chemically with the getter alloy. The molecules of this gas which strike the getter surface dissociates on it. The individual H atoms give their unique electron to the mass and diffuse into the bulk as protons, forming a solid solution. This solution has the characteristic of reversibility. An increase of the temperature of the getter causes the release from the bulk of some of the hydrogen sorbed at lower temperatures and vice-versa.

As an example, when 1 mg of St 101 alloy is heated to 400°C in a constant \( \text{H}_2 \) pressure of \( \sim 1 \times 10^4 \) Torr it is able to pick up \( \sim 1 \) cm³ Torr of this gas. (See point 1 of Fig. 3)

If the \( \text{H}_2 \) pressure on the getter is increased to \( \sim 1 \times 10^4 \) Torr; maintaining the getter at 400°C, 1 mg of St 101 alloy sorbs up to \( \sim 6 \) cm³ Torr of this gas. (Point 2)

When 1 mg of St 101 alloy has already sorbed \( \sim 6 \) cm³ Torr of \( \text{H}_2 \) at 400°C, most of this gas may be removed from it by increasing the getter temperature (for example to 600°C) and pumping away the \( \text{H}_2 \) evolved. When the equilibrium pressure is stabilized (\( \sim 1 \times 10^8 \) Torr), the residue \( \text{H}_2 \) within 1 mg of St 101 alloy has decreased to \( \sim 5.5 \times 10^2 \) cm³ Torr. (Point 3)

In using St 101 alloy for sorbing hydrogen, it is recommended not to exceed a load greater than about 20 cm³ Torr/mg of this gas to prevent the risk of embrittlement of the powder.
REACTIVATION OF St 101 GETTERS

Whenever it is felt that the sorption speed of the getter towards active gases has been excessively reduced because of a severe contamination of its surface, a "REACTIVATION" can be performed. This can be achieved using times and temperatures similar or slightly lower than those used at the first activation.

This possibility gives more flexibility in manufacturing techniques and can be used as a final step after the tube ageing or seasoning for reconditioning the getter.

During the activation or reactivation process of St 101 getters, the gas pressure within the device may be observed to rise. This pressure rise may be associated with the release of the small quantity of residual hydrogen in solution within the St 101 alloy. However, it is quickly repumped as the getter device cools down. Traces of other gases may also be noticed during first activation or even on reactivation. These may originate from local overheating of the areas in contact with, or subject to radiation from the getter during the activation steps.
KINDS OF GETTERS AVAILABLE

Tablets, rings, coated strips, pump cartridges, modules and others products are available. St 101 alloy powder is compacted without using organic or inorganic binders thus maintaining the alloy free of any possible contaminants.

The most common types of St 101 based getters are described in the enclose data sheets.

ADVANTAGES PROVIDED BY THE USE OF St 101 GETTERS

The use of the St 101 alloy in SAES GETTERS non-evaporable products gives the following advantages:

— availability of a wide range of getters having different sizes and shapes and easily adaptable to different applications;
— large getters capacities for active gases even at moderate temperatures (in excess of 200°C);
— convenient and versatile activation conditions compatible with high production rates. In some cases an activation step may not be necessary;
— ability to regenerate the getter after partial saturation;
— elimination of all problems connected with inter-electrode leakage and capacitance effects which are commonly associated with the use of barium;
— elimination of barium films when not desired.

FIELDS OF APPLICATION OF St 101 GETTERING DEVICES

The principal fields of application for St 101 getters are:
— electron tubes and devices, cooker magnetrons, vacuum interrupters, power tubes, lasers, vidicons, H.V. rectifiers, photomultipliers;
— self-ballasted lamps, metal halide lamps, high pressure sodium lamps and in high wattage incandescent lamps.
— particle accelerators, fusion machines, sputtering and MBE systems.
SOME PRACTICAL HINTS ON THE USE OF St 101 GETTERS

Storage: St 101 getters are packed in sealed cans under a protective atmosphere. This method of packing allows practically indefinite storage. Once the original packing has been opened it is suggested that long exposure of the getter to the ambient atmosphere should be avoided to prevent contamination of the products by foreign particles and humidity. Prolonged storage of getters after the original packing has been opened should always be in containers under vacuum or in a dry atmosphere.

Handling: St 101 getters may be safely handled in the atmosphere for mounting in the device in which they are to be employed. However, to avoid contamination the use of finger cots is strongly suggested. Cotton or nylon gloves should be avoided.

Sealing: During the sealing operation of the device it is advisable to avoid overheating the St 101 getters in the presence of either air or forming gas. In fact, if the getters are overheated in the presence of these gases, to temperatures in excess of 300°C - 350°C, partial oxidation and hydriding of the St 101 alloy can occur. This can result in faulty behaviour of the St 101 alloy. If such overheating cannot be avoided it is advisable to protect the getters by flowing a rare gas through the device (*). Whenever possible the gas flow should be directed in order to remove heat from the getter.

Exhaust: During the exhaust and bake cycle of the device it is suggested that the temperature of the getter is not raised above 400°C - 450°C to prevent possible partial saturation of the getter. If these temperatures are unavoidable they should be maintained for the shortest possible time or at pressures below about 1.10⁻² Torr (≤ 1 Pa).

Activation: It is generally recommended to activate the getter as the last step before tip-off. Should the getter become gassy (because of hydrogen picked up during device manufacture) it should be degassed, possibly as the last step before activation. In some devices activation occurs during the tube processing or during functioning.

Reactivation: After tip-off, after tube seasoning and even during tube life, the getter can always be reactivated (if necessary) in order to restore a high gettering efficiency.

(*) Nitrogen gas may be also used, but only when the getter temperature during processing does not exceed – 400°C.
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