Preparation and characterization of zirconium porous getters

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Abstract: This paper presents the development of a powder metallurgy process to obtain porous pieces with specific pore size distribution. The porosity is controlled by the processing variables and by the addition of a pore forming substance. These pieces are to be used as gas absorbers (getters) in a capacitive membrane type High Accuracy Pressure Measurement device, where a high surface area is important. Ammonium bicarbonate was added to the zirconium powder to achieve a sintered density around 50% of the theoretical density of zirconium.
The gas absorption conditions were obtained with getters containing a bimodal pore distribution (density of 3.6 g/cm^3). The best getter activation results were obtained in temperature range of 850 to 900 °C. Concerning gas absortion, the best temperature range was 770 to 790 °C, where the absorption time was three minutes.

1. INTRODUCTION

A getter is a component which can be used to obtain a vacuum or maintain a system under a previously specified vacuum [1]. Its function when used in a capacitive membrane type High Accuracy Pressure Measurement device is to preserve low pressures in sealed components, that have been submitted to ultra high vacuum [2].

This paper describes the processing and characterization of metallic zirconium getter to be used in a capacitive membrane type High Accuracy Pressure Measurement device.

2. GETTER CHARACTERISTICS

Table I presents the density and porosity distribution of a zirconium getter.

Table I - Getter characteristics

Material	Density (g/cm^3)	Porosity distribution
Zirconium	3.0 to 3.5	70 % from 100 to 200 μm 30 % from 2.0 to 3.0μm

3. METHODOLOGY

3.1 - Determination of sintering behavior of Zr powder

Porous pieces fabricated by powder metallurgy are generally subject to a methodology that includes the processing stages shown in the flowsheet in Figure 1.

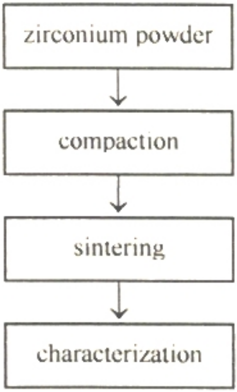
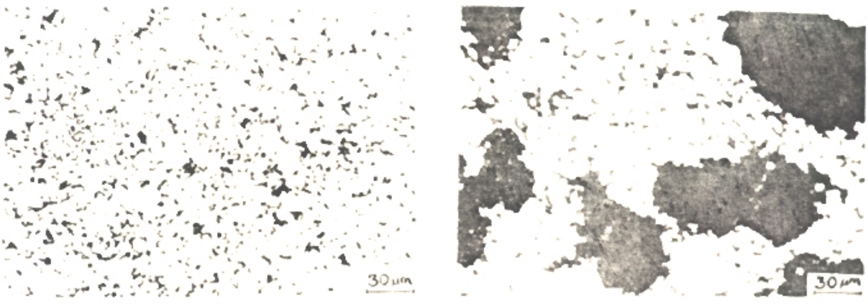


Figure 1 - Powder metallurgy getter processing steps.

The zirconium powder of 97 % purity and specified for getters was acquired from Flucka. It presented mean particle size of 4.4μm (Fisher Subsieve Size) and apparent density of 2.2 g/cm^3. The sintering conditions were determined by following the flowsheet shown in Figure 1. Experiments were performed in which a constant pressure of 150 MPa was maintained and the sintering temperature varied between 950 and 1200 °C. The choosen conditions were 950 °C under a vacuum of 1.3×10^{-2} Pa (10^{-4}mm Hg) and the micrograph of a getter obtained under these conditions is shown in Figure 2a. The mean density was 5.2 g/cm^3. This micrograph shows a homogeneous distribution of pores whose size are of the expected order.



(a) (b)

Figure 2 :Getter optical micrographs :(a)Without pore forming substance, (b)With pore forming substance

3.2 Bimodal porosity distribution

In order to obtain rough porosity (biger pores) a pore forming material which dissociates upon heating was used. An additional processing stage was required where amonium bicarbonate powder in the size range 104 and 124 μm was added to the zirconium powder [3]. The density value obtained earlier corresponds to that desired for fine porosity distribution. The mass of pore former was obtained by using the density value in equation 1

$$mpf = dpf . m \left[(1/df) - (1/dfg) \right] \qquad (1)$$

where
df = desired final density = 3.3 g/cm^3
dfg = density obtained without pore former
dpf = density of amonium bicarbonate = 1.58 g/cm^3
m = mass of zirconium
mpf = mass of pore former to be added

The getter to be used in a High Accuracy Pressure Measurement device must have a specified geometry, and for this, a compacting die was developed. In the micrograph shown in Figure 2b, the microstructure of the getter is presented and the bimodal porosity distribution can be seen. The fine porosity is similar to that previously obtained, and the size of the rough pores is close to expected value. The mean density was 3.6 g/cm^3.

4. GETTER PERFORMANCE

In order to characterize the getter with respect to its service performance, an ultra high vacuum device with a working pressure of 10^{-7} Pa (10^{-9} mbar) was utilized (Figure 3). The pressure of the gases selectively introduced in the system are controlled by a capacitive membrane type device and the corresponding mass measurements made with an on line mass spectrometer. This residual gas analyser (EQ 80F Edwards Model) permits a direct measurement of the gas partial pressures.

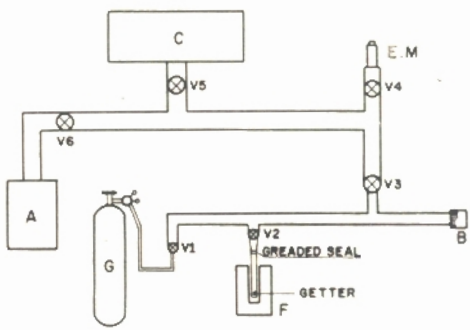


Figure 3: Getter analyser device: (A) Chemical sorption pump, (B) Capacitive membrane type pressure measurer, (C) Titanium pump, (G) Gas container, (F) Furnace, (EM) Mass spectrometer.

An activation treatment is necessary to clean the surface of the getter, by removing surface oxide formed during its preparation and to remove absorved hydrogen. This treatment is carried out at high temperature under high vacuum. The ideal conditions for activation were, heating in the range 850 to 950°C for two hours.

After activation and cooling of the getter to room temperature, the H_2, N_2 and CO_2 absorption curves were obtained. The purpose was to determine the optimum temperature range for the absorption of these gas contaminants. These curves are presented in Figure 4, where it can be observed that absorption increases above 600°C. An operanting temperature range of 770 to 790°C was defined. In this range, hydrogen, the main gaseous contaminant in this kind of measuring device, is quickly absorved, in the first few minutes (Figure 5). Comparison of the two curves in this figure shows that better results are obtained with the getter activated between 850 to 900°C, as shown by curve A.

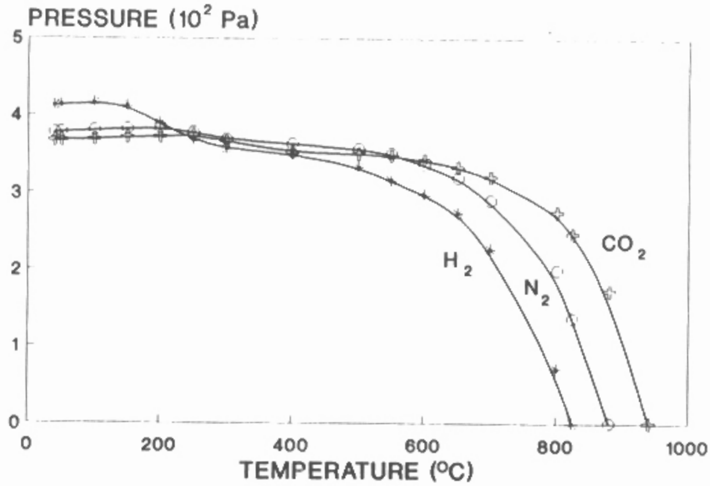


Figure 4 - Getter gas absorption curves (H_2, N_2 and CO_2).

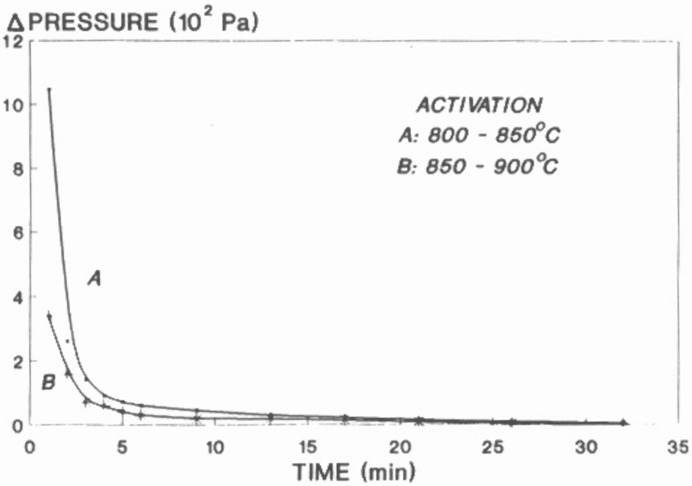


Figure 5 - Getter hydrogen absorption curves.

5. CONCLUSION

The processing variables to fabricate a zirconium getter with a bimodal pore distribution were determined. Adequate pore distribution was obtained by using a pore forming substance (ammonium bicarbonate). The results obtained concerning gas absorption and mainly H_2, permit the conclusion that the getter is adequate for use in capacitive membrane type High Accuracy Pressure Measurement devices

6. REFERENCES

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