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Hydrogen detection by SnO_2 gas sensors

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ABSTRACT

Tin dioxide microsensors have been used for hydrogen detection in nitrogen. The aim of this study is the development of a device which could detect quickly a leak of hydrogen on launchers equipped with hydrogen-oxygen motors. In order to evaluate the performances of industrial sensors made by Coreci Company, several tests have been realized on a laboratory bench. The experiments are related to the determination of the sensitivity and the response time and also to the influence of operating conditions like the room temperature and the presence of low levels of oxygen in the carrier gas. The obtained results show that these sensors are able to solve the different problems depending on this application, especially in regards of the particular conditions like hydrogen detection in pure nitrogen with a short response time.

1. INTRODUCTION

For the Ariane vehicle system development, studies leaded to prevent fire and explosion risks mainly on account of hydrogen and oxygen on board of the launcher: the leakage detection (O_2 , H_2) was one of the studies axis. This activity concerned the detection systems of H_2 and/or O_2 in terms of operational needs for a launcher: measure principle, instrumentation used in industry or in Research/Development, performances and reliability.

Hydrogen detection is possible with various physical or chemical technics. The choice of the method depends on the performances which are inquired for a special application: on one hand, the measurement performances (sensitivity, selectivity, stability, reproducibility, calibration needs, ...) and on the other hand, the operational parameters such as cost, dimensions, weight, power supply, ...

An evaluation of these detection systems (catalyst detector, thermal conductivity, electrochemical oxidation, optical interferometry, thin film detector, ...) based on Nasa data [1] showed the interest of the semi-conductor sensors: nevertheless an accurate evaluation of these sensors performance is essential to consider their possible utilization for Ariane 5.

Also, a research activity, beared by the CNES (the French Space Agency: Ariane Launcher Direction) and managed by the AEROSPATIALE (Industrial Architect of Ariane 5) was leaded by Saint-Etienne Mines School. The aim was to evaluate the SnO_2 semiconductor sensors performance, e.i. their selectivity, sensibility, response linearity, response delay, drift during time, ... For all these parameters, the effect of the temperature and oxygen traces was studied.

2. SnO_2 SENSORS AND TESTING BENCH

The tin dioxide sensors used are the commercial gas sensors A 5001 developed by the CORECI company [2] [3]. The sensing material is a miniaturized tin dioxide bar ($0.5 \times 0.5 \times 2$ mm) obtained by sintering of cold pressed powder. This sensing element is fixed on a heating element in order to control the operating temperature of the sensor (400°C for this study). The weight of the sensor is 1.8 g. For explosive atmospheres, its necessary to use an explosion-proof head (noted "ADF", weight 250 g). The associated electronic (AIRCOR 30) allows the temperature regulation of the sensors, the setting of the sensitivity range and the conversion of the signal (0-5 volts or 4-20 mA) for computer interface.

The two kinds of sensors (without or with "ADF" head) have been tested in a special testing bench controlled by a computer (for sensors and gas). The main characteristics of this testing bench are: control of the concentrations of hydrogen (0.01 to 2%) and oxygen (0.01 to 2%) in the nitrogen carrier gas, special procedures for response time determinations, control of the temperature of sensor cells.

3. RESULTS

The aims of this study is to determine the response of the commercial sensors (value of the signal and response time) for hydrogen detection in nitrogen in the range 0-2%. The external parameters are the oxygen concentration (0-2%) and the ambient temperature in the range -10°C to 40°C .

3.1. Hydrogen detection in pure nitrogen

The signal of the sensor is continuously recorded versus time. The sensor response at 20°C and in absence of oxygen is reported on figure 1 for differents injections of hydrogen in pure nitrogen. It can be noticed the high sensitivity, the very good reversibility of the sensors and also the reproducibility which can be observed with the second run of injections. In general manner, all the experiments have been recorded for many runs and the sensors do not presented drifts during several weeks.

The comparison of the sensitivities under hydrogen in pure nitrogen for the two kind of sensors (without and with "ADF" head) is reported on figure 2. The limit of detection is near 100 ppm.

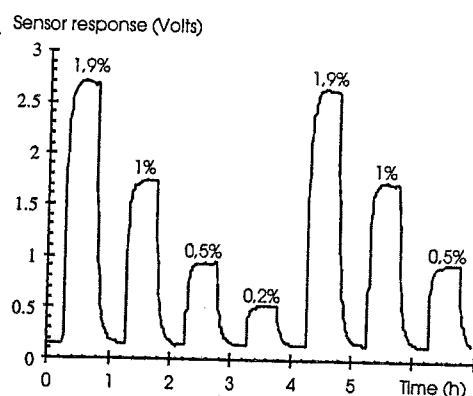


Figure 1: Sensor response for 4 hydrogen concentrations in nitrogen.

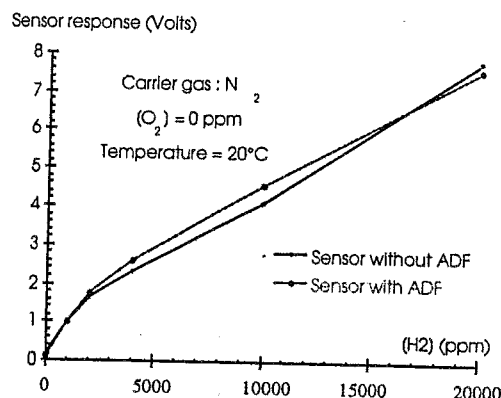


Figure 2: Comparison of the sensitivity for the two types of sensors.

3.2. Influence of external conditions on the sensitivity

The influences of the oxygen concentration in the nitrogen carrier gas and of the room temperature have been evaluated on the response of the sensors.

When oxygen is introduced in the carrier gas, the sensitivity for hydrogen is decreased (figure 3). The result is a relative deviation on the measure of the hydrogen concentration: 30% with 0.2% oxygen and moreover with 2% oxygen. Results of figure 3 are obtained with a temperature of the measuring cell fixed at 20°C but similar values have been measured all over the range -10°C to 40°C.

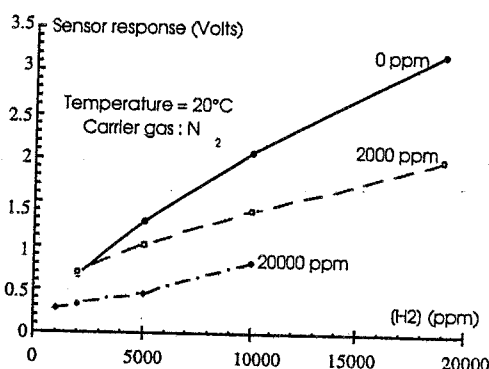


Figure 3: Influence of the oxygen concentration in the carrier gas.

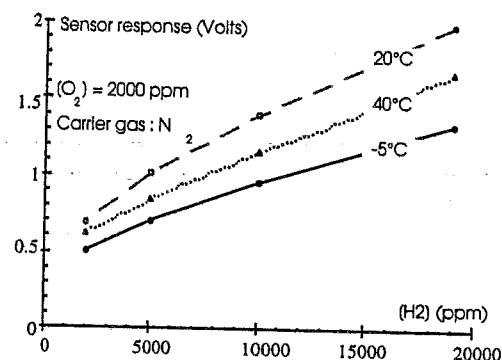


Figure 4: Influence of the ambient temperature on the sensor response.

Concerning the influence of room temperature, the relative variations of the response under hydrogen are less important. For instance, when the temperature of the sensor cell is changed from -5°C to 40°C, the relative deviation on the measure of the concentration of hydrogen do not exceed 15%. Results of figure 4 are obtained with 0.2% oxygen in the carrier gas but similar influences are measured under pure nitrogen or with 2% oxygen.

3.3. Evaluation of the response time

The determination of the response time of a sensor is generally difficult in a testing bench because it depends on the measuring conditions: flows, volume of the cells, layout of canalizations, ... Moreover the absolute value depends on the definition of the response time. However the comparison of times obtained in fixed conditions allows some evaluations.

For instance, on figure 5 is reported the time to reach 10% of the absolute signal under fixed experimental conditions. The time does not depend, on one hand on the value of the hydrogen concentration, and on the other hand, on the external parameters (room temperature and oxygen concentration). The relative deviation does not exceed 20%. By way of illustration on the difficulty to determine the real response time, the influence of the volume of the measuring cell is reported on figure 6. For instance under 1.9% hydrogen, the time to reach 50% of the total signal changes from 10 to 40 seconds with the nature of the cell.

Taking into account the operating conditions, the calculated response time are: 1.5 second for the hydrogen detection (alarm) and 5 seconds for the measure of the hydrogen concentration. The use of an explosion-proof sensor doubles the response time.

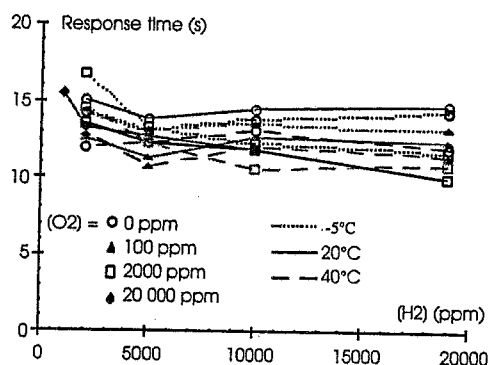


Figure 5: Influence of external conditions ($[O_2]$ and T ($^{\circ}C$)) on the response time.

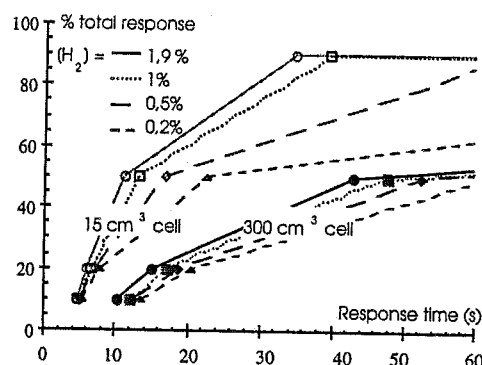


Figure 6: Influence of testing conditions (volum of cells) on the response time.

4. CONCLUSION

A major result is the fact that hydrogen detection is possible in pure nitrogen with tin dioxide sensor for which the electrical conductivity generally depends on their stoichiometry deviations. The experiments point out that the signal of these sensors is perfectly stable and hydrogen response are perfectly reversible in absence of oxygen.

The performances obtained with commercial tin dioxide sensors demonstrate that their use for hydrogen detection in nitrogen can be consider for space application: weak dimensions (and mass), conventional signal (4-20 mA), good detection level (100 ppm) sufficient precision for hydrogen concentration determinations, relative deviation with ambient conditions (temperature and oxygen concentration) less than 30% and response time evaluated to few seconds.

Next experiments will concern the tests of these sensors directly on a motor-bench for their final validation for their use on launchers.

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5. REFERENCES

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