ADSORPTION AND DESORPTION KINETICS IN ZrO$_2$ – TiO$_2$ CERAMICS BY PHOTOACOUSTIC TECHNIQUES

A. Pinto Neto[1], D. Moura[2], C. Kuranaga[3], M. D. Silva[3] and L. C. M. Miranda[3]

1 – Universidade Federal do Maranhão – UFMA – Brazil
2 – Universidade de Taubaté – UNITAU – Brazil
3 – Instituto Nacional de Pesquisas Espaciais – INPE – Brazil – marcosd@dir.inpe.br

Abstract. In this paper we report on the photoacoustic (PA) characterization of ZrO$_2$-TiO$_2$ ceramic wafers as a sensing element for solvent adulteration evaluation. The experiments consisted of photoacoustic time dependent monitoring of the sorption and desorption of a droplet of a solvent deposited on the outer face of a ceramic wafer. The used solvents were isopropanol and chloroform. For the polar isopropanol molecule the results shown diffusion into the sample, with a characteristic diffusion time τ_1, accompanied by the evaporation at a rate with a time constant τ_2. Indeed, for the non polar chloroform, wetting-drying kinetics is adequately described by a simple diffusion-evaporation.

1. INTRODUCTION

The different PA techniques have been successfully applied over the years for monitoring time evolution processes, as well thermal properties evaluation [1-4]. In this paper we present the preliminary results of our investigations on the potentialities of conventional photoacoustic detection for monitoring solvent sorption in porous ceramics. This is part of a program aiming the development of ZrO$_2$-TiO$_2$ ceramics with controlled porous distribution for solvent adulteration sensors. The central aspect in these PA studies is to find out if conventional PA detection is able to provide us with a simple and precise way to single out a characteristic of solvent sorption-desorption kinetics in these ceramics potentially useful as a sensing parameter.

2. EXPERIMENTAL PROCEDURE

The experimental apparatus is shown in Fig 1. The photoacoustic signal was measured using a conventional PA cell. Two types of measurements were carried out. The first one consisted of a conventional modulation frequency scanning of the amplitude and phase of the PA signal of our dry ceramic sample in order to determine its thermal diffusivity. The second set of measurements consisted in the monitoring of the PA signal, at a fixed modulation frequency, as a function of time, after dropping 25 µl of an organic solvent on the external surface of the porous ceramic sample. In this case, the aim was to investigate the solvent sorption – desorption and evaporation mechanisms in the sample. We have used two types of solvents, one, a polar one, namely, isopropanol, and the other one a non-polar solvent, namely, chloroform.

The samples used were ZrO_2-TiO_2 ceramic discs of 13 mm diameter and 530 μm thick, compacted at 120 MPa and sinterized at 1100 º C for 3 h. Their specific surface area was found to be of 1.48 m^2/g, whereas their porosity was of the order of 43% with an average pore diameter of roughly 0.6 μm. In Fig 2 we present the pore distribution as obtained from the mercury intrusion porosimetry. In order to insure no vapor diffusion into the gas sensing chamber, at the same time that a surface heating condition is assured, a black painted Al foil 60 μm thick was glued to the inner surface of the ceramic sample as indicated in Fig 1.
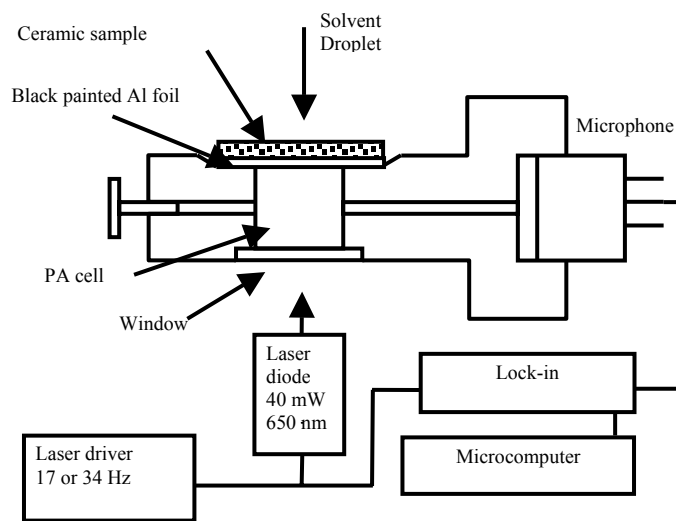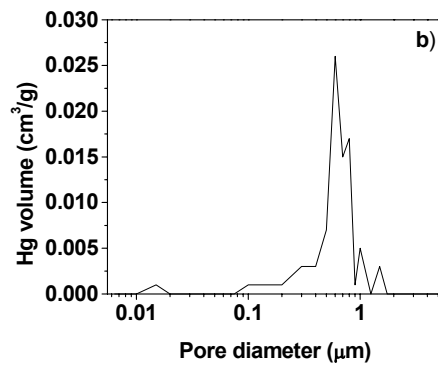

Figure 1 – Experimental setup

Figure 2 – Pore distribution

3. RESULTS

The behavior of the photoacoustic signal amplitude as a function of the modulation frequency, f, exhibited a f^{-1} dependence indicating that, indeed, the thermoelastic mechanism is the main responsible for the PA signal generation. The dry sample thermal diffusivity was found to be 0.12 ± 0.01 cm^2/s from the PA signal phase data fitting as a function of the modulation frequency, following the procedure outlined in [1] and [6].

Having determined the main mechanism producing the PA signal we have next carried out the time monitoring of the solvent sorption in our samples. According to the existing models [1], the PA signal amplitude due to the thermoelastic mechanism varies with the inverse of the sample heat capacity [1,6,7], namely,

$$ S \propto \frac{1}{\rho c} \qquad (1) $$

These experiments were performed at a fixed modulation frequency of 34 Hz. We note that in the above equation we are explicitly neglecting the effect of the Al foil on the PA signal. In other words, we are assuming that the condition of surface light into heat conversion still holds for our sample. This is a reasonable assumption for the low modulation frequency regime used in this paper. For a 60 μm thick Al foil the thermal diffusion time is of the order of 39 μsec, so that, for low modulation frequencies, we may assume that heat is instantaneously diffused through the Al foil. Initially, the dry sample PA signal is recorded for approximately 5 min, so that a "dry" sample signal is defined. After this initial stage, a solvent droplet of 25 μl is deposited on the outer sample surface and the resulting changes of the PA signal amplitude are recorded as a function of time. In what follows, the origin of the time scale is assumed the time at which the solvent droplet was poured onto the sample surface, and the changes of the PA signal are presented in terms of the signal amplitude at a given time normalized to the "dry" sample signal. Accordingly, the inverse of this normalized signal is simply the ratio of the wet to the dry sample heat capacity. In Fig 3 we plot the inverse of the normalized signal relative to unity (that is, $1/S_N - 1$), as a function of time for the case of isopropanol. It consists basically of a sharp peak followed by a long tail. The overall behavior may be understood as follows. The initial fast rising is attributed to the wetting of our porous sample resulting from the diffusion of the isopropanol molecules displacing the air in the pores and capillaries of our sample. This is followed by the evaporation of the free isopropanol molecules, that is, those molecules that are weakly bounded to the pores. The liquid near the outer surface evaporates first generating a gradient of liquid concentration through the sample which, in turn, forces the liquid in the inner parts to rise to the surface due to the capillary forces. This simultaneous evaporation and diffusion of the liquid molecules defines a profile of liquid distribution throughout the sample thickness such that the liquid concentration near the outer surface is smaller than that in the inner parts. However, due to the polar nature of isopropanol, a fraction of the alcohol molecules gets bounded to the pores. As result it takes longer for these bounded molecules to evaporate. This corresponds to the long tail observed.

The solid line in Fig 3 corresponds to the data fitting to the simple model outlined above describing the wetting and drying of our ZrO$_2$-TiO$_2$ ceramic sample. Accordingly, we have assumed the following expression to describe the above wetting-drying process:

$$ f = A(1 - \exp(-t/\tau_1))\exp(-t/\tau_2) + B\exp(-(t-t_b)/\tau_3) \qquad (2) $$

The first term in equation (2) corresponds to the isopropanol molecule diffusion into the sample, with a characteristic diffusion time τ_1, accompanied by the evaporation at a rate with a time constant τ_2. To this term, describing the free liquid molecules dynamics, we have added a second one describing the

slow evaporation of the bounded liquid molecules. This is represented in equation (2) by the second term in which t_b corresponds to the time for the onset of the bounded molecules desorption at a rate with a time constant τ_3.

This model was applied to the measurements with both solvents. The results are shown in Fig 3 and the values of the fitting parameters are summarized in table 1.

The interesting point to be noted in Fig 3 is the marked difference of the wetting-drying kinetics of the two solvents in our ceramic sample. The chloroform diffusion into the sample tends to be faster, as compared to the isopropanol case. However, its evaporation regime is quite different from that of isopropanol. The isopropanol drying regime corresponds to an initially fast drying following by a relatively long tail. In contrast, for the case of chloroform, the drying process is essentially a single-step monotonic process. This is reflected in table 1 by the small value of the parameter B found for the case of chloroform indicating that, indeed, the chloroform wetting-drying kinetics is adequately described by a simple diffusion-evaporation process as given by the first term of equation (2).
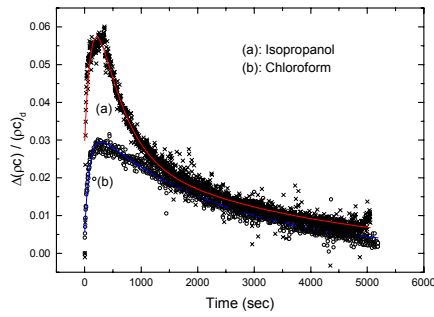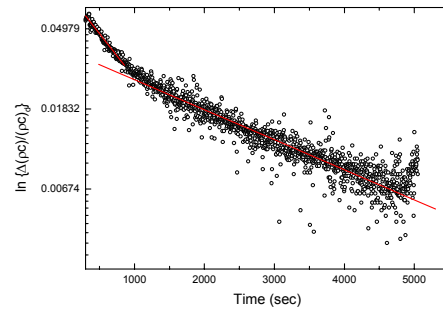

Figure 3 – Plot of the $1/S_N - 1$

Figure 4 - monolog plot of the data to the solvent desorption for the isopropanol case

Table 1. Numerical values of the fitting parameters.

Solvent	A	τ_1	τ_2	B	t_b	τ_3
Isopropanol	0.073	189.15	437.46	0.022	889.18	3505.75
Chloroform	0.030	91.04	2368.96	0.002	2558.78	2770.16

In Fig 4 we present the monolog plot of the data corresponding to the solvent desorption regime for the isopropanol case. Figure 4 clearly indicates that the evaporation, for the case of isopropanol wetting-drying, is a two-step process as indicated in our simple model outlined above. In contrast, for the case of chloroform wetting, as can be seen from the value of B in table 1, the contribution of the bounded molecules is negligibly small. This is essentially due to the non-polar nature of this solvent as compared to the polar isopropanol case.

Acknowledgments

References
[1] H. Vargas and L. C. M. Miranda, Phys. Reports, 161, 43 (1988).
[2] A.C. Pereira et al., Plant Science 96, 203, (1994).

[3] A. Torres-Filho, L.F. Perondi, and L.C.M. Miranda, J. Appl. Pol. Sci. 35, 103 (1988)
[4] N. Cella et al., J. Pol. Sci. C: Pol. Letters, 27, 313 (1989)
[5] S.A. Tomás et al, Meas. Sci. Technol. 9, 803, (1998).
[6] L.F. Perondi and L.C.M. Miranda, J. Appl. Phys., 62, 2955 (1987)
[7] W. Jackson and N.M. Amer, J. Appl. Phys., 51, 3343 (1980)