XIX IMEKO World Congress
Fundamental and Applied Metrology
September 6–11, 2009, Lisbon, Portugal

USE OF MIRAGE EFFECT FOR THE DETECTION OF ADSORPTION OF ORGANIC MOLECULES ON THE SURFACE Pt – 10% Ir ALLOY OF MASS STANDARD

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Abstract − One among factors responsible of the instability of mass standard is the adsorption and desorption induced by the cleaning products. An optical non-contact method based on mirage effect is proposed to investigate the adsorption/desorption of cleaning solvents on the surface of mass standards at conditions close to normal temperature and pressure (NTP). A model developed for the mirage effect when physical adsorption occurs on a non-porous sample under NTP conditions is recalled. The experimental results of the mirage deflection obtained, in the case of platinum iridium alloy with ethanol\nitrogen and ether\nitrogen mixture, and the relation between the phase of the mirage deflection and the adsorption isotherm allow the measurement of the parameters characterizing the adsorption process, such as the amount of adsorbed matter in the first monolayer.

Keywords: mirage effect, adsorption.

1. INTRODUCTION

The handling and the condition of storage and use of the mass standards made from platinum iridium alloy, superalloys based on cobalt or nickel or austenitic stainless steel affect the stability of this reference. Among the phenomena contaminating mass standards are: oxidation and corrosion; dust particle deposits; adsorption\desorption. In view of the complexity of the problem and its metrological importance, a number of laboratories in different countries have undertaken a long-term study of the stability of standards. The mission given to the French metrology institute (LNE−Cnam) as a part of a project financed by French National research Agency (ANR) is to control the conservation and treatment condition of mass standards by physicochemical studies.

The main solvents used to clean mass standards are ethanol, ether, isopropanol, ethanol\ether mixture and water-vapour jet [1]. The main materials investigated in LNE−Cnam are platinum iridium (90% Pt − 10% Ir), which is the alloy of the international prototype and most of national prototypes of the kilogram, and special alloys such as XSH Alacrite and cobalt or nickel which are used for the fabrication of secondary and reference mass standards [2].

Several techniques used for these investigations (gravimetric methods, thermal desorption mass spectrometry (TDS), X-ray photoelectron spectroscopy (XPS)…) [3-4]. The difficulty with the XPS and TDS techniques is that the samples studied are placed under vacuum. Molecules having the smallest desorption energy are thus quickly desorbed and the contamination layer is modified even before analysis starts. Hence it was important to use a non-destructive method, such as the mirage effect device.

Mirage effect method also called optical beam deflection (OBD) is optical non-contact method based on local heating via absorption of modulated light flux at the surface. The detection can be achieved by detecting the pressure variations produced by the periodic adsorption and desorption and by measuring the deflection of a light beam skimming the surface with a position sensor.

In this paper, we present in the first section a theoretical description of the mirage effect with explaining that the origins of the phenomenon lie in the presence of thermal and mass gradients close to the solid surface. A direct model relating the thermal and mass concentration gradients to the mirage signal, published in previous papers [5], is recalled to describe the main parameters influencing the mirage signal. Particular attention is paid to the BET adsorption isotherm which directly linked to mass concentration gradient. In the section two and three we explain briefly the experimental set-up and we present the results obtained for platinum iridium alloy with two different mixture gases ethanol\nitrogen and ether\nitrogen.

2. THEORY

The mirage technique which exploits the optical beam deflection due to a refractive index gradient is currently used as a very effective tool for optical spectroscopy, thermal measurements and imaging in solids. A hot body heats up the surrounding medium so as to generate a refractive index gradient (RIG) directed away from its surface. An optical beam (probe beam) propagating normal to the RIG and parallel to the hot surface suffers deflection from the original beam path (mirage effect Fig. 1.). The amount of deflection is a function of the magnitude of the RIG in the vicinity of that surface and this in turn will depend on the

ISBN 978-963-88410-0-1

various thermal parameters of the sample as well as the distance between the sample surface and the detector together with the relevant geometrical factors. The first quantitative explanations of the phenomenon were given by Silva et al. [5], who demonstrated that the mirage effect combines two contributions (thermal and mass concentrations) and is directly sensitive to the gradient of concentration of the absorbable molecules very close to the sample surface.

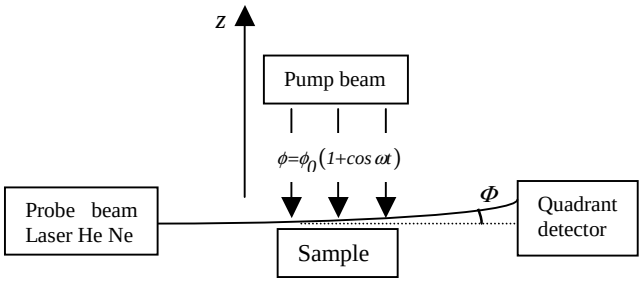

Fig. 1. Principle of detection by mirage effect, the probe beam is deflected in going through the heated area near the sample.

In the case of homogeneous solid sample at temperature T with presence of a mixture of two gases, A (non-condensable) and B (condensable) with C_A and C_B the respective amounts of matter per unit volume (mole concentration), we suppose that a thin film of adsorbed molecules B is formed at the surface of S which receives a uniform modulated flux of light (pump beam, see Fig. 1.); that the film is transparent; and that the pump beam is totally absorbed at the sample surface (metal). This film is partly vaporized during the half-period of illumination of the sample inducing a deflection of second beam (probe beam) with an angle Φ_n due to the gradient of the gas refractive index n produced along z by both the temperature gradient and the concentration gradient [5]:

$$\Phi_n = \frac{L}{n}\frac{RT_0}{P_0}\left\{\left[C_A\left(n_A^0-1\right)+C_B\left(n_B^0-1\right)\right]\frac{1}{T}\frac{\partial T}{\partial z}-\left(n_B^0-n_A^0\right)\frac{\partial C_B}{\partial z}\right\} \quad (1)$$

The first term in (1) represents the contribution of the thermal gradient and the second term the contribution of the concentration gradient. These two gradients have been calculated analytically for a sinusoidal modulation and finally the complex expression of the periodic angle is given by:

$$\Phi_n = -(1+i)\frac{L}{n}\frac{T_{g_0}T_0}{T^2}\frac{P}{P_0}\left\{\left[C_A\left(n_A^0-1\right)+C_B\left(n_B^0-1\right)\right]\frac{e^{-(1+i)(z-l_f)/\mu_g}}{\mu_g}\right.$$
$$\left.-\left[C_B\left(n_B^0-n_A^0\right)\frac{(1-X)(q/RT-1)}{1-X+(1-i)X(\mu_D/2l_g)(1+lg/Y_PRTX)}\right]\times \quad (2)\right.$$
$$\left.\frac{e^{-(1+i)(z-l_f)/\mu_D}}{\mu_D}\right\}$$

where R is the molar gas constant, X is the molar fraction of condensable gas, T_{g0} is the complex amplitude of the periodic sample surface temperature, L is the length of interaction between the probe beam and the heated gases, l_f is the thickness of adsorbed gases, q is the isosteric adsorption heat, μ_g and μ_D are respectively the thermal and mass diffusion length and the index zero denotes quantities evaluated at NTP conditions (pressure P_0 and temperature T_0). Y_P is the derivative of adsorption isotherm with partial pressure at a given temperature T.

Brunauer, Emmett and Teller proposed a model (BET equation) [7] for the case of multilayer adsorption :

$$Y = Y_1\frac{C_1 x}{(1-x)(1+(C_1-1)x)}$$

where $x=P_B/P_{sat}$, P_{sat} the vapour saturation pressure, Y_1 represents the amount of adsorbed matter per unit surface in the first layer, and C_1 is a parameter related to the difference between the heat of adsorption on the first monolayer and the heat of condensation, characterizing the type of adsorption.

3. EXPERIMENTAL SET-UP

The experimental procedure and set-up have been presented elsewhere [6] and are described here only briefly.

The main parts of the experimental set-up are: the sample cell and the balloon for preparation of the gas mixture. The top surface of the sample is illuminated by a modulated light beam from a 12 V, 50 W tungsten filament lamp. The sample, a 1 cm diameter cylinder enclosed in a 40 cm^3 glass cell with silica windows, is fixed to a copper holder pressed against the cold surface of a Peltier element used to vary the sample temperature. The whole cell is placed on a rotation plate fixed to a vertical translation stage, allowing alignment and positioning of the sample surface relative to the probe beam from a He-Ne laser. The temperature of the sample is measured with a thermistor introduced through the sample holder. The deflection of a probe beam from the periodically oscillating thermal bump, caused by local laser heating, is detected by quadrant detector.

4. EXPERIMENTAL RESULTS

The results of laser beam deflection, presented in Fig. 2., were obtained for a platinum iridium sample and a mixture of ethanol, as the adsorbable vapour, and nitrogen. The experimental conditions are: the molar fraction of ethanol 0.07; sample/probe-beam distance 150μm; modulation frequency 225Hz; surface temperature 285K.

From (2) it is possible to simulate the experimental phase of the mirage signal and after we can deduce the adsorption isotherm by the computation of Y_1 and C_1 parameters. From Fig. 2. we can determine that the mirage model introduced above represents well all the physical phenomena and we can conclude that the BET adsorbed isotherm, used in the theoretical model, give a good description of the adsorption phenomenon.

Fig. 3. shows the derivative adsorption isotherms deduced from these experimental data and the inversion procedure introduced by Taillade et al. [8]. In our case, the values of Y_1 and C_1 are respectively 2×10^{-6} mol m^{-2} and 2.7×10^{-2}. By referring to the BET adsorption type, we found that when $C_1 < 1$, the type of adsorbed isotherm is III. The heat of adsorption is then equal to or less than the heat of condensation of ethanol and the adsorption tends to produce aggregates of molecules that grow into droplets, the diameter of which increases with time; further adsorption and desorption will then take place mainly at the meniscus of these droplets

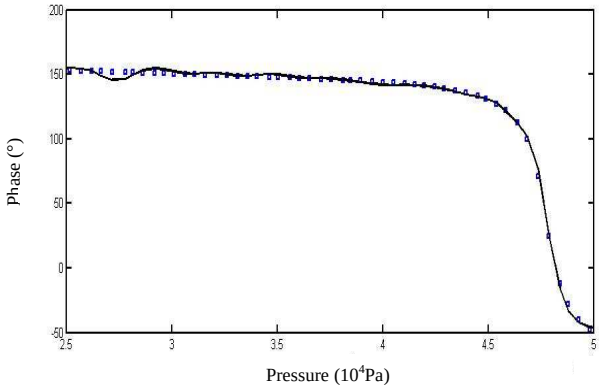

Fig. 2. Experimental (line) and theoretical (square) phase obtained for an ethanol-nitrogen mixture on platinum iridium alloy.

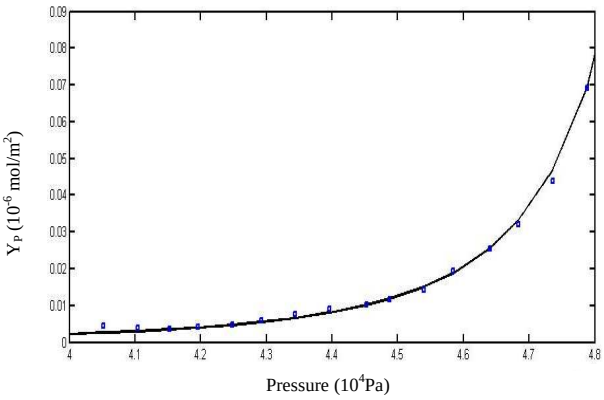

Fig. 3. Adsorption isotherms reconstructed from experiments of Fig. 2. (square) and BET adsorption isotherm (line).

The same study has been made for platinum iridium sample with ether-nitrogen gases mixture, the molar fraction of ether and the temperature surface are fixed respectively at 0.27 and 265K. the results obtained shows that the amount of adsorbed molecules in this case is 1.8×10^{-6} mol/m^2 less than measured with ethanol.

5. CONCLUSIONS

As a result of our study we found, that the mirage method could be a useful quantitative tool to measure the adsorption of organic molecules. The main advantage of this method is its non-destructive character, as it operates at NTP conditions. The mirage technique, adopted in our experiment, allows to found as well as the amount of adsorbed matter per unit surface in the first layer matter. The two parameters values Y_1 and C_1 which defined the BET adsorption type have been calculated by simulation the phase of experimental mirage signal in the case of ethanol\nitrogen and ether\nitrogen mixture. The theoretical procedure is based on the BET adsorption isotherm which neglects the lateral interaction between the adsorbed atoms or molecules. A new theoretical approach should be developed to better understand the dynamics of the growth of the layers.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the 'Agence National de Recherche (ANR)' for its support in this study.

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