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Dirt reference standard for surface cleanliness measurements

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Abstract Thin films based on polymer poly(isobutyl methacrylate) (PIBMA), doped with carbon black particles deposited on steel plate substrates are proposed as dirt reference standards for cleanliness accreditation methods, particularly for instruments based on laser ablation. The films were made with the spin-coating method, obtaining layers with thickness between 4 and 17 µm. Carbon black particles with sizes smaller than 100 nm and concentrations between 1 and 27.6 mgr/cm^3 were used. Characterization of the films was made by using absorbance measurements and laser ablation-induced photoacoustic.

1 Introduction

Cleanliness is a critical issue in many industrial and technological processes as well as in quality control of products [1–3]. Usually, the main problems are to define what level of cleaning of the surface is necessary for a certain quality standard and how to measure it [4]. Regularly cleanliness determination is made by comparing a measurement of some typical parameter of the dirt with respect to the same measurement in an arbitrary sample reference, in most cases defined ad hoc [5]. Most of the cleanliness methods are chemical laboratory procedures that determine indirectly the amount of dirt in a surface [6–8]. Laser cleaning methods have been developed during the last 20 years, including patents and an important theoretical background related to the mechanisms involved [9–12].

Recently, new methods based on laser ablation have allowed real-time measurement of the relative or absolute amount of dirt present on different types of surfaces [13–16]. These methods are based on the ablation of the dirt film by a short laser pulse and the measurement of the emitted sound or the luminescence of the plasma produced after laser ablation. The intensity of the sound and the intensity of the light are proportional to the amount of dirt in the surface and provide a direct measurement of the cleanliness of the sample. When using acoustic detection, a simple model that gives the amount of dirt as a function of the characteristic parameters of the dirt, that is, its thickness, concentration and particle size can be used [16].

In general, there are no well-accepted standards that can be used as references for cleanliness measurements, mainly because the production of dirt in a controlled way is a very difficult task. When using instruments that allow automatic measurements, and for a wide range of applications, well-defined and controlled dirt reference standards are required for calibration purposes [17–20]. On the other hand, any dirt reference standard used is not generally applicable for all types of dirt, since the composition of the contaminant could certainly affect calibration.

In this work, we developed and characterized a dirt reference standard (DRS) for laser ablation measurements of the cleanliness of surfaces contaminated with dirt composed of a thin film of organic substances, such as oil or grease, in which a more or less homogeneous distribution of small black particles mainly of carbon is present (i.e., produced by hand manipulation, candle soot, during the cold-rolled steel production).

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The DRS developed is based on thin films made with PIBMA acrylate doped with IRB#6 black carbon particles of up to 100-nm sizes and concentrations between 1 and 27.6 mg/cm^3. These films have special characteristics for this purpose: The material is cheap, easily to obtain and the films can be made in reproducible conditions with a controlled thickness between 4 and 17 µm and a wide range of concentrations. We present the manufacture procedure to prepare the film standards: a method for the determination of the thickness of the films based in absorbance measurements and the correlation between the acoustic signals measured after ablation with the carbon concentration in the sample.

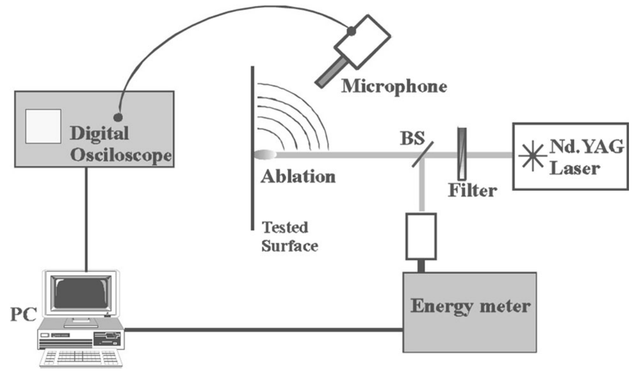

Fig. 1 Experimental setup used for laser ablation-induced photoacoustic. *BS* beam splitter, *PC* personal computer

2 Experimental

2.1 Manufacture of the dirt reference standards

For the preparation of the DRS, first, we made a solution (0.1 g/cm^3) of PIBMA in toluene. Then, different quantities of IRB#6 nanoparticles in suspension in toluene were added to this solution. This suspension was before sonicated to prevent particle agglomeration. Finally, thin films were made with a spin-coating method.

As substrates, we used pieces of 40 × 80 × 1.5 mm steel plates, cleaned at room temperature for 50 min, using acetone-isopropyl alcohol 50/50 v% solutions in an ultrasonic cleaner. Two centimeter of both ends of the substrate was covered with sticky tape.

Once the film was made, this tape is removed and it is used to measure the absorbance of the PIBMA + IRB#6 films obtained. Absorption measurements of the sticky tapes with the film were taken by using a double beam spectrophotometer (Shimadzu UV-1650 PC) at $\lambda = 1064$ nm. Tapes without the film were used as reference.

The spin coater was operated at 4000 rpm, obtaining films of thickness between 4 and 17 µm. Finally, the samples were dried putting them in an oven 30 min at 60 °C. This temperature is compatible with the PIBMA glass transition temperature (40 °C) and the toluene evaporation points. The final result is a uniform film, firm and very stable, of easy handling and storage.

2.2 Setup for laser ablation-induced photoacoustic (LAIP) measurements

The setup used for LAIP is shown in Fig. 1. A Q-switched Nd:YAG laser with pulse duration of 15 ns (FWHM) operating at a fundamental wavelength (1064 nm) impinges normally to the sample surface. The sample is moved perpendicularly to the laser beam with a step motor, so each laser shot impinges on a different region, and the measurement is made with only one shot. A neutral density wedge filter is used to change the energy of the laser pulse (from 0.8 to 20 mJ). An electret condenser microphone (Panasonic WM-61A) picks up the emitted sound which was amplified using a homemade amplifier and registered on a digital oscilloscope (Sample rate: 300 MHz). The amplitude of the first peak to peak acoustic signal (S) was measured as a function of the laser fluence. The pulse energy was measured using an energy meter with a pyroelectric detector, splitting the laser pulse by means of a calibrated beam splitter. Taking into account the non-homogeneous spatial energy distribution of the laser pulse and the effective area of the laser spot, the fluences F calculated in this work have an uncertainty of c.a. 10 %.

3 Results

3.1 Measurement of the DRS thickness

The thickness $\boldsymbol{D}$ of the DRS films can be determined by using Eq. (1)

$$\boldsymbol{D} = A/\boldsymbol{\alpha c} \tag{1}$$

where A is the absorbance of the sample, $\boldsymbol{\alpha}$ is the total average particle cross section (assumed constant), and $\boldsymbol{c}$ is the IRB#6 concentration. $\boldsymbol{\alpha}$ can be determined from an independent experiment, by plotting the absorbance at 1064 nm measured in a solution with different concentrations of IRB#6 particles in toluene and optical path length of 1 mm (see Fig. 2). From the slope of the curve in the linear region of this plot, a value $\boldsymbol{\alpha} = 1.4 \pm 0.02$ cm^3/mg mm was obtained.

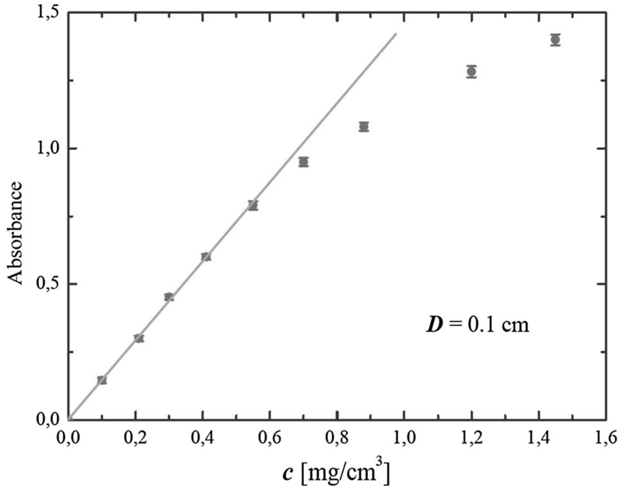

Fig. 2 Absorbance as a function of the concentration of IRB#6 particles in toluene

Table 1 A = Absorbance at $\lambda = 1064$ nm, c = IRB#6 particles concentration and D = thickness of DRS

Sample	A (±0.001)	c (mg/cm^3)	D (μm)
M_1	0.026	1.04	17.3
M_2	0.025	1.04	16.6
M_3	0.035	2.09	11.6
M_4	0.062	4.17	10.3
M_5	0.053	5.21	7.0
M_6	0.078	10.39	5.2
M_7	0.124	17.45	4.9
M_8	0.140	24.75	3.9
M_9	0.143	23.50	4.2
M_{10}	0.160	27.60	4.0

By measuring the absorbance of the sticky tapes with the DRS film and using Eq. 1, assuming that the value of c is known, the thickness D of each sample was determined. Table 1 shows the thickness of the different samples manufactured in this work.

3.2 Photoacoustic (LAIP) measurements

Figure 3 shows the dependence of the peak to peak amplitude of the acoustic signal (S) as a function of the laser fluence for the DRS samples already described in Table 1. The laser ablation threshold fluence ($F_0 = 50$ mJ/cm^2) is the same, as expected, for all concentrations of IRB#6. This threshold fluence is the same as the one that was obtained in previous work for dirt in cold-rolled steel plates [21]. A linear relationship S versus F was observed for all the samples, for laser fluences up to F_0, and below 300 mJ/cm^2.

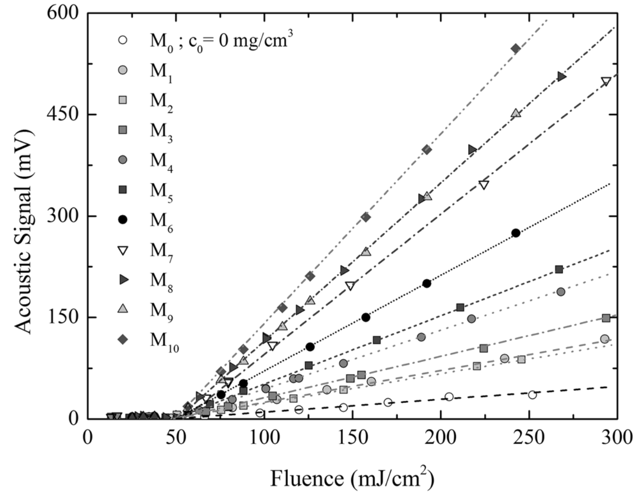

Fig. 3 Acoustic signal amplitude as a function of the laser fluence. Data obtained in ten different reference standards and for PIBMA pure without the addition of particles

3.3 Calibration curves and dirt reference standard measurements

Figure 4 shows the dependence of $S/(F - F_0)$, the normalized acoustic signal (NAS), obtained from the slopes of Fig. 3, as a function of the sample absorption $[1 - \exp(-A)]$, where measured values of $A = \alpha c D$ (see Eq. 1) are presented in Table 1.

As shown in Fig. 4, a linear relationship between the fluence-normalized acoustic signal and the DRS absorption was found. Hence, the acoustic signal can be represented by the equation [16]:

$$S = K\,(F - F_0)\,(1 - \exp(-\alpha c D)) \qquad (2)$$

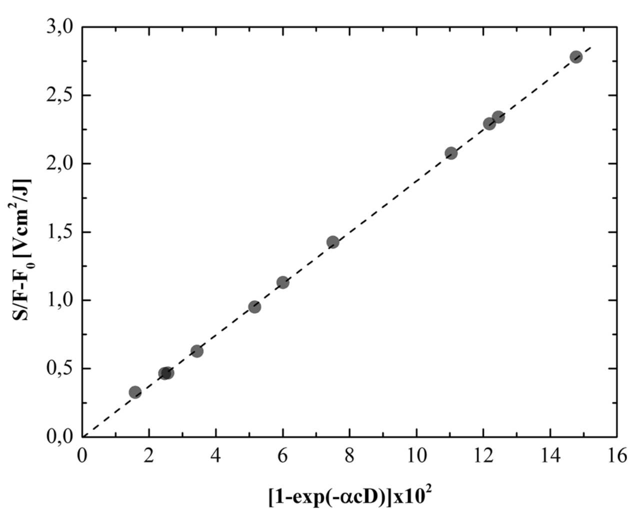

Fig. 4 Dependence of the normalized acoustic signal obtained from Fig. 3 as a function of the DRS film absorbance A

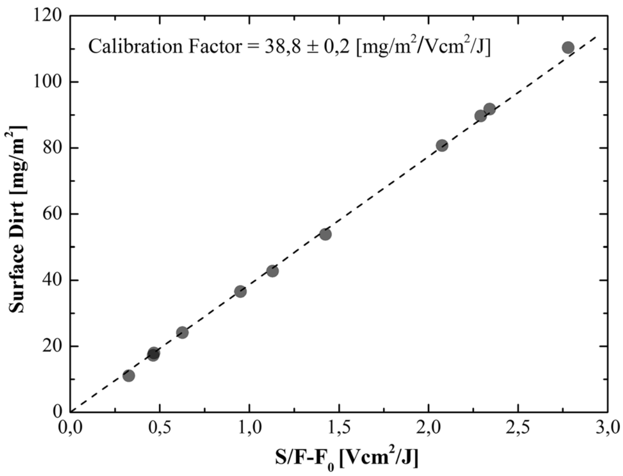

Fig. 5 Dirt reference standards calibration

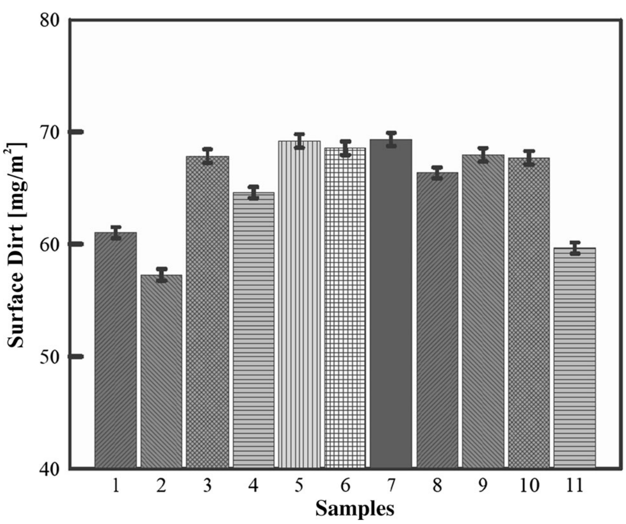

Fig. 6 Amount of dirt of different samples of cold-rolled steel plates. Work fluence $F_w = 250$ mJ/cm^2

where $K = 18.80 \pm 0.05$ Vcm^2/J is a constant that depends on the nature of the sample, the detector geometry and sensitivity.

By expressing the IRB#6 concentration ***c*** in milligrams per cubic meters and ***D*** in meters, the product ***cD*** is the amount of surface carbon in milligrams per square meter.

Calibration curves for the measurement of the cleanliness of surfaces contaminated with dirt of the same characteristics of the DRS can be obtained with this data.

Figure 5 shows the dependence of the amount of carbon per unit area (*Surface Dirt*) in the DRS sample as a function of the NAS. As shown, a linear plot was obtained.

Figure 5 shows a good linear dependence of the acoustic measurement as a function of the dirt concentration in the range 10–110 mg/m^2. This is the dirt concentration range for which the DRS can be used. DRS with concentrations up to 110 mg/m^2 is very difficult to prepare, because formation of particle clusters takes place.

By measuring the fluence-normalized acoustic signal produced during the ablation of surface dirt, and using a calibration factor obtained for the DRS (like in Fig. 5), the amount of surface dirt of a sample, in grams per square meter, can be then determined.

Figure 6 shows an example of the determination of the amount of surface dirt of cold-rolled steel plates by using the photoacoustic technique. We used the DRS samples and the calibration procedure described in the previous sections. Measurements were taken at a fluence of $F_w = 250$ mJ/cm^2, a value between F_0 (50 mJ/cm^2) and the ablation threshold of the substrate (800 mJ/cm^2). It is worth mentioning that for this type of samples, F_0 is the same as that determined for the developed dirt reference standards. Also, the optical properties and the thickness of the dirt deposited on cold-rolled steel plates are very similar to the DRS.

4 Conclusions

PIBMA reproducible films doped with carbon black particles (IRB#6, 100 nm diameter, at concentration between 1 and 27.6 mg/cm^3) have been designed and manufactured. These reference standards can be used for laser ablation-induced photoacoustic measurement of the cleanliness of surfaces contaminated with dirt of the same characteristics of the reference standard developed (i.e., composed of a thin film of an organic substance, such as oil or grease, with a more or less homogeneous distribution of small black particles). The result is a uniform, strong and very stable film, very easy to manipulate and store. This type of reference standards have optical properties and other characteristics that are very similar to the surface dirt deposited on cold-rolled steel plates. Then, they can be used to calibrate instruments used in the siderurgical industry for cleanliness measurements.

It is interesting to mention that in a previous work [16], we developed a reference sample made with printed dots (PDR). The main difference between this reference and the DRS developed here are: In the PDR, thickness was not included and then it is considered negligible. But this is not the real case. On the opposite, the DRS developed here include this parameter. Also, the DRS can be calibrate in mg/m^2, while in the printed dots, it can be determined only the covered area. Finally, the DRS laser ablation threshold is of the same order that it was measured for the applications of interest, in particular surface dirt of cold-rolling steel plates.

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