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Photothermal radiometry on nickel (pigmented aluminium oxide) selective solar absorbing surface coatings

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Abstract

Photothermal radiometry (PTR) is applied to characterize nickel-pigmented aluminium oxide solar absorbing coatings. A modulated laser beam is used to heat the solar samples. The subsequent emission of thermal radiation is measured as a function of modulated frequency in the range of 10 Hz to 10 kHz. A simple one-dimensional model is used to fit the experimental PTR results, allowing for the extraction of some thermal parameters for the solar absorbing coatings. Finally, comparison of the emissivity measured by traditional technique and the photothermal radiometry is made.

Keywords: Photothermal; Radiometry; Solar coatings

1. Introduction

The solar irradiance which reaches the earth is mainly restricted in the wavelength range of 0.3–2 μm. A selective absorbing surface which absorbs efficiently in the above

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[1] To the memory of Professor J.P. Traverse who passed away last February.

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range heats up and emits thermal radiation. In regard to the above information a good selective solar absorber must absorb energy in the range where solar radiance lies and have low emittance at the blackbody range defined by its temperature. In other words its absorption should be near unity within the solar spectrum whereas its emittance should be near zero for thermal reradiation. Recently, increased interest in solar energy applications has led to a very active development of selective surfaces [1]. Some of the most widely used selectively solar absorbing surfaces are metallic Ni particles embedded in anodic Al_2O_3, "black chromium" which is a complex composite of metallic chromium and dielectric Cr_2O_3, anodized black coloured aluminium using electrolytic and integral techniques, metal–insulator composites made by coevaporation, cosputtering and ion implantation. The characterization of these solar selective films has been achieved using various methods some of which involved photothermal and photoacoustics techniques. McClelland and Kniseley [2] proposed the use of the reflection photoacoustic effect for determining photothermal conversion surface efficiencies. Two years later Yun [3] used the photoacoustic effect to determine the absorption coefficient for a selective surface. In 1981, Cahen [4] used the photoacoustic technique for comparative studies of the conversion efficiency of the solar convertor. An interesting review concerning photothermal characterization of various types of coatings has also been published by Busse and Walther [5].

In this paper we demonstrate for the first time the use of photothermal radiometry [6, 7] (PTR) for the characterization of solar absorbing coatings. Light from an argon laser is used to heat up the solar material. This in turn emits infrared radiation which is measured using an infrared HgCdTe detector. This PTR technique along with a simple mathematical model is used as a non-destructive means of evaluating and characterizing Al_2O_3–Ni solar coatings.

2. One-dimensional theoretical model

In this section we will give a brief overview of a theoretical model describing the PTR signal obtained from the solar coatings in this work. Consider a sinusoidally modulated light source with intensity $\frac{1}{2}I_o[(1+\cos(\omega t)]$ incident on the sample as shown in Fig. 1. I_o is the peak intensity of the laser and ω is the laser modulation frequency. The light source is assumed incident on the coating material which has thickness L. Thermal waves generated in the coating are assumed to be partially reflected and transmitted at the material interface, and similarly at $z=0$ for waves travelling in the negative z-direction. The thermal wave diffusion equation in the coating can be written as follows:

$$\frac{\partial^2 \Delta T(z,t)}{\partial z^2} = \frac{1}{\beta_c}\frac{\partial \Delta T(z,t)}{\partial t} - \frac{\alpha\eta(1-R)I_o}{2k_c}[1+\exp(i\omega t)]\exp(-\alpha z), \tag{1}$$

where R is the surface reflection coefficient, β_c is the thermal diffusivity (m^2/s) of the coating and k_c is the thermal conductivity (W/mK) for the coating. α and η are the optical absorption coefficient and non-radiative efficiency, respectively. Similarly, for

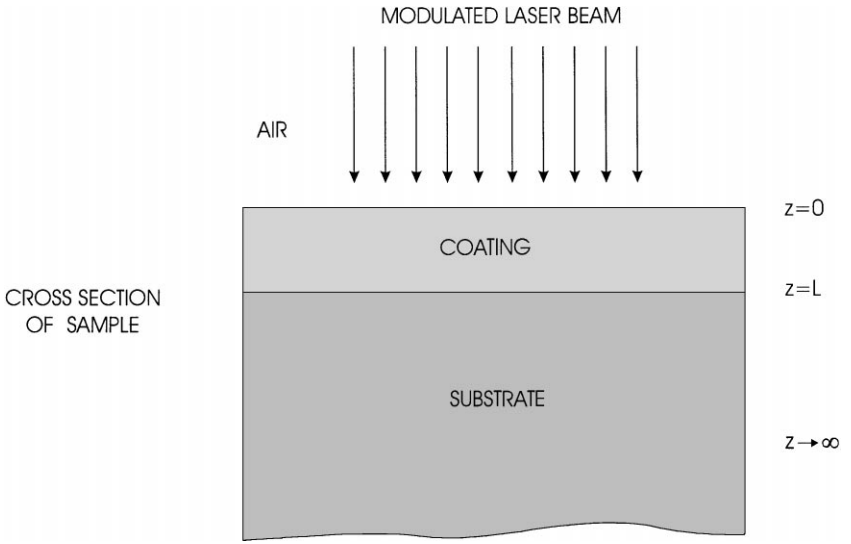

Fig. 1. A cross section of the sample used in the mathematical model. The coating thickness is assumed to have length $z = L$ and the substrate z. In this experiment the substrate was aluminium and the gas was air.

the substrate and air, the thermal diffusion equations are as follows:

$$\frac{\partial^2 \Delta T_s(z,t)}{\partial z^2} = \frac{1}{\beta_s}\frac{\partial \Delta T_s(z,t)}{\partial t} \quad z \geqslant L, \tag{2}$$

$$\frac{\partial^2 \Delta T_g(z,t)}{\partial z^2} = \frac{1}{\beta_g}\frac{\partial \Delta T_g(z,t)}{\partial t} \quad z \leqslant 0, \tag{3}$$

where the subscript s and g indicate the substrate or gas, respectively. In view of the fact that the selective coating is extremely thin (submicron) with respect to the thermal wave, we can assume that the main contribution to the signal originates from the surface of the substrate. The measured temperature change is therefore given by the following equation [8]:

$$\Delta T = \frac{\alpha \eta I_o (1-R)}{2k_c(\alpha^2 - \sigma_c^2)} \times \left[\frac{(1-r)(b+1)\exp(\sigma_c L) - (r+1)(b-1)\exp(-\sigma_c L) + 2(b-r)\exp(-\alpha L)}{(g+1)(b+1)\exp(\sigma_c L) - (g-1)(b-1)\exp(-\sigma_c L)}\right], \tag{4}$$

where

$$b = \frac{k_s \sigma_s}{k_c \sigma_c} \quad g = \frac{k_g \sigma_g}{k_c \sigma_c}, \quad r = \frac{\alpha}{\sigma_c}, \tag{5}$$

σ_c, σ_g, and σ_s, are the complex propagation coefficients for the coating, gas and substrate, respectively, given by

$$\sigma_c = \frac{1+i}{\sqrt{2\beta_c/\omega}} \quad \sigma_g = \frac{1+i}{\sqrt{2\beta_g/\omega}} \quad \sigma_s = \frac{1+i}{\sqrt{2\beta_s/\omega}}. \tag{6}$$

A direct consequence of the modulated temperature change, is a change of the total radiant emissive power of the body. As Stefan's law states, the total radiative emissive power of a body W, is related to its temperature T, with the relation

$$W = \varepsilon\sigma T^4, \tag{7}$$

where ε is the emissivity of the body, and σ is Stefan's constant. In a first approximation the change ΔW of the emissive power is directly proportional to ΔT [6]

$$\Delta W = 4\varepsilon\sigma T^3 \Delta T. \tag{8}$$

Since ΔT is a function of the modulation frequency, the emissive power change ΔW is directly proportional to it and it can be detected with the use of a lock-in amplifier.

3. Experimental part

3.1. Preparation of the samples

The samples under investigation are four nickel-pigmented alumina Al_2O_2–Ni solar absorbers. These solar-selective materials were made via the electrochemical process. The thickness of the solar coating for the various samples were obtained with an electron scanning microscope. Coatings 1 and 2 were estimated to be 0.250 μm, whereas coating 3 was measured to be 0.320 μm and finally coating 4 was 0.480 μm. A brief description of the process used in the preparation of the substrate as well as of the thin film, is given below.

3.1.1. Preparation of substrate

An 1050_α Al alloy (99.95%) was used as the substrate with dimensions 20×40 mm^2. The samples were first cleaned using ethylene trichloride for 5 min at a temperature of 60°C. This process was followed by etching using a sodium hydroxide (100 g/l, 15 min) at 60°C. Finally, in order to neutralize the surface it was immersed in nitric acid (20%W, 2 min) at room temperature. Following each step the samples were rinsed in distilled water.

3.1.2. Formation of alumina layer by anodization

Selective surfaces were obtained using different acids during anodization to create an Al_2O_3 deposit on the above Al substrates. The best results were reached with phosphoric acid (H_3PO_4). During optimization, the different parameters were kept in the following range:

- Acid concentration: $0.5\ \text{M} < X < 3\ \text{M}$.
- Anodization voltage: $5\ \text{V} < U < 25\ \text{V}$.

Table 1
Parameters of the black solar samples

Sample	Potential U(V) impregnation	Impregnation time t (min)	ε (%)[a]	Thickness (μm)	κ_c (W/mK)	Total signal
1	9.0	3.0	12.5	0.250	1.7	0.065
2	9.0	4.0	21.5	0.250	2.8	0.116
3	9.3	3.0	16	0.320	1.8	0.085
4	9.5	3.0	19	0.480	3.1	0.133

[a]Emissivity measurements by an absorptionmeter.

- Anodization time: 10 min $< t <$ 25 min.
- Distance between electrodes: 4 cm.
- Temperature of treatment: 20°C.

The parameters for optimal anodization (minimum ε and maximum α) were found to be: $X = 0.8$ M, $U = 18$ V (current density of 15 A/m^2), and $t = 18$ min.

3.1.3. Nickel impregnation

This electrochemical process will give the Aluminium oxide its selective properties for photothermal conversion. During experimentations, the nickel bath was composed as follow [9]:

- $NiSO_4$: 30 g/l, H_3BO_3: 20 g/l, $(NH_4)_2SO_4$: 20 g/l and $MgSO_4$: 20 g/l.
- Impregnation voltage varying from 5 to 15 V (AC) – Ambient temperature.
- Time of treatment confined between 1 and 5 min.

Table 1 includes the impreganation parameters for the samples utilized in this experiment.

3.2. Photothermal radiometric technique

Photothermal radiometry is one of the most widely used non-destructive techniques for characterizing various type of thin films [6, 7]. A modulated laser source is used to generate a thermal wave within the coating under investigation. The absorption of the laser light by the solar-coating material will eventually result in a change of the temperature of the material. This temperature change will be detected as a change in the infrared radiation emitted by the sample. The experimental arrangement consists of a continuous wave Ar ion laser operating in a multiline mode configuration at 488 and 514 nm. An acousto-optic modulator placed directly in-line with the Ar ion laser is used to modulate the laser beam, the modulation frequency of which is controlled with the help of a frequency function generator. The modulated laser beam is then directed into the sample chamber, used in isolating the detector and sample from the rest of the environment. Most of the laser incident power is absorbed by the sample due to the black coatings. This absorbed laser energy will be converted into heat and eventually some will be emitted as thermal radiation from the sample. This infrared radiation is collected and collimated by two off-axis paraboloid mirrors

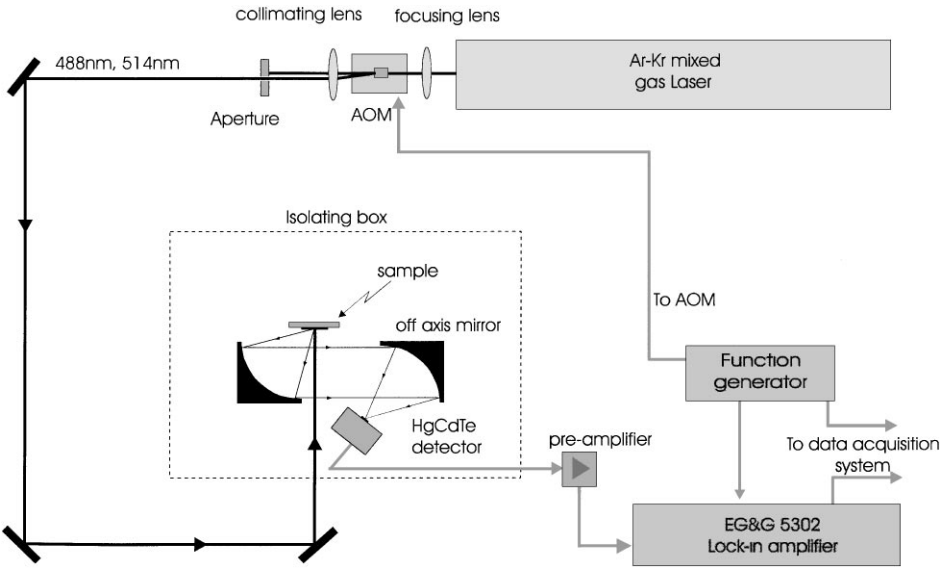

Fig. 2. A schematic of a typical photothermal radiometry technique (PTR). An Ar laser emitting 300 mW of combine 488 and 514 nm laser light is used to heat the samples. The beam is modulated with an acousto-optic modulator between 10 to 10 kHz. Infrared radiation measurements in the range of 2–12 μm are made with a HgCdTe detector using a phase-sensitive technique (lockin amplifier).

and focused into an infrared HgCdTe detector. The detector is cooled down to liquid nitrogen temperature (77 K) and has a wavelength sensitivity of 2 to 12 μm. A Ge filter covers the detector and has the effect of blocking the visible fundamental laser radiation and transmits the infrared radiation emitted by the sample. The signal from the detector after going through a preamplifier stage is passed to a lock-in amplifier which is set to detect at the modulated frequency of the acousto-optic crystal. Fig. 2 shows a schematic of the experimental set-up. The four Ni/Al solar samples were investigated using this photothermal radiometry technique. The laser beam which was approximately 300 mW was directly incident on the sample (unfocused) with a spot size approximately 5 mm. Experimental PTR results for the various samples are represented as points in Fig. 3a and Fig. 3b. Fig. 3a is a log–log plot of the amplitude of the PTR signal as a function of the modulation frequency, whereas Fig. 3b shows the phase of the PTR signal as a function of the modulation frequency. It is interesting to point out that the only noticeable change between the different samples occurred in the amplitude of the PTR signal, whereas the phase appears to be the same for all the samples.

4. Results and discussion

The experimental data of both Fig. 3a and Fig. 3b were fitted with the one-dimensional model described in Section 2. The simulation curves are shown as lines

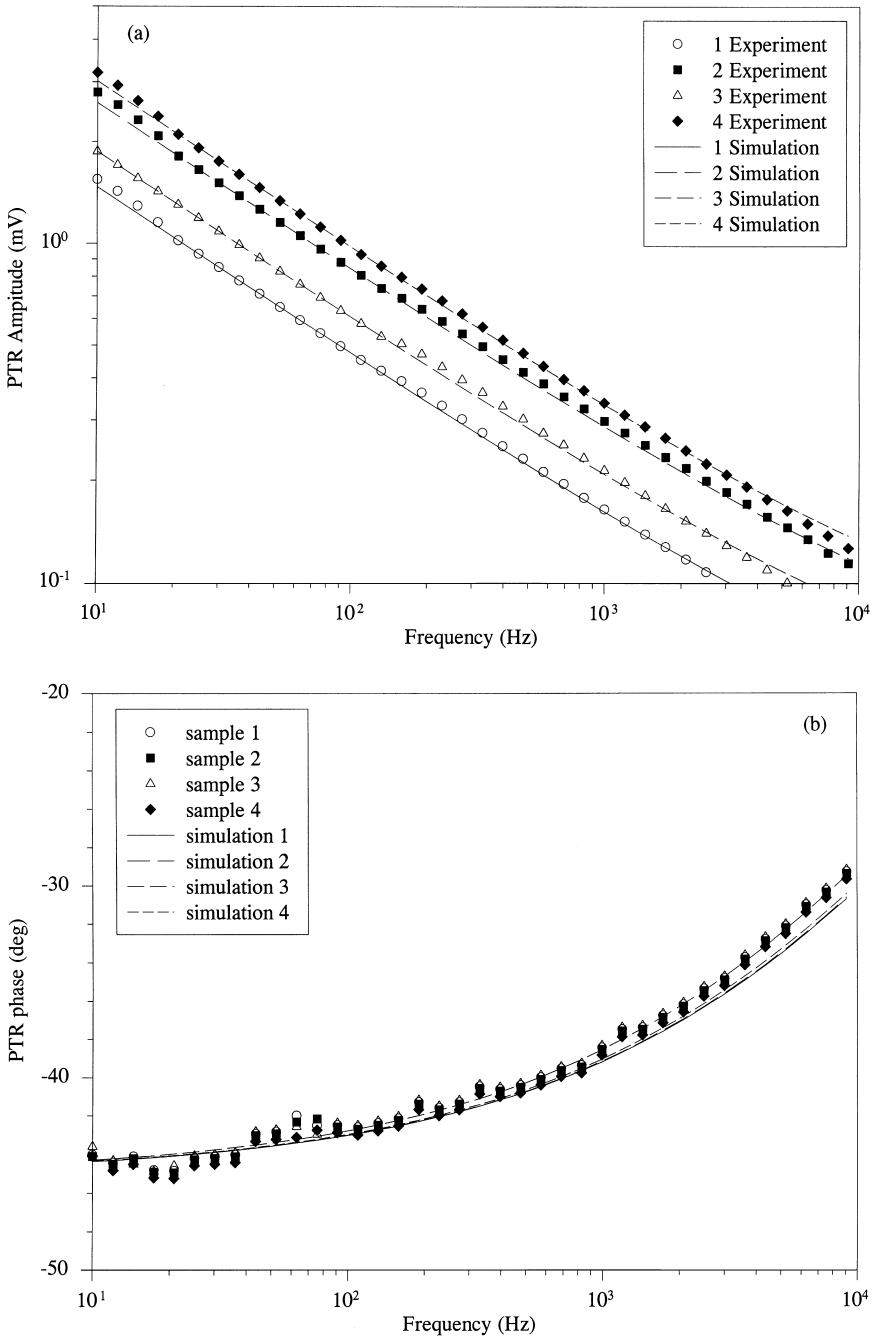

Fig. 3. PTR results for the four Al/Ni-coating solar samples: (a) PTR amplitude as a function of modulated frequency plotted on a log–log graph. The experimental data are represented by the various symbols whereas the curves represent the fitted results from the one-dimension model; (b) PTR phase experimental (symbols) and theoretical (curves) results.

on the graphs of the experimental data. These fits were obtained by varying the absorption coefficient α, the thermal diffusivity β_c and the thermal conductivity k_c of the coatings. However, variations in the absorption coefficient and thermal diffusivity had a very small effect on the fitting curves. Thus, from our fittings it is difficult to determine the exact values of these two coefficients. Nevertheless, Table 1 shows the average fitted values (α, β) which are considered as an order of magnitude approximation. All other parameters (parameters of air and substrate) were kept constant since all samples had the same substrate. The following fitting parameters for air and substrate have been used [10]: $k_g = 0.024$ W/mK; $\beta_g = 0.19 \times 10^{-4}$cm^2/s; $k_s = 201$ W/mK and $\beta_s = 0.75$ cm^2/s $\times 10^{-4}$. All fitted curves appear to be in very good agreements with the experimental data. Table 1 shows the various parameters obtained from the above simulations. In this table the constant ε is the emission coefficient which was measured by using traditional absorptionmetric technique (see next paragraph) and L is the thickness of the coating. The critical parameter in obtaining a good fit to the experimental data was the thermal conductivity of the Al/Ni coating. Sample 1 had the smallest measured total PTR signal from all the samples, which is in agreement with the measured emissivity (see Table 1). Samples 2 and 4 on the other hand, have the highest PTR signal which is again in good agreement with the emissivity results from other experiments.

The emissivity measurements seen in Table 1 (column 4), were obtained using a conventional technique. In fact, the total hemispherical emittance (ratio between the energy emitted by the surface and the energy emitted by a black body at the same temperature, i.e. 70°C) was measured by an absorptionmeter (Elan Informatique EL520) [9]. These measurements indicate that sample 1 has the lowest emissivity value, followed by samples 3, 4 and finally sample 2. It is interesting to point out that the total PTR amplitude signal in effect gives a direct measure of the emissivity. This clearly provides a new means in obtaining emissivity values for the various black coating solar samples. In view of the geometry of the PTR technique and signal collection, it is an extremely difficult task to obtain the total emissivity signal. However, in most cases, the interest is with the relative emissivity signal, which allows successful comparison between different samples.

The order of the total signal which resulted from the PTR measurement is sample 1 with lowest signal, then comes 3, 2 and finally sample 4. The order of the emissivity obtained from the PTR measurements is different for samples 2 and 4 than that obtained from the conventional technique. These samples, however, have very similar values according to the conventional emissivity measurements technique. It is our belief that these differences may be explained due to the large error (close to 15%) in the conventional technique in measuring emissivity.

5. Conclusions

Photothermal radiometry was applied and demonstrated as a non-destructive technique for the evaluation of solar selective coatings. Although the PTR technique in its present arrangement lacks absolute values for emissivity it is extremely useful as

a non-destructive technique for characterizing and improving solar-selective coatings. It is important to note that due to the simplicity of the photothermal technique it can easily be implemented in industry for in-line characterization during production. Finally, it has been shown that the theoretical one-dimensional model which is used to fit the experimental PTR results, allows the extraction of some key parameters of the solar absorbing coatings.

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