White Paper

Fundamentals of Photothermal Coating Thickness Measurement

Photohermal coating thickness measurement is a proven technology for non-contact determination of the thickness of coatings on metallic and non-metallic substrates. In this article, we present the underlying physical principles and provide information on the prerequisites for the successful application of this flexible, non-destructive and precise measurement method.

Introduction

In almost all industrial sectors, components are coated for a wide variety of reasons. To ensure the quality and efficiency of a coating process, it is essential to be able to reliably measure the thickness of the applied coating. For this reason, there are various technologies for coating thickness measurement, many of which have special requirements for the components to be measured. Measurement methods based on eddy current or induction require a metallic or even ferromagnetic substrate. Just like measuring methods based on ultrasound, they are also contacting and are therefore not suitable for measuring wet coatings or unbaked powder coatings. Photothermal coating thickness measurement, on the other hand, is an optical measurement technique that works without contact and is qualified for almost all material combinations of coating and substrate. The basis for this is the photothermal effect.

Photothermal effect

It has been known since 1880 that materials can absorb optical radiation and convert it into heat. How pronounced this so-called photothermal effect is depends on the specific material properties. Put simply, the component to be measured must be illuminated with optical radiation that is absorbed as well as possible by the coating. For non-metallic coatings, light from the near-infrared part of the optical spectrum ($\lambda > 850\,\mathrm{nm}$) is suitable, whereas for metallic or transparent coatings, the use of ultraviolet light ($\lambda < 400\,\mathrm{nm}$) may be necessary. The light hits the coating of the component, which absorbs part of it and converts it into heat – the actual photothermal effect. This results in a temperature change on the top of the coating, causing it to emit blackbody radiation in accordance with Planck’s law of radiation. The maximum of this thermal radiation is in the mid to long-wavelength infrared and can be detected using appropriate sensors. However, the heat generated by the excitation light does not remain on the surface of the coating, but diffuses through the coating towards the substrate. Physically, this diffusion is described by the heat conduction equation, which is given in Eq. (1) for the one-dimensional case.

$$\frac{\partial T(x,t)}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \tag{1}$$

The heat input takes place at the location $x = 0$ at the time $t = 0$, in this example the component occupies the half-space $x > 0$. The only material property occurring in Eq. (1) is the thermal diffusivity $\alpha = {}^{k}/_{\rho\cdot c}$, a quantity consisting of the thermal conductivity k, the density ρ and the specific heat capacity c. As the thermal properties of substrate and coating usually differ, the thickness h of the coating determines when the heat reaches the substrate if the material properties are known. By recording the blackbody radiation over time, starting from the time of excitation, information about the coating structure of the component can be obtained, which is the basis of photothermal coating thickness measurement.

Thermal waves

With a single excitation, the heat diffuses through the component and the coating cools back down to ambient temperature shortly after the excitation. Although

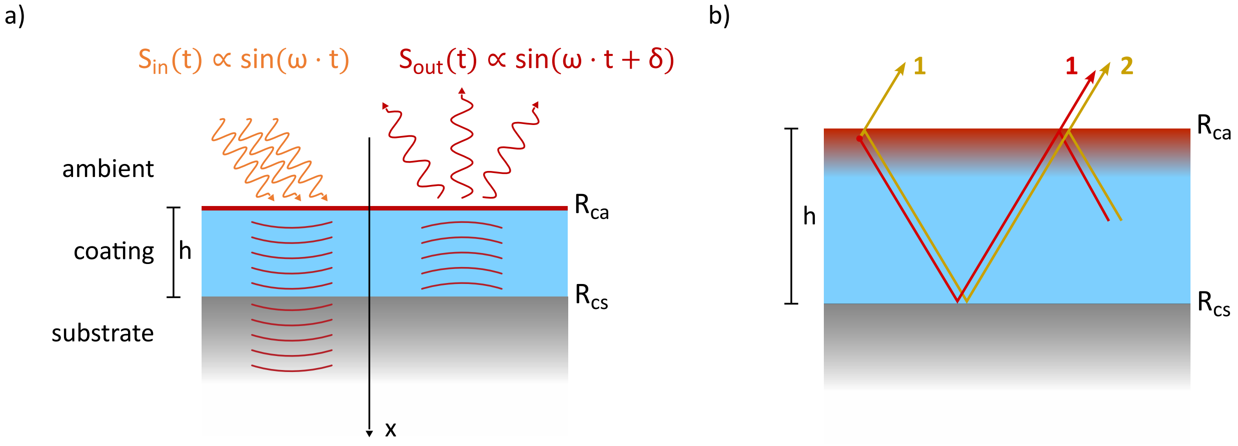

Figure 1: a) Overview of the photothermal effect and the excitation of thermal waves by a periodic light source. A substrate with a coating of thickness h is considered. The reflectivity of the thermal waves at the material transitions is described by R_{ca} and R_{cs}. b) Generation of thermal interference in a sample through the superposition of different wave trains. The temperature at the surface of the coating ultimately results from a superposition of the respective partial reflections of the original thermal wave.

the use of a single excitation pulse already allows the coating thickness to be determined, the precision can be significantly increased by using a periodic excitation, ideally sinusoidal. Physically, the periodic excitation causes a periodic heat input into the coating, resulting in a so-called thermal wave. Thermal waves are solutions of Eq. (1) if a temporally modulated heat flow with frequency $\omega = 2\pi \cdot f$ is specified as a boundary condition. This situation is sketched in Fig. 1 (a). The temperature curve within the component is then also periodic and can be described by Eq. (2).

$$T(x, t) = \frac{Q_0}{\sqrt{4e^2\omega}} \cdot \exp\left(-\frac{x}{\mu}\right) \cdot \sin\left(\omega t - \frac{x}{\mu} - \frac{\pi}{4}\right) \quad (2)$$

Here, $e = \sqrt{\rho c k}$ is the thermal effusivity, which can again be attributed to the same material properties as α. Eq. (2) shows similarity to an exponentially damped plane wave from classical optics. The attenuation coefficient μ, which occurs both in the attenuation term and in the oscillating part of Eq. (2), is referred to as the thermal wavelength.

$$\mu = \sqrt{\frac{2\alpha}{\omega}} \quad (3)$$

The thermal wavelength thus defines the penetration depth of the thermal wave into the coating. It can be tuned by selecting the excitation frequency ω: The lower the excitation frequency, the greater the penetration depth. This makes the excitation frequency an important measurement parameter, which is usually selected depending on the expected coating thickness or optimized as part of a calibration.

Although the heat conduction equation is not a wave equation, thermal waves behave like electromagnetic waves in many ways. When they hit a material transition, they are reflected and transmitted proportionally. Based on the effusivities of the materials involved, for example the coating e_c and the substrate e_s, a thermo-optical refractive index can be defined:

$$n_{cs} = \frac{e_s}{e_c} \quad (4)$$

Similar to classical optics, ratios can be specified for the reflected and transmitted components R and T of the thermal wave at a boundary layer.

$$R_{cs} = \frac{1 - n_{cs}}{1 + n_{cs}} \quad (5)$$

$$T_{cs} = \frac{2}{1 + n_{cs}} \quad (6)$$

If the effusivities of the coating and substrate differ only slightly, the thermal refractive index and therefore the reflectivity of the material transition is low. In such cases, photothermal coating thickness measurements are hardly possible. However, the component can simply be measured at a different stage of the coating process. If, for example, the thermal refractive index of a dried or baked coating on a substrate is too low, the measurement can be performed on the still wet or unbaked coating, which has different thermal properties.

Photothermal coating thickness measurement now exploits the fact that thermal waves in thin layers show interference effects analogous to electromagnetic waves, as illustrated in Fig. 1 (b): The periodic excitation excites thermal waves at the surface of the coating, which propagate through the coating according to Eq. (1). A distinction can be made between two wave trains: One wave train is first reflected at the transition to the ambient atmosphere and then propagates towards the substrate, whereas another wave train propagates directly from the heating zone towards the substrate and is reflected for the first time at the transition to the substrate.

$$\tan(\delta) = \frac{R_{cs}(1 + R_{ca})\exp(x)\sin(x)}{1 + R_{cs}(1 - R_{ca})\exp(x)\cos(x) - R_{cs}^2 R_{ca}\exp(2x)} \quad \text{with} \quad x = -\frac{2h}{\mu} \tag{7}$$

The superposition of both wave trains on the surface of the coating then results in a temperature curve on the surface of the coating that is out of phase with the excitation. A closed analytical expression can be formulated for this phase shift, see Eq. (7). In addition to the reflectivities R_{cs} (transition coating substrate) and R_{ca} (transition coating ambient), the thermal wavelength μ and the thickness h of the coating are also included in this expression for $\tan(\delta)$. Fig. 2 (a) shows an example of the calculated curve of $\tan(\delta)$ as a function of h for painted aluminum.

If the material properties are known, a coating thickness h can be calculated from a measured phase δ. However, it is even more feasible to empirically determine a curve for converting the measured phase into a layer thickness as part of a calibration. The phase progression shown in Fig. 2 (a) can be well described by a low-order polynomial in the range of 50 µm to 150 µm layer thickness, possibly even by a straight line. During calibration, the phases of ideally three or more reference samples with known coating thicknesses are measured for a fixed excitation frequency. A corresponding polynomial can then be fitted to these data points of coating thickness and phase, serving as a calibration curve and enabling the conversion of a phase into a coating thickness within a corresponding thickness range.

Measurability

In principle, photothermal coating thickness measurement is suitable for all coated materials, provided that the excitation light is well absorbed by the coating. The first obstacle to absorption is the reflection of the excitation light on the coating, quantified by the optical reflectance. As reflected light is not available for heating the coating via the photothermal effect, a high reflectance automatically implies a low measurement signal. This applies to light-colored materials, for example, which often have a reflectance above 0.9 in the relevant spectral range. Dark materials, on the other hand, can have reflectance values below 0.1. If the heating is too low for a specific measurement task due to the high reflectance, the wavelength of the excitation light can be adjusted.

If, on the other hand, there is only a low reflection, the majority of the excitation light can penetrate the coating and heat it through the photothermal effect. This requires a sufficiently high optical absorption coefficient, which is the reciprocal of the penetration depth of the excitation light into the coating. The greater the absorption coefficient, the greater the heating of the sample and therefore the stronger the signal available for measurements. Typical values range from around $10^6\ \mathrm{cm}^{-1}$ to $10^7\ \mathrm{cm}^{-1}$ for non-transparent materials to close to 0 for transparent materials in the relevant spectral range. In the case of periodic excitation, the magnitude of the absorption coefficient is also decisive for the induced temperature change θ_0 at the surface. For a strong optical absorption, corresponding to a high absorption coefficient, the following applies:

$$\theta_0 \propto \frac{1}{\sqrt{\omega}} \tag{8}$$

Weak optical absorption on the other hand yields:

$$\theta_0 \propto \frac{1}{\omega} \tag{9}$$

In the first case, θ_0 decreases proportionally with the square root of the excitation frequency, whereas in the second case it decreases proportionally with the excitation frequency itself. This behavior can be measured

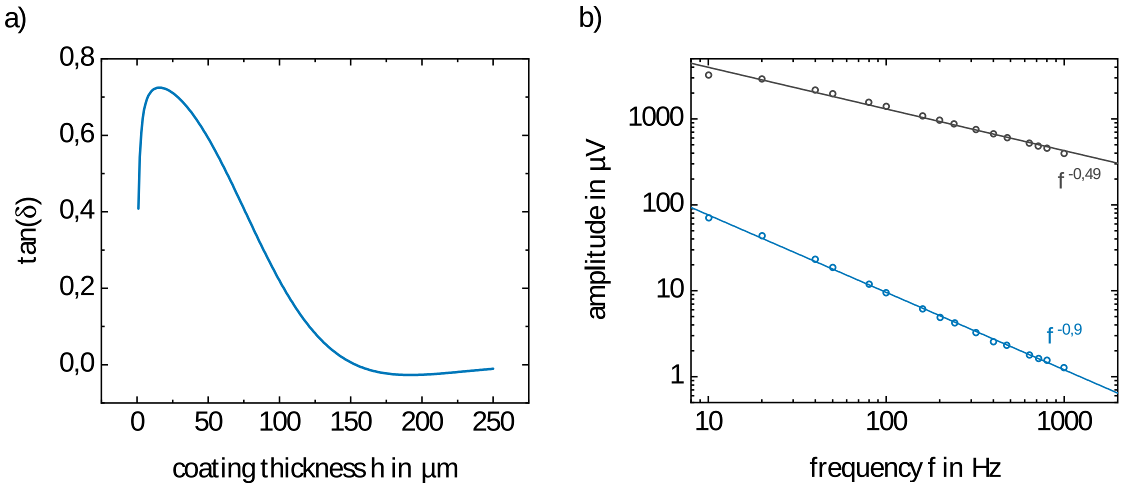

Figure 2: a) Dependence of tan(δ) on the layer thickness h calculated for painted aluminum and a excitation frequency of $\omega = 2\pi \cdot 5\,s^{-1}$. b) Amplitudes of the registered signal for a clear coat sample with weak optical absorption (blue) and a solid rubber sample with high optical absorption (black). The amplitude is proportional to the induced temperature change at the surface, the curves reproduce the corresponding equations (8) and (9) very well.

very well, as Fig. 2 (b) shows. Here, the signal amplitudes are shown for varying excitation frequency for solid black rubber (black circles) and a clear coated sample (blue circles). The exponents −0.49 for rubber and −0.9 for the clear coat sample match the expectations from Eq. (8) and (9). The deviation for the clear coat originates from the opaque substrate of this sample. These measurements demonstrate that the choice of excitation frequency not only has an influence on the penetration depth, as discussed above, but also on the signal amplitude.

After the component has been heated, the dimensionless emissivity ultimately determines the extent to which the heat introduced into the coating by the photothermal effect is emitted again in the form of detectable thermal radiation. An idealized black body radiator has an emissivity $\epsilon = 1$, a grey radiator is characterized by $\epsilon < 1$ and a non-grey radiator has a wavelength-dependent emissivity $\epsilon = \epsilon(\lambda) < 1$. The emissivity directly influences the intensity of the emitted radiation according to the Stefan-Boltzmann law. Most non-metal coatings, resists, paints and plastics can be assigned to the gray emitters in the infrared range with $\epsilon > 0.9$. The heating of these materials induced by the photothermal effect can therefore usually be measured very well with appropriate detectors.

Accuracy and repeatability

As described above, the measured phase is translated into a coating thickness via a calibration. Hence, the accuracy of a photothermally determined coating thickness depends significantly on the accuracy of the independently measured coating thicknesses of the reference samples used for the calibration. In addition, the approximation of the phase progression by a polynomial, which is often carried out as part of a calibration, is only meaningful and possible for a finite thickness range. Coating thicknesses outside this range may not be determined correctly. In summary, the accuracy of the measured coating thickness due to the calibration is influenced by the quality of the reference samples.

The repeatability, on the other hand, depends on the technical implementation of the photothermal measurement. It is typically quantified by the standard deviation of individual measured values of the same sample recorded repeatedly under the same conditions. With periodic excitation, the more periods per measurement are detected, the more accurately the phase signal can be determined. This is a significant advantage compared to a single excitation pulse, for example with a single flash. For a measurement with a excitation frequency of 150 Hz, for example, exactly 150 periods are available for a measurement time of 1 s to determine the phase and thus the thickness. With only 100 ms measurement time, only 15 periods are available. The short-

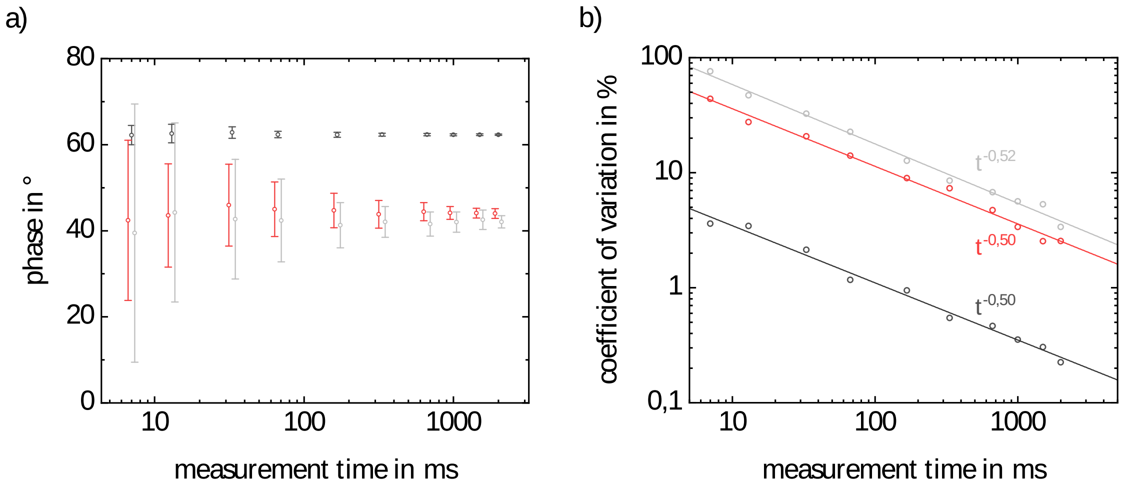

Figure 3: a) Dependence of the mean value and the standard deviation of the measured phase for 50 individual measurements on the measurement time of the individual measurement for 10 µm red and white colored clear coat and a black matt color coating on stainless steel. It can be clearly seen that the measured values show the lowest standard deviation for the black matt coated sample. Regardless of the coating, the standard deviation decreases the longer the measurement time of the individual measurement is. b) The coefficient of variation, a normalized measure for the standard deviation that is the quotient of the standard deviation and the mean value, clearly follows a $^1/\sqrt{t}$ law.

est measurement time is therefore in the order of the reciprocal of the excitation frequency. Since low excitation frequencies are required to measure very thick layers due to the penetration depth of the thermal waves, the minimum measurement time required for thick layers is greater than for thin layers.

To illustrate the relationship between precision and measurement time with periodic excitation, Fig. 3 shows the results of test measurements in which lock-in amplification is used to determine the phase. The excitation frequency is 150 Hz, which results in a minimum measurement time of around 7 ms. The test is carried out on painted stainless steel sheets, all of which are coated with an approximately 10 µm thick layer of paint of different colors. Measurements of the phase are carried out for different measuring times for each 50 and the arithmetic mean and standard deviation are calculated.

Fig. 3 (a) shows the mean value and the standard deviation (error bar) as a function of the measurement time. First of all, it can be seen that the black coating can be measured with a significantly higher precision overall, corresponding to a lower standard deviation. As described in the section on measurability, the black coating absorbs the excitation light very well and therefore generates a strong signal. The red and especially the white clear coat, on the other hand, reflect a large proportion of the excitation light, which means that the resulting signal is lower and the standard deviation is higher. Nevertheless, the mean value for these coatings remains extremely stable even with very short measurement times. This shows that with a combination of periodic excitation and lock-in amplification, even short measurement times are sufficient to obtain a robust measured value for the phase. In Fig. 3 (b) it is also shown how the quotient of standard deviation and mean value (coefficient of variation) decreases with increasing measurement time. It follows a $t^{-1/2}$ law, which is expressed in the selected double-logarithmic axis scaling as a straight line with slope $-^1/_2$. A hundred times longer measurement time thus reduces the standard deviation by a factor of 10.

Conclusion

In this article, we have described the fundamentals of photothermal coating thickness measurement and illustrated them with individual calculations and measurements. Important material properties are effusivity (heat penetration coefficient) and diffusivity (thermal diffusivity), both of which can be traced back to the fundamental material constants of density, thermal conductivity and specific heat capacity. Effusivity in particular is of crucial importance: measurements are only possible if the effusivity of the coating and substrate differ. In practice, however, this is almost always the case.

In addition, the coating must absorb the excitation radiation with as little reflection as possible, which can be ensured by selecting the excitation wavelength for the specific application. Photothermal coating thickness measurement is therefore suitable for a wide range of material systems. The precision of the measurement can be individually increased by a freely selectable measuring time, but in principle, measuring times in the range of half a second are sufficient in many cases to obtain robust values for the coating thickness. This makes photothermal coating thickness measurement using periodic excitation the ideal method for almost any substrate and any coating.

Further reading

D. P. Almond and P. M. Patel, Photothermal Science and Techniques, 1st ed. (Chapman & Hall, London, 1996).

D. Rothermel und T. Schuster, Development of a Generalized Photothermal Measurement Model for the Layer Thickness Determination of Multi-Layered Coating Systems, Appl. Sci. **13**(7): 4185 (2023).

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