INVESTIGATION ON THE ACCURACY OF THERMAL-WAVE INTEFEROMETRY IN THE THERMOPHYSICAL CHARACTERIZATION OF COATINGS

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Abstract: Thermal wave interferometry (TWI) is used for the thermophysical characterization of coatings. The characterization procedure is influenced by the magnitude of the signal-to-noise ratio and also by the amount of experimental data available. These issues are analyzed theoretically via a sensitivity formalism. This has allowed the identification of the critical factors that determine the accuracy and the limitations of the technique. Thermal diffusivity and effusivity data resulting from TWI experiments on ceramic and metallic coatings plasma sprayed onto copper substrates are presented. Their comparison with those obtained using reference techniques confirms the predictions resulting from the sensitivity analysis.

Introduction: Thermal barrier coatings (TBCs) are increasingly used to protect the base metal and allow against high operating temperatures in gas turbine and diesel engine components. Plasma-sprayed coatings can reduce the heat flow and thus the cooling requirements by up to 80%, depending on the thickness and thermal conductivity of the coating material. It is necessary to non-destructively evaluate their thermal properties in order to know their effectiveness as thermal barriers.

There have been a number of non-destructive methods used to determine the thermal properties of TBCs. The majority of these methods rely on laser-modulated or pulsed-heating techniques [1-14]. Modulated techniques have been shown to be potentially appropriate for the characterization of thermally sprayed coatings. They can be used for the quantitative evaluation of the coating thickness or thermal properties, and to image adhesion defects at the interface as well [1, 5, 7, 9]. However, the practical accuracy of those techniques and the influence of the thermophysical parameters on the characterization have never been reported.

The present article, which deals with TWI, discusses the effect of the thermal characteristics on the accuracy of the method. This was investigated using a sensitivity analysis for various values of the thermal properties. The critical factors that determine the accuracy and the limitations of the technique were established. To validate these factors, the technique was applied to the characterization of tungsten plasma sprayed onto copper substrates. The results were compared to thermal diffusivity measured by the laser flash method [8, 10, 11] and to the heat effusivity estimated from the combination of the latter measured diffusivity and the specific heat of the coating. This one was calculated using the specific heat of tungsten and air, and the air porosity in the coating measured via scanning electron microscopy (SEM). Discrepancies confirm the range of applicability of TWI in determining the thermal properties and are discussed in terms of coating thermal thickness. At the end of the description of the investigation regarding the tungsten specimens, for comparison reasons, we give the main results that were obtained in a previous work [14] that dealt with plasma-sprayed zirconia coatings. Zirconia is a much better thermal insulator than tungsten.

Results: In the TWI technique, the coating surface is heated periodically and the resulting periodic thermal response, governed by the heat diffusion equation, is monitored. The basic principle of TWI is that, when thermal waves are generated in a coating-substrate sample, they propagate diffusively to the interface, where they are effectively partially reflected and return to produce interference effects at the surface. The interference between the reflected and the incoming thermal waves leads to variations in the surface temperature phase, with respect to an uncoated surface. According to theoretical modeling [1, 4], the phase change in the complex surface temperature caused by TWI for an opaque coating material is given by:

$$\varphi = -\tan^{-1}\left[\frac{2R\exp(-x)\sin(x)}{1-R^2\exp(-2x)}\right]$$

in which $x=2L/\mu$, L is the coating thickness, μ is the thermal diffusion length $\mu=(\alpha_c/\pi f)^{1/2}$, α_c is the normal thermal diffusivity, and f is the frequency. R is the thermal wave reflection coefficient defined as $R=(1-b)/(1+b)$, and $b=[(\rho C_p k)_s/(\rho C_p k)_c]^{1/2}$ gives the ratio of the substrate and coating thermal effusivities e_s and e_c.

Typical interferometric patterns of the phase change φ, with respect to an uncoated surface, against the reduced coating thickness L/μ are shown in Figure 1 for a range of the coating/substrate reflection coefficients. A negative value of R indicates a phase lead and a positive value indicates a phase lag. The greater the magnitude of R, the larger the phase changes. Maximum interference effects occur when the coating thickness is less than a thermal diffusion length because of the heavily damped nature of thermal waves.

The TWI technique provides an effective means for characterizing coating thermal parameters or thickness. A non-linear least squares fitting of phase versus frequency measurements can be used to identify the characteristic time $t_c=L^2/\alpha_c$ and the reflection coefficient R. The coating thermal diffusivity is obtained from the characteristic time if the coating thickness is known, and the coating thermal effusivity is obtained from the reflection coefficient if the substrate effusivity is known. In order to check the identifiability and the reliability of the unknown parameters, some issues have to be considered. One of them is the influence of the measurement noise on the unknowns. Another is the choice of the suitable experimental data for the identification procedure in order to avoid any risk of correlation between parameters. This has already been dealt with elsewhere [14] using a sensitivity analysis and only the main conclusions are given here:

- Diffusivity and effusivity are not correlated, which means that simultaneous identification of both parameters is theoretically possible.
- Accurate effusivity estimation will be very difficult for cases where phase data are limited to larger thermal thickness. This may happen, for example, for certain experimental designs limited to low frequencies when characterizing thermally thick coatings.
- Large absolute values of the reflection coefficient lead to more precise estimations of the diffusivity.
- The precision of the estimated effusivity is almost constant when the absolute value of the reflection coefficient changes.
- It is easier to better identify the diffusivity than the effusivity when the reflection coefficient is large, $|R| > 0.65$. On the contrary, when the reflection coefficient is small, it is easier to better identify the effusivity than the diffusivity. It is worth noting that for those small values of R, the maximum sensitivity to effusivity is located near the maximum of the phase curve.
- The extremum value of the sensitivity to the diffusivity occurs in the decreasing region of the phase signal. Specifically, it occurs at the inflexion point of the decreasing part of the phase, at a thermal thickness close to 1. This is applicable for any value of the reflection coefficient.
- The sensitivity to diffusivity cancels out (exact zero value) when the thermal thickness corresponds to the maximum of the phase curve. This means that an estimation using data in the maximum phase region, and particularly a maximum point identification procedure, are not suitable for effective identification of the diffusivity.

To validate the above sensitivity conclusions, we carried out experimental trials on four coating samples prepared by the plasma-spraying process. The four samples were tungsten plasma sprayed onto a copper substrate. The coatings were obtained with commercial tungsten powder of granulometry 5.6 - 45 μm (H.C. Starck, Amperit 140.3). The powder spray rate was adjusted to get a deposition rate of 12 μm/pass. The carrying argon gas flow was set at 7 $L.min^{-1}$. The plasma-spraying torch was laterally scanned at 0.6 $m.s^{-1}$. The torch was a Plasmadyne SP-100 with a No.129 cathode, No.145 anode and No.130 gas injector. The power was 28 kW (800 A and 35 V). The arc gas was argon and the auxiliary gas was helium (32% helium, with 50 $L.min^{-1}$ for argon and 24 $L.min^{-1}$ for helium). The standoff distance during spraying was 76 mm. The substrate was cooled with a nitrogen jet, while the front surface was air-blasted to eliminate aerosols.

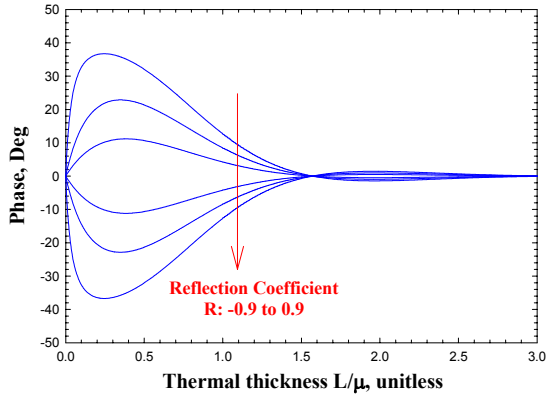

Figure 1. Phase angle variation with coating thermal thickness for various coating/substrate reflection coefficients ($R = \pm 0.90, 0.60, 0.30$).

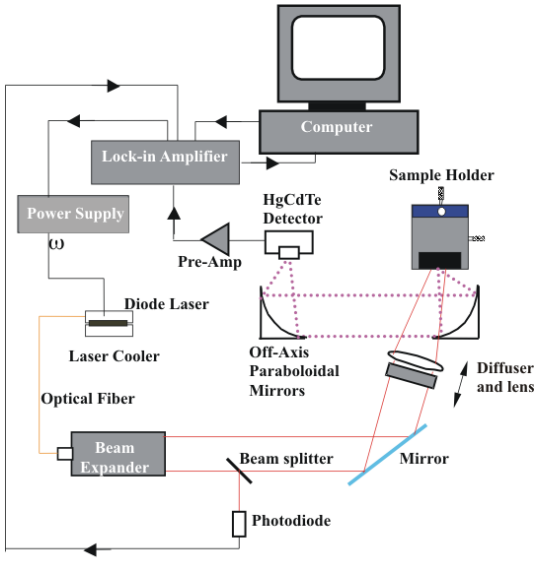

Figure 2. Schematic representation of the thermal-wave-interferometry testing system.

The experimental system for sample frequency scans is shown in Figure 2. A high power 20-W laser (Jenoptik JOLD-X-CPXL-1L) was current-modulated using a Thor Labs high power laser driver with a maximum modulation-frequency capability of 10 kHz and minimum frequency capability of 0.1 Hz. The largely anisotropic multi-mode laser beam was expanded, collimated and then directed onto the surface of the sample. The infrared (Planck) radiation from the optically excited sample surface was collected and collimated by two silver-coated, off-axis paraboloidal mirrors and then focused onto a liquid nitrogen cooled HgCdTe (Mercury-Cadmium-Telluride) detector (EG&G Judson Model J15016-M204-S01M-WE-60). The heated area of the sample was at the focal point of the one mirror positioned near the sample and the detector was at the focal point of the other mirror. The HgCdTe detector is a photoconductive element that undergoes a change in resistance proportional to the intensity of the incident infrared radiation. Our detector had an active square-size area of 1mm x 1mm and spectral bandwidth of 2-12 μm. An anti-reflection coated germanium window with a transmission bandwidth of 2-14 μm was mounted in front of the detector to block any radiation from the laser. Prior to being sent to the digital lock-in amplifier (EG&G Instruments Model 7265), the photothermal radiometric (PTR) signal was amplified by a low-noise preamplifier (EG&G Judson PA101), specially designed for operation with the HgCdTe detector. The lock-in amplifier, which was interfaced with a PC, received and demodulated the pre-amplifier output (thermal-wave amplitude and phase). The process of data acquisition, storage and frequency scanning was fully automated.

Frequency scans from 0.1 Hz to 200 Hz were performed with large laser beam size (> 1.5 cm) to keep the photothermal response one-dimensional. System transfer function normalization was achieved by performing the same one-dimensional experiment with a homogeneous (untreated) sample, a Zr alloy, and using this frequency scan to normalize the frequency scans of the coated samples. Normalization problems due to the inadequacy of our reference sample were observed in the data below approximately 0.3Hz. Calculations of the thermal diffusion length showed that for very low frequencies, the thermal diffusion lengths of copper and zirconium were longer than the depth of the samples themselves. For this reason, the first ten points of the normalized data have been set aside as "ignored data". These data can be used as long as we normalize the points by a proper semi-infinite reference sample. In the unnormalized form they have relative value and can also be used to observe signal trends. The normalized phase data above ~ 0.3 Hz have been plotted in Figure 3. By comparing the phase-versus-frequency curves reported in Figures 1 and 3, the reflection coefficient R was expected to be around –0.90. As previously mentioned in the conclusions resulting from the sensitivity analysis, this case (large R value) is very suitable for accurate diffusivity estimation. The effusivity should also be accurately estimated because it still has quite a high sensitivity at thin thermal thickness. As a result, owing to the fact that useful experimental phase data

were not available for frequencies below 0.3 Hz, we did not expect to obtain precise estimations of effusivity for thermally thick coatings, namely Samples 3 and 4. However, diffusivity measurements were expected to be quite accurate. Indeed, the maximum sensitivity to diffusivity is within the decreasing part of the phase versus frequency curve, and the lack of data at low frequencies did not have a serious effect on its estimation. Figure 4 shows a typical example of the non-linear numerical fitting of experimental data for Sample 1 (L = 123 µm). Table 1 summarizes the results obtained from all the samples analyzed by the TWI technique. We also mention for reference that because of the low level of the roughness compared to the coating thickness, effects of roughness were neglected in the frequency range (0.3-200 Hz) used during the processing of the phase data. This assumption is based on the fact that for low roughness levels, the phase signal is affected by roughness only at very high frequencies and less influenced at low frequencies where it exhibits the behavior of a homogeneous coating.

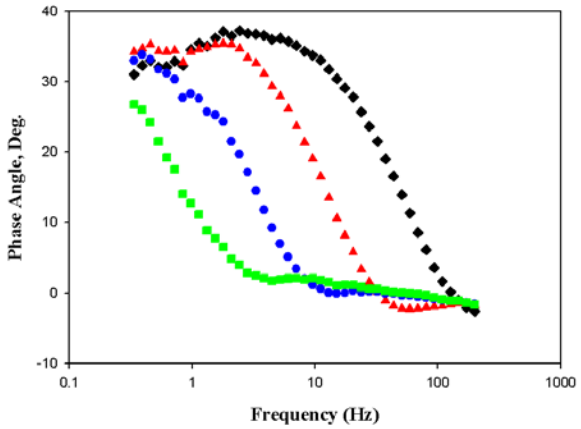

Figure 3. Normalized phase versus frequency curves of copper substrate with tungsten coating of thickness 123 (□), 223 (▲), 449 (() and 835 µm (%).

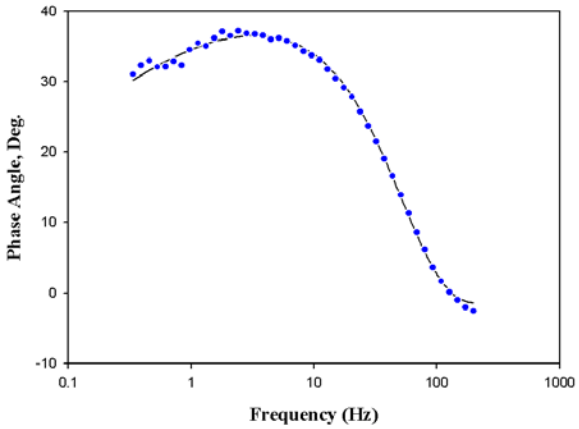

Figure 4. Numerical fitting of the thermal diffusivity and effusivity for the thinner tungsten coating (Sample 1, thickness L = 123 µm).

To validate the thermal diffusivity and effusivity measured by TWI, we performed comparison measurements using the flash and SEM experiments. To carry out the latter techniques, it was necessary to separate the coatings from the substrates. This was done by chemical etching for 2 h in a 50 % water solution of nitric acid, which did not substantially attack tungsten. The flash method is considered to be a very reliable and accurate technique for diffusivity measurement (better than 5 % precision). In this experiment, we projected a YAG laser pulse, of nearly 600 µs duration and 10 J energy, over the full front face of the sample so that the heat transfer could be considered as one-dimensional. The temperature evolution with time at the center of the back face was monitored by an InSb infrared detector. The temperature data were first processed to determine the characteristic time $t_c=L^2/\alpha_c$. To estimate the diffusivity from the latter characteristic time, the coating thickness L was subsequently measured using the coating cross-section images provided by SEM. Figure 5 shows a typical microscopic image obtained from a tungsten coating (Sample 3). Measured coating thickness is reported in Tables 1 to 4. Thermal diffusivities measured by the flash method are reported in Table 2. Knowing the diffusivity α_c measured by the flash method, it was possible to evaluate the effusivity of the coating using the following relationship: $e_c=(\rho C_p)_c\,(\alpha_c)^{1/2}$. The specific heat of the coating $(\rho C_p)_c$ is simply given by: $(\rho C_p)_c = (\rho C_p)_{air}\,F + (\rho C_p)_w\,(1\text{-}F)$, where F is the coating porosity, $(\rho C_p)_{air}$ and $(\rho C_p)_w$ are the specific heats of air and tungsten, respectively. The coating porosity F was determined from the processing of the images obtained from SEM taken at 500x in backscatter mode. For each coating, the porosity was calculated from ten images randomly selected on the coating cross section. The estimated thermal effusivities are reported in Table 3.

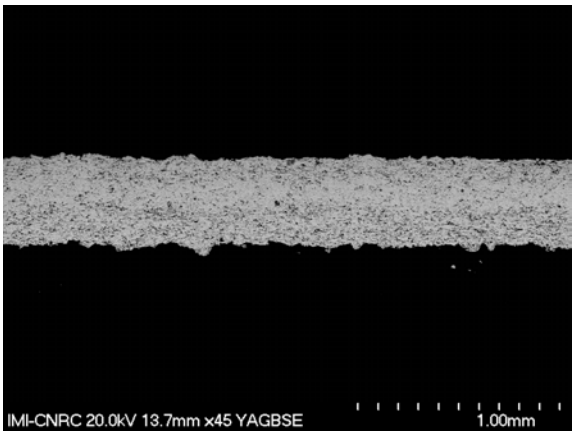

Figure 5. Typical image obtained via SEM of the cross-section of the 449-µm-thick tungsten coating. The image is used to the accurate thickness and porosity of the coating.

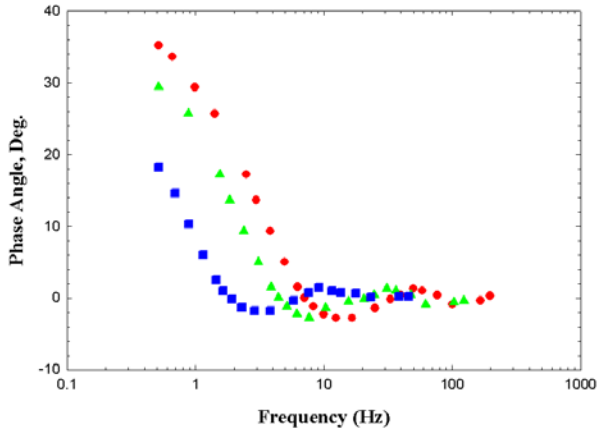

Figure 6. Normalized phase versus frequency curves of copper substrate with zirconia coating of thickness determine 252 (), 317 (▲) and 494 µm (%).

In a previous study that was reported elsewhere [14], we used the same strategy to analyze the accuracy of TWI in characterizing the thermal properties of a plasma-sprayed zirconia coating. Only important results will be recalled here, the reader may refer to the above-mentioned article for a detailed description of the study. Compared to tungsten, zirconia has a lower thermal diffusivity (5 to 8 times lower). On the other hand, the thinnest zirconia coating that was investigated had a thickness of 252 µm. As a consequence, the investigated zirconia coatings had a much higher thermal thickness than the tungsten specimens described in this work. Moreover, the TWI experiment that was employed at that time to test the zirconia specimens was limited by its lock-in amplifier to frequencies higher than 0.5 Hz. All these facts caused the TWI measurement to be restricted only to the decreasing part of the phase signal as shown in Figure 6. This figure shows the experimental data for the three zirconia coatings, L = 252, 317 and 494 µm. Again, according to the sensitivity analysis conclusions, we did not expect to obtain precise estimations of the effusivity for the zirconia samples. However, diffusivity measurements were expected to be quite accurate.

Discussion: It can be seen from Tables 1 to 3 that TWI provides diffusivity values comparable to those obtained with the flash method. Table 4 summarizes the relative deviations between the thermal properties provided by the TWI technique and those given by the flash and the SEM measurements. The diffusivity errors were less than 7 %, which is comparable to the standard precision of the flash method, 5 %. With regard to effusivity, the agreement was acceptable only for the thin tungsten coatings (L = 123 and 223 µm), where the absolute relative discrepancy did not exceed 8.43 %. For thick coatings (L = 449 and 835 µm), the discrepancy in effusivity measurements was quite high, more than 20 %. This confirms the conclusions of the sensitivity analysis for the determination of the effusivity in the case of thermally thick coatings when the experimental design provides useful data only in the high-frequency range. In the experimental apparatus used in this work, the useful frequency range was limited to frequencies larger than 0.3 Hz.

Table 5 summarizes the discrepancies between the thermal properties provided by the TWI technique and those given by the flash and modulated differential scanning calorimetry (MDSC) measurements for the zirconia specimens. It can be seen clearly that the identification of the diffusivity by TWI is quite acceptable. The diffusivity errors were less than 7 %. On the other hand, the absolute effusivity error was in the range 14 to 71 %. These percentage errors are not comparable to standard effusivity evaluation techniques (accuracy < 5 %) and are too high to be acceptable. However, it should be pointed out here

that these results for zirconia coatings were obtained in unfavorable evaluation conditions: large coating thickness and low thermal diffusivity.

Summary: This work deals with the analysis of the accuracy of TWI in estimating the thermal properties of coatings. First, we characterized four plasma-sprayed tungsten coatings, each with a different thickness. Then, we compared the TWI results with those obtained using the flash method and the scanning electron microscopy. The discrepancies were discussed in terms of lack of useful data in the low frequency range, below 0.3 Hz. Indeed, the experimental arrangement used during TWI experiments did not provide useful phase data in the latter frequency range. The study has shown that the lack of data at low frequencies did not affect diffusivity measurements. However, it had a strong effect on the characterization of effusivity of thermally thick coatings. The experimental results confirmed the conclusions obtained by a theoretical sensitivity study that has previously been performed [14] to determine the critical parameters that influence the accuracy of TWI.

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Table 1. Diffusivity and effusivity of tungsten coating obtained by thermal wave interferometry

Sample No.	L (μm)	α (10^{-6} $m^2.s^{-1}$)	R	e ($J.m^{-2}.°C^{-1}.s^{-1/2}$)
1	123	2.24	-0.897	3135
2	223	3.40	-0.879	3691
3	449	4.70	-0.808	6132
4	835	5.24	-0.681	10931

Table 2. Diffusivity of tungsten coating obtained by the flash method

Sample No.	L (μm)	α (10^{-6} $m^2.s^{-1}$)
1	123	2.32
2	223	3.22
3	449	4.39
4	835	5.51

Table 3. Effusivity of tungsten coating obtained by the combination of the diffusivity measured by the flash method and the specific heat calculated using the coating porosity measured with SEM, as well as the specific heats of tungsten and air

Sample No.	L (μm)	α (10^{-6} $m^2.s^{-1}$)	F (%)	ρC_p (10^6 $J.m^{-3}.°C^{-1}$)	e ($J.m^{-2}.°C^{-1}.s^{-1/2}$)
1	123	2.32	16.4	2.17	3244
2	223	3.22	15.7	2.19	4030
3	449	4.39	10.5	2.32	5029
4	835	5.51	15.7	2.19	5004

Table 4. Discrepancies of TWI with respect to the flash and the SEM measurements for the tungsten coatings

Sample No.	L (μm)	$\Delta\alpha/\alpha$ (%)	$\Delta e/e$ (%)
1	123	+3.43	-3.38
2	223	-5.67	-8.43
3	449	-7.03	+21.92
4	835	+4.81	+118.43

Table 5. Discrepancies of TWI with respect to the flash and the MDSC measurements for the zirconia coatings

Sample No.	L (μm)	$\Delta\alpha/\alpha$ (%)	$\Delta e/e$ (%)
1	252	+6.95	+24.31
2	317	+3.16	-14.32
3	494	-3.93	-71.57