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Thermal Transport-Property and Contact-Conductance Measurements of Coatings and Thin Films[1]

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There is an intense and growing demand for knowledge of the thermal transport properties and contact conductances of coatings, thin films, and interfaces. The laser flash technique is uniquely suited for many of the measurements. The usefulness and limitations of this technique for coatings, greases, and joining techniques are described in some detail. Several alternate techniques, namely, step heating, multiproperty, and photoacoustic techniques, are briefly examined.

KEY WORDS: adhesives, coatings; contact conductance; thermal barrier coatings; thermal conductivity; thermal diffusivity; thin films.

1. INTRODUCTION

Thermal transport properties of thin coatings such as thermal barrier coatings (TBCs) used in airplane engines and other thin films present special challenges to the researcher. These difficulties arise from extreme sensitivities associated with uncertainties and nonuniformity of the sample thickness, with possible gradations in properties of very thin films, with contact conduction between coating and substrate, and with the general problems of dealing with small or fragile samples. When one adds the complications of measuring over very wide temperature ranges and two-dimensional properties, the necessity of having a variety of techniques becomes evident.

2. LASER-FLASH TECHNIQUE

The laser flash method [1] to measure thermal diffusivity (α) combined with differential scanning calorimetry (DSC) to measure specific heat

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(C_p) and bulk density (ρ) values calculated from sample geometry and mass has been an effective method to determine thermal conductivity (λ). Thermal conductivity values are calculated as the product of these quantities, i.e., $\lambda = \alpha C_p \rho$. This approach enjoys the advantages of using small samples of simple shapes, the ability to measure over wide temperature ranges rapidly (and hence being cost-effective, and having a relatively high degree of accuracy when properly performed with suitable geometry samples. The laser flash method, ASTM E 1461-98 involves holding a sample, normally about 12.7 mm square, at the desired measurement temperature. The front surface receives a pulse of energy from the laser, which soon raises the back-face temperature. The rear-face temperature response is normalized and compared with the theoretical model based on Carslaw and Jaeger's solution to one-dimensional heat flow [2]. Using that model, thermal diffusivity values can be obtained at any percent rise of the curve.

Layered structures have been studied extensively [3–5]. The dimensionless rearface temperature-rise history following an instantaneous heat pulse to the front of a layered sample composed of layers whose diffusivity ratios are less than about 10 : 1 is the same as that for a homogeneous sample, provided that there is no contact resistance between the layers.

Lee and Taylor [4] and Lee et al. [3] developed computer programs which calculate the thermal diffusivity of one layer of a two-layer or three-layer composite from the half-time, $t_{1/2}$, measured in the conventional manner by the flash technique. Programs were also written and tested to compute the contact conductance between two layers whose thermal properties are known. Lee et al. [3] also established the criteria for distinguishing between a resistive and a capacitive layer. It is interesting to note that reversing the direction of heat flow does not affect the response curve.

3. EXPERIMENTAL RESULTS OBTAINED BY THE FLASH TECHNIQUE

3.1. Thermal Barrier Coatings

Even though samples of free-standing TBCs have been measured, it was often necessary to add thin coatings to the front surface to prevent laser beam penetration. In addition, we usually had to apply a very thin coating on the rear surface to prevent an infrared (IR) detector from viewing into the sample and thus not giving an accurate temperature rise curve for the rear surface. In general, the presence of a rear surface coating did not have to be accounted for because it takes only a very thin layer to prevent the IR, detector from viewing into the sample interior. However, preventing a relatively severe laser burst from penetrating into the samples may require a significant protective coating, depending upon the translucency of the TBC. In cases of a substantial front layer, the presence of the protective coat must be accounted for and the experiment becomes a two-layer case (see below). It should be noted that in the case of TBCs mounted on a metal substrate, there is no need for a protective front layer, since the metal substrate provides this, i.e., the substrate side is always positioned toward the laser.

The agreement in the conductivity values for TBC samples of 0.43- and 1.42-mm thicknesses was generally within 4%, even though the half-time values were different by a factor of about 10 [6]. This is a strong indication that the results are valid (along with on-line comparisons of experimental to theoretical rise curves) and that the translucency problem is taken into account.

While we routinely determine the thermal conductivity of one layer bonded to another, the accuracy strongly depends upon the absolute and relative values of the individual layers. The input parameters which enter into a two- (or three)-layer calculation are the thicknesses, densities, and specific heat of each layer, the diffusivity of one (or two) layers, and the measured half-rise times. The sensitivity of each of these parameters also depends on the relative values between these parameters for the various layers, i.e., the relative magnitudes of the layer thicknesses, the relative magnitudes of the diffusivity/conductivity ratios, etc. The situation is further complicated by the fact that the calculations of the diffusivity/conductivity value of the unknown layer is based upon parameter estimation (i.e., iterative) procedures. Therefore, several cases have been examined. These cases all involve superalloy substrates whose conductivity/diffusivity values increased substantially with increasing temperature and TBCs of relatively low diffusivity/conductivity values which were relatively temperature-independent. This means that the relative magnitudes of the diffusivity/conductivity values for the substrate and coating increases substantially with increasing temperature. For example, the conductivity ratios of substrate to coating were of the order of 10:1 at 100°C and greater than 20:1 at 1000°C.

The effects of uncertainties in the input parameters for the case of a 0.28-mm coating bonded to a 0.635-mm substrate at 500°C are examined in Fig. 1 [6]. The calculated conductivity values are most sensitive to the uncertainty in the coating thickness and the measured half-times. However, it should be possible to obtain sufficiently accurate input parameter values to obtain reasonable results for this case. But when we consider a 0.083-mm coat on a 3.05-mm substrate at 500°C (Fig. 2) [6], the extreme sensitivities of the calculated conductivity value to errors in substrate thickness, diffusivity, and half-rise times preclude meaningful results. For example, a ±1%

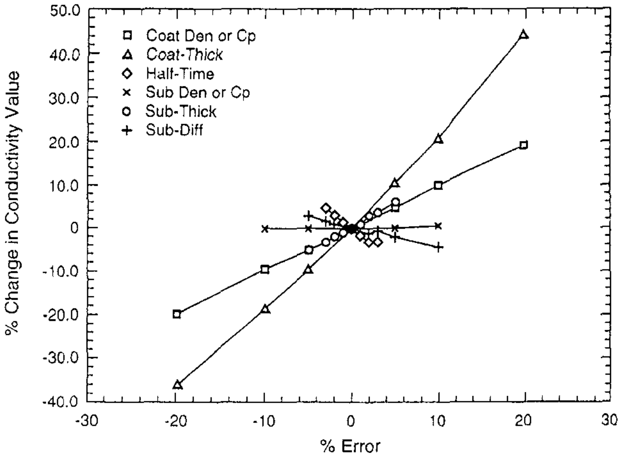

Fig. 1. Percentage change in computed thermal conductivity values based on percentage errors in input parameters (0.28-mm TBC coating on a 0.635-mm superalloy substrate).

change in the value assigned to substrate thickness results in changes of +60 and −28% in the conductivity values. A ±2% change in the measured half-time value from 0.34089 s (i.e., 0.34089 ± 0.00682 s) results in changes in the calculated conductivity values of +65 to −30%.

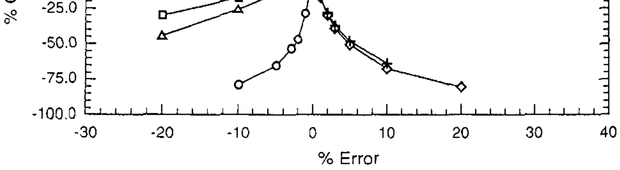

Fig. 2. Percentage change in computed thermal conductivity values based on percentage errors in input parameters (0.083-mm TBC coating on a 3.05-mm superalloy substrate).

As mentioned earlier, these sensitivities also depend upon the relative magnitudes of the diffusivity/conductivity values of the substrate and TBC. The larger this ratio, the better is the experiment, i.e., more accurate values of the conductivity are obtained. This is the reason that the conductivity values for the layered composites approach those for the free-standing coatings at higher temperatures. It is interesting to note that coating conductivity values could be determined fairly accurately under the conditions of Fig. 2 if their values were one-tenth of the value normally encountered.

To summarize our experiences with the laser flash technique applied to TBC coatings, we routinely obtain very good results for 0.51-mm coatings, less accurate results for 0.25-mm coatings, and much less accurate results for 0.13-mm or thinner coatings, depending upon the manufacturer's ability to furnish accurate information on layer thicknesses and densities.

3.2. Paints, Adhesives, and Greases

We have measured hundreds of samples of paints, adhesives, greases, or scales on substrates. Again, we must know the properties of the substrate and the layer thicknesses accurately in order to get reliable results. We must also take precautions to ensure that the IR detector does not view into the sample. The measurement of the conductivity of paints, whose values often lie in the 0.002 to 0.006 $W \cdot cm^{-1} \cdot K^{-1}$ range, have not proven to be very difficult.

Many suppliers have attempted to increase the conductivity of adhesives and greases by adding particles of high conductivity. Invariably they have been very disappointed to find out that averaging conductivity values does not apply, i.e., they thought that adding 25% particles of a high-conductivity material to the adhesive or grease would cause the conductivity of the mixture to be about 25% that of the high-conductivity particles. There are numerous equations to predict the conductivity of such two-phase systems [7]. We often found the Bruggeman-variable dispersion equation to be the most accurate [8]. However, the actual increase in conductivity is also dependent upon factors such as particle shape and size, particle dependency to "clump" instead of to disperse uniformly, etc.

3.3. Scales and Anodized Surfaces

The problems caused by scales have varied widely. In the case of rolling mills, for example, the effective conductivity was not appreciably altered by the formation of a scale on the rolling surface—probably because of the pressures and temperatures encountered. On the other hand, scales formed on the interior walls of pipes and heat exchangers have been found to have significant consequences.

A particular intriguing case involves anodized aluminum. We measured the case of a 0.15-mm-thick anodized, layer on a 3.99-mm-thick aluminum alloy substrate. Based on our experiences with TBCs and other materials, we expected a difficult task. However, the results were very good, as there were large differences between the measured half-times for the substrate and the substrate plus coating. It turns out that the conductivity of the anodized layer is only 0.011 $W \cdot cm^{-1} \cdot K^{-1}$, compared to 1.65 $W \cdot cm^{-1} \cdot K^{-1}$ for the aluminum alloy—a factor of 150. In fact, the presence of the relatively thin anodized layer on the surface reduced the effective conductivity of the material by a factor of eight. The conductivity of anodized aluminum is much different from that associated with Al_2O_3. This is undoubtedly due to a large difference in structures of the two—as the large oxygen atoms interact with the relatively small aluminum atoms in attempting to form the closest packing of oxygen spheres with aluminum atoms in the interstices. The ease in measuring this system compared to measuring the diffusivity of correspondingly thick TBC layers on a superalloy support the statements made with regard to the sensitivity analysis, i.e., changing the conductivity ratio from 10 : 1 to 150 : 1 makes it easy to determine the conductivity values for the coatings.

3.4. Contact Conductance and Joints Between Dissimilar Members

When the properties of two layers are known, the contact conductance (H) between the layers can be determined using the laser flash technique [1]. An example of the normalized rear-face temperature rise for a sample of silicon wafer/grease/aluminum heat sink under no-load conditions compared to the perfect thermal contact case is shown in Fig. 3. The large differences between the two normalized curves is evident. This normalization procedure involves dividing the measured temperature by the maximum rise (Y-axis) and dividing measurement times by the half-rise time (X-axis). It was quite easy to measure the increase in contact conductance (i.e., the decrease in interfacial resistance) with applied pressure. It must be remembered that conductance (ending in *-ance*) is not an intrinsic property (such as conductivity, which ends in *-ity*). Thus, the thicknesses of the layers contribute to the magnitude of H, and a simple statement that H is a certain value other than zero or infinity is not definitive. However, with a knowledge of the values of H and the thicknesses and conductivities of each layer, the effective conductivity of the sample can be calculated.

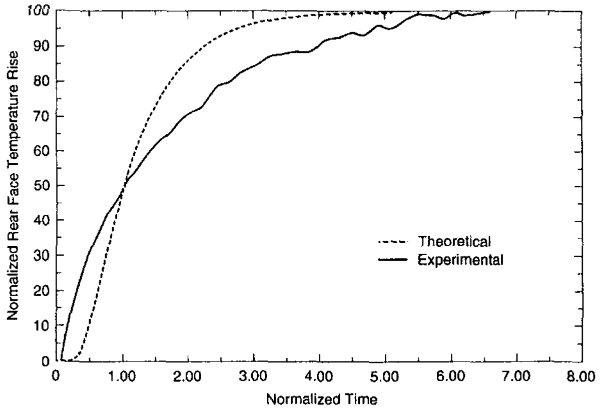

Fig. 3. Comparison of experimental normalized rear-face temperature rise curve with theoretical normalized curve without interfacial resistance (silicon wafer/grease/aluminium system under no applied pressure).

4. STEP HEATING

The step heating technique involves flooding the front face of a sample with a constant or long-time heat source and measuring the temperature response at the rear surface or at several locations [9, 10]. It has been successfully applied to insulations and large-grained materials, neither of which are very well suited for the laser flash technique. We have modified the technique for use in studying high-conductivity films in the in-plane direction [11]. In this case, the method is similar to the periodic techniques of Hatta et al. [12], except that the method is DC and uses temperature rise curves as opposed to frequency shifts. The technique was checked using foil samples of tantalum, copper and molybdenum. The results for two CVD diamond films are shown in Fig. 4. The peak values for Sample A and Sample B occur near 200 and 280 K, respectively. The thermal conductivity of both samples roughly follows the T^3 rule in the low-temperature region (below 200 K) where boundary phonon scattering is dominant. However, at relatively high temperatures, the thermal conductivity is relatively less sensitive to T and the boundary phonon scattering is less important. The scanning electron microscope results for Samples A and B in Fig. 4 show that their grain sizes are about 20 and 2 μm respectively. Phonon theory indicates that the effect of the smaller grain size will depress

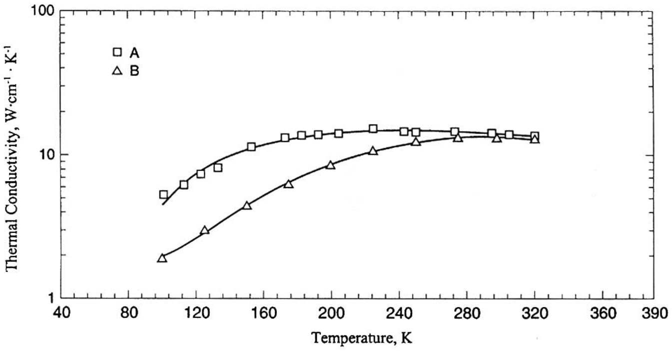

Fig. 4. In-plane thermal conductivity of diamond films.

the conductivity at very low temperatures and shift the peak value to a higher temperature. The measured data of the polycrystalline films (Fig. 4) approach the value for single-crystal diamond [13] near room temperature, which indicates that boundary phonon scattering is not the dominant phenomenon in CVD diamond in this region.

5. MULTIPROPERTY APPARATUS

This technique [14] involves Joule heating of an electrically conducting sample enclosed in a vacuum system. Power generated in the central portion of the sample where temperature gradients are negligible is equated to heat losses. Electrical resistivity and total hemispherical emissivity values are calculated from measured voltage drops, current flow, sample geometry, and temperature. Recently, TBC-coated thin-walled metal tubes were examined. From the temperature gradient across the TBC coating, thermal conductivity values for the coating could be calculated. The conductivity values obtained were about one half of those usually encountered for TBCs of this chemical composition. However, the structure of the deposited TBC was deliberately different from the usual structure in such a manner that the conductivity should be considerably smaller. Thus, it appears that this technique may be a useful method to determine conductivity values for TBCs. However, additional studies are required before the method is put "on-line." The advantages of this technique include the linear dependence of conductivity on coating thickness rather than the quadratic dependence inherent in diffusivity methods, and the possibility of better effective averaging of uncertainties in thickness. The major disadvantage is the necessity of coating larger specimens and determining temperature gradients across the TBC.

6. PHOTOACOUSTIC TECHNIQUES

We are investigating photoacoustic techniques [15]. The obvious advantage of this approach is the elimination of a knowledge of coating thickness. The major disadvantage is the difficulty in covering an extended temperature range. We may use this technique to determine the values near room temperature and calculate the effective thickness of the layers for laser flash experiments.

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