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Thermophysical properties of thermal barrier coatings

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Abstract

Thin layers of thermal barrier coating (TBCs) are applied to metallic components of heat engines to reduce metal temperatures and to provide environmental protection. This results in increased engine efficiency and prolonged operational life. Of special current interest is the use of TBCs in aircraft engines. The TBCs, often yttria-stabilized zirconia (YSZ), are deposited on nickel or cobalt-based superalloy components used in high-temperature environments. The thermophysical properties (especially thermal conductivity) of the coatings are extremely important since, together with the coating thickness, they control the temperature drop across the coating. Accurate determinations of the thermal conductivity of the coating are critical in designing the engines and in research aimed at decreasing the thermal conductivity of TBCs. Such research includes very thin multiple layers, compositional changes and deposition techniques. The number of potentially applicable techniques is limited because of the sample configurations. Consequently, the reproducibility of results from a technique or agreement between the results from different techniques may not be satisfactory.

Keywords: Thermal barrier coatings; Thermal conductivity; Thermal diffusivity; Thin layers; Zirconia

1. Introduction

Thin layers (usually 5–10 mil thick) of thermal barrier coatings (TBCs) are applied to metallic components of heat engines to reduce their operating temperatures, increase environmental protection and extend the life of the components. Currently of special interest is the use of TBCs in aircraft engines. Values of the thermophysical properties, especially thermal conductivities of these coatings, are extremely important since temperature drops across the coatings are controlled by the thermal conductivity and operating temperature. Thus, accurate determinations of the thermal conductivity are critical in designing the engines and in research to improve (in this case to decrease) the thermal conductivity of TBC coatings. A number of techniques have been used to determine the thermal conductivity of TBC coatings, but there has been no summary paper published on an inter-comparison of results by different techniques under controlled conditions — although the scatter of results even from the same technique have sometimes been substantial. Unfortunately, poor results from measurements on improperly sized samples have been published, whereas excellent results measured using the same techniques on near ideal samples have not been released for publication. Thus, analysts may draw erroneous conclusions concerning the validity of techniques as well as the magnitude of the thermal conductivity values.

2. Measurement techniques for thermal conductivity determination

Although a number of techniques have been employed, the overwhelming majority of the measurements have been performed by three methods: (1) laser flash diffusivity, (2) 3-omega, and (3) photoacoustic. These methods are all described extensively in the literature; only brief descriptions will be given here.

The laser flash technique [1,2], which is an ASTM standard method (E1461), involves subjecting the entire front surface of a small (coin size) specimen to a very short burst of energy from a laser. The irradiation times are typically less than 1 ms. The resulting temperature rise curve for the rear surface is recorded and analyzed (Fig. 1). The analysis includes comparing this experimental curve with that calculated from the mathematical solution of a semi-infinite specimen initially at a constant

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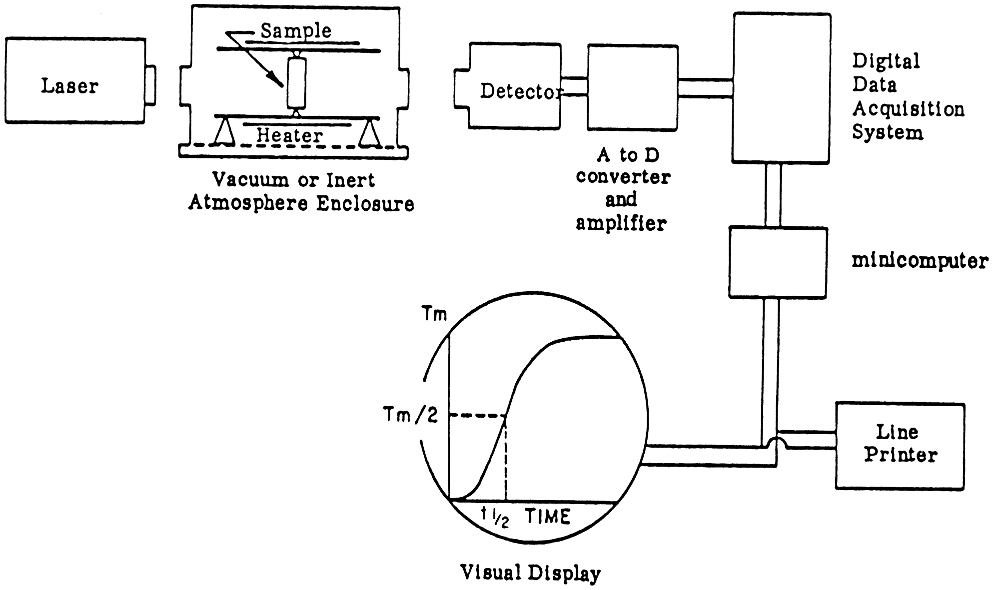

Fig. 1. Schematic of laser flash technique.

temperature subjected to a flash of energy. A large number of diffusivity values can be calculated from the rise curve. The equation is $\alpha = K_x \ell^2 / t_x$ where α is the thermal diffusivity, K_x are known constants corresponding to different percentage rises, ℓ is the sample thickness and t_x is the elapsed time for the rear face temperature to rise to $x\%$ of its maximum. The maximum rise is typically about 1°C, so all the diffusivity values are based on essentially the same ambient temperature. The raw data can be examined on-line and appropriate corrections made for heat losses, [3] finite pulse time offset [4] or non-uniform heating. This elegant, rapid, well-developed method uses small samples of simple geometry and is useful over an extremely large range of diffusivity values and measurement temperatures. Well over one-half of the conductivity values measured since 1980 have been obtained by this technique. In order to convert diffusivity results to thermal conductivity values, the diffusivity results are multiplied by the bulk density (d) and specific heat (C_p). Both of these properties are thermodynamic properties, relatively insensitive to microstructure, small variations in composition, etc., and are relatively easy to determine. Therefore, the conversion of diffusivity values to conductivity values generally is not of major concern, and the diffusivity, specific heat, density route is usually more accurate than heat flux, temperature gradients and sample geometry determinations.

The 3-omega technique was developed by Cahill [5]. It is similar to the hot-wire technique in that it utilizes radial flow of heat from a single element that is used as both heater and thermometer. The major difference is the use of the frequency dependence of a temperature oscillation instead of a time domain response. A narrow heating element is deposited on the sample to form a narrow line source of heat on the surface of an infinite half volume using either photolithography or evaporation through a mask. An a.c. power of controllable frequency is supplied to the heater, and the temperature response of the heater is determined from its resistance. The thermal conductivity is determined from the power and the third harmonics of the voltage oscillations. The method is useful for very thin films, but so far, it has been limited to temperatures below 500°C.

The photoacoustic technique [6] involves periodic heating of the surface of the sample by a radiant heat source. The sample is in a small acoustic chamber. The surface heating causes acoustic waves that are detected by microphones. A schematic of the experimental apparatus for the photoacoustic measurement is shown in Fig. 2. The diffusivity of the sample is determined from the phase lag between the heat source and the acoustic wave and/or the ratio between the amplitude of the acoustic signal of the sample and the amplitude of the acoustic signal of a reference with known thermal and optical properties. Theoretical relations between the phase lag and thermal and optical properties and the geometry of the sample have been well established [6]. In practice, to improve the measurement accuracy, the unknown thermal diffusivity is obtained from a procedure of curve-fitting of the measured phase lag or amplitude ratio in the frequency range used in the experiment. Generally, the photoacoustic signal is measured in the frequency range between 100 and 20 000 Hz. The maximum temperature rise at the sample surface is estimated to be less than 0.5°C. The method is limited in temperature range due to the microphones.

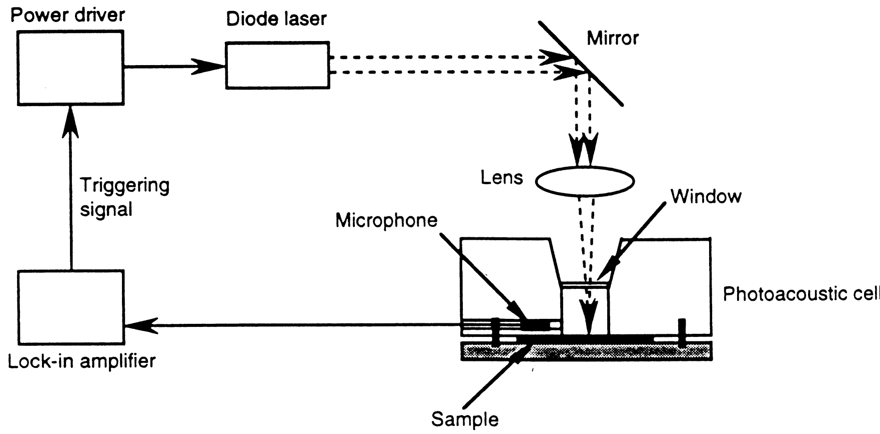

Fig. 2. Schematic of the photoacoustic technique.

3. Sensitivity study of laser flash technique

Sensitivity studies of the laser flash technique for measurements on TBCs have been carried out. The input parameters that enter into a two-layer calculation are the thicknesses, densities and specific heats of each layer, the diffusivity of one layer 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 and the relative magnitudes of the diffusivity/conductivity values of the coating and substrate. The calculations of the properties of the unknown layer is based upon parameters estimation (i.e. iterative) procedures. The results of a sensitivity analysis for a 11 mil YSZ layer bonded onto a 25 mil superalloy substrate are shown in Fig. 3 [7]. The abscissa is the percentage error in an input parameter, and the ordinate is the resulting change in the calculated thermal conductivity value. For example, a 10% error in coating thickness, i.e. 0.0010 inches (1 mil), causes a 20% error in the calculated conductivity values. However, a curve that is almost horizontal, such as that for substrate density or specific heat, indicates that the errors in those parameters have a negligible effect. For the same configuration of a 4.1 mil coating on a 24 mil substrate, the most sensitive parameters are the substrate thickness, substrate diffusivity and measured half-times [7]. In other words, several parameters associated with the substrate dominate the accuracy of the calculated conductivity values of the coating. This is due to the fact that the major portion of the transit time for the heat pulse is associated with the substrate. The time associated with the coating is relatively small, and errors in the substrate parameters have a large effect on this value. The same study [7] showed that measuring the conductivity values of a 3.3 mil YSZ layer on a 120 mil superalloy was untenable by the usual flash technique.

An unpublished study at TPRL based on 5 mil TBC coatings on 14 mil superalloy substrates, demonstrated that accuracies and reproducibilities of several per cent could be achieved from 100 to 1200°C (Fig. 4). Thus, the laser flash technique is quite capable of yielding useful data for coatings of the thicknesses contemplated for aircraft engine use.

4. Comparison of results by different measurement techniques

There has been no published account of a round-robin program specifically aimed at inter- comparing results on the same TBC/superalloy composite samples. However, several samples were measured using the laser flash method at TPRL and by the photoacoustic technique at Purdue University. Only the amplitude method was used in the calculations for the photoacoustic technique since the TBC layer was too thick for the use of the phase lag method. The major source of error in using the amplitude method comes from the uncertainties in determining the surface reflectivity. Since the surface of the TBC sample is fairly rough, the uncertainty of measuring the reflectivity, which includes both the diffuse and the specular components, is estimated to be $\pm 10\%$. Using the numerical analysis, this uncertainty in reflectivity causes about $\pm 10\%$ of uncertainty in determining the conductivity values of the sample 1758. Samples 1736 and 1787 are also measured using the amplitude method and are subjected to the same uncertainty analysis.

The results for the two techniques are compared in Table 1. It can be seen that the results obtained from the two techniques agree with each other within the experimental uncertainty range. However, the agreement for Sample 1736 may be fortuitous. The uncertainty in the layer thicknesses of this sample is large. This sample

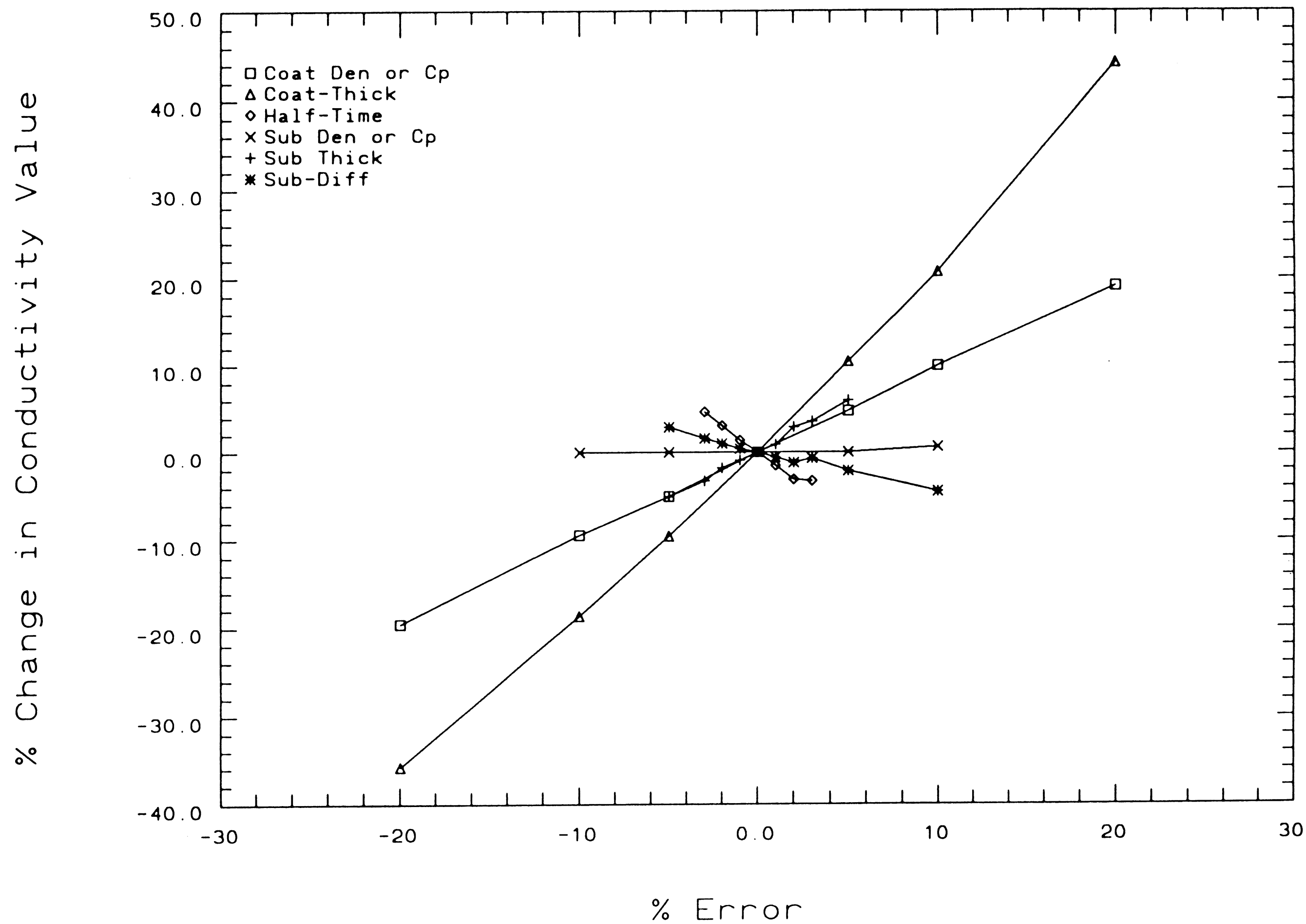

Fig. 3. Errors in calculated conductivity values for a 11 mil YSZ layer bonded onto a 25 mil superalloy substrate caused by errors in input parameters.

consisted of 2.6 mil TBC on 110 mil substrate, and this is a very poor ratio for the laser flash. As discussed previously, for the laser flash method, the uncertainty in thickness greatly affects the thermal conductivity results. However, the thickness value is not needed when the photoacoustic method (the amplitude method) is used. The data obtained from the photoacoustic method should be more reliable for this sample.

Although 3-omega measurements were not performed on these samples, it was stated that 3-omega and laser flash measurements have yielded comparable results where near optimum type samples were employed [8].

5. TBC studies

There are three obvious ways to attempt to lower the thermal conductivity of TBCs. These are: (1) to make the TBCs of many thin alternating layers to create a significant interfacial resistance; (2) to increase and control porosity; and (3) to decrease the inherent thermal conductivity of the TBC by increasing atomic scale disorder.

Taylor [7], Josell et al. [9] and Lee et al. [10] have all shown that the interfacial resistance of TBCs consisting of many thin YSZ layers is small. Thus, the conductivity values of such composites are essentially equal to those calculated from the conductivity values of the constituents and their volume fractions, and no advantage is gained by fabricating TBCs consisting of many thin layers.

The general effects of porosity on thermal conductivity of mixtures have been extensively studied. There are numerous equations relating thermal conductivity to porosity. These are usually based on equations for binary mixtures, with the pores being a discontinuous phase with negligible conductivity [11]. Equations that take into account pore geometry such as spherical, platelets (laminae) and cylinders and orientation have been derived or determined empirically [11]. Since the various equations yield a variety of values, it is usually possible to fit porosity data reasonably well to at least

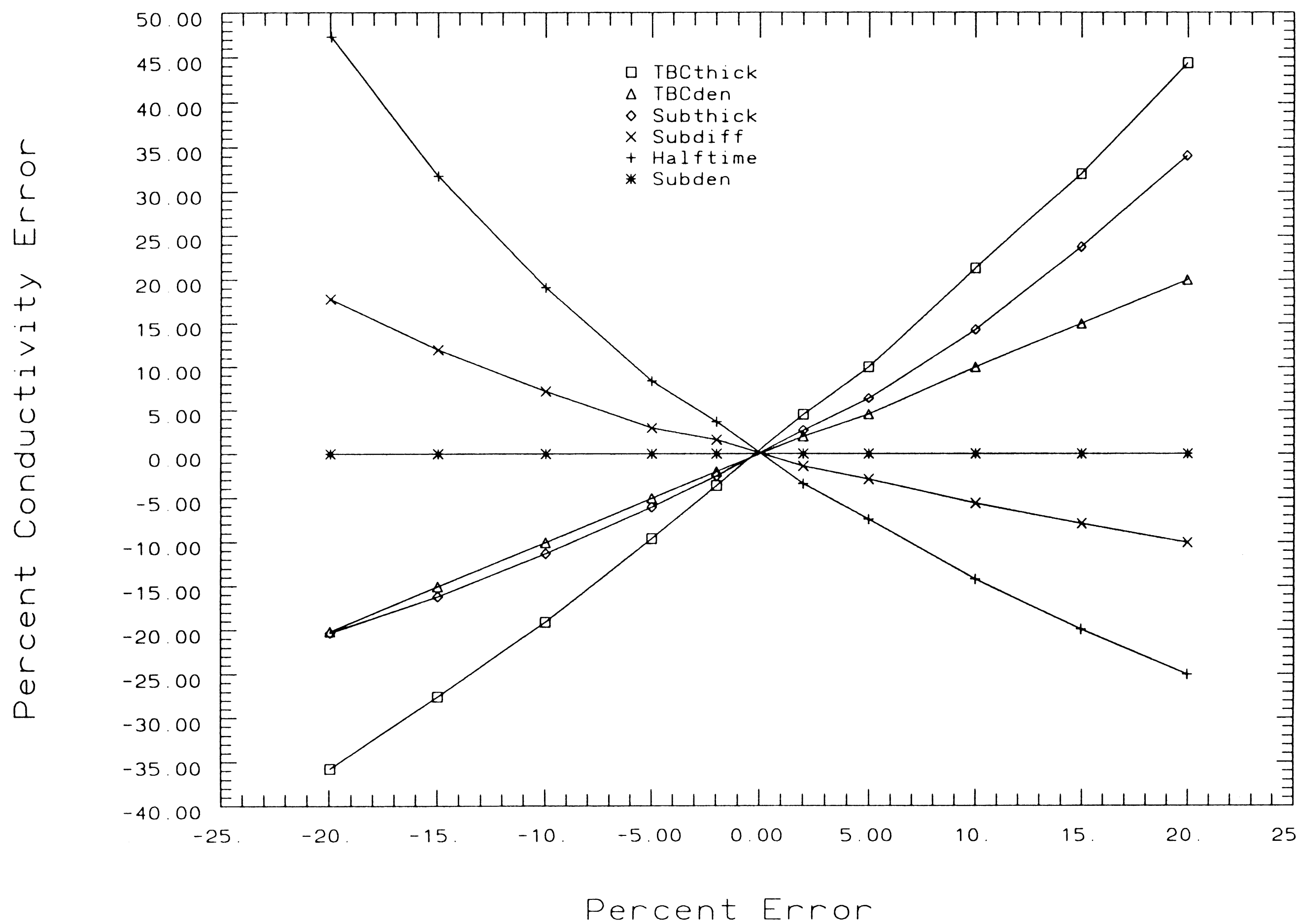

Fig. 4. Errors in calculated conductivity values for a 5 mil YSZ layer bonded onto a 15 mil superalloy substrate caused by errors in input parameters.

one equation. A study specifically aimed at studying the effects of grain size and porosity of bulk yttria-stabilized zirconia is under way at the University of Connecticut under the direction of Professor N. Padture [12]. The first results show that the conductivities of dense polycrystalline and single crystal YSZ are the same. Data on the relation between the thermal conductivity and the pore size and total porosity have been obtained and are in the course of publication [12].

The microstructure of TBCs is well known to substantially influence the thermal conductivity. The problem with producing low conductivity coatings by this approach is that the conductivity values may increase substantially during heating. Thermal diffusivity values for an as-sprayed TBC and sister samples heat-treated for 36 h at 1090°C (36-1093), 5 h at 1371°C (5-1371) and 100 h at 1371°C (100-1371) are shown in Fig. 5 [7]. The density values for these samples were 5.100, 5.104, 5.006 and 5.066 g cm^{-3}, respectively. The increase in diffusivity values with increasing heat treatment is evident, and the changes are substantial. Because the specific heat values (Table 2) are essentially unchanged and the density changes are relatively small, the conductivity value changes mirror the diffusivity value changes. Since the material is to be used in high-temperature engines with a long operating life, these changes are important [7].

Table 1
Comparison of conductivity values

Sample I.D.	Laser flash ($W\ cm^{-1}\ K^{-1}$)	Photoacoustic ($W\ cm^{-1}\ K^{-1}$)
1736	0.0042[a]	0.0045
1758	0.0066	0.0061
1787	0.0096	0.0098

[a] 2.6 mil TBC on 110 mil substrate according to supplier. Very non-optimum for laser flash. Value uncertain within ±20% due to uncertainty in thicknesses.

6. Summary and conclusions

The thermal conductivity values for ZRO_2 and TBCs are low (in the range of 0.004–0.012 W cm^{-1} K^{-1}) and are not strongly temperature-dependent. The low

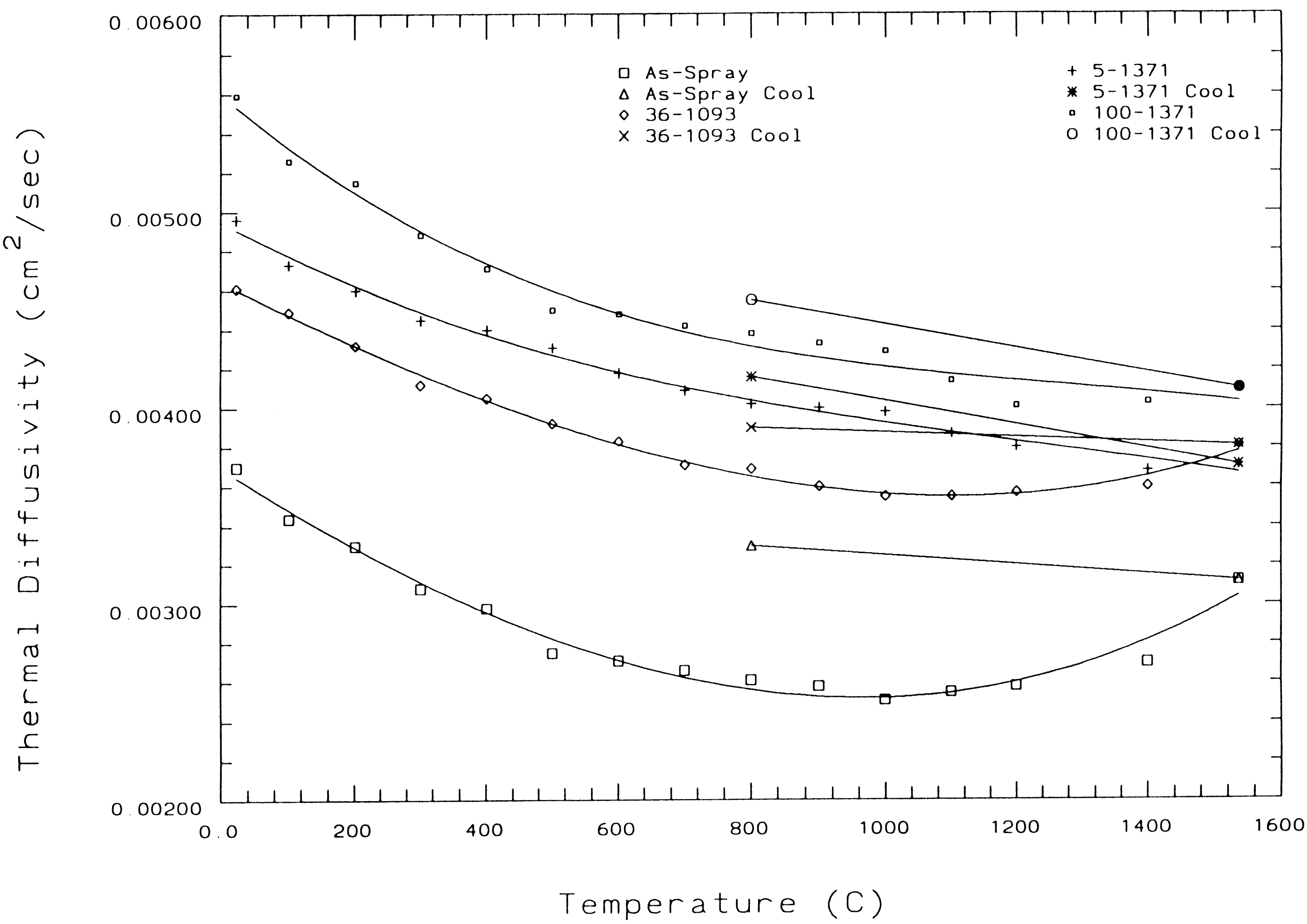

Fig. 5. Thermal diffusivity values of plasma-sprayed YSZ subjected to heat treatment for various times (h) and temperatures (°C). 'Cool' refers to cooling curve data.

values are caused by atomic disorder, and thus grain boundary scattering and interfacial resistance do not play a major role. Reliable thermal conductivity values for TBCs can be obtained on free-standing or TBC/substrate composites by the laser flash, photoacoustic or 3-omega techniques under specified conditions. Each technique has its advantages and disadvantages. The laser flash technique can readily be used from below room temperature to the melting point of the substrate, whereas the other techniques are useful only at lower temperatures. However, the flash technique depends critically upon the coating and substrate thickness, whereas the other techniques do not. A particularly attractive approach is to measure the values near room temperature using both the laser flash and the photoacoustic (or 3-omega) techniques and then use the flash technique for higher temperature measurements. A comparison of the near room temperature values by the other techniques can be used to determine the effective coating and substrate thicknesses for the flash experiments.

Table 2
Specific heat values

Temperature (°C)	Specific heat (J/g C)
23	0.469
100	0.499
200	0.542
300	0.569
400	0.593
500	0.605
600	0.618
700	0.621
800	0.630
900	0.637
1000	0.645
1100	0.647
1200	0.649
1400	0.653
1500	0.655

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