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Problems for determining the thermal conductivity of TBCs by laser-flash method

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Materials

ABSTRACT

Purpose: The purpose of this paper was to investigate the parameters which effect the results of determining the thermal conductivity of thermal barrier coatings (TBCs) by laser-flash method.
Design/methodology/approach: The air plasma-spray (APS) technique was used to deposition of two- and three-layered samples. Two-layered samples were composed of metal substrate (321 stainless steel), and ceramic top coat (8YSZ). Three-layered samples were composed of metal substrate (321 stainless steel), bond coat (NiCrAlY) and top coat (8YSZ). Thermal diffusivity of each layer have been measured in the temperature range from room temperature (RT) to 900ºC by laser-flash method. The thermal conductivity was calculated with respect to density, specific heat and diffusivity of the materials.
Findings: Obtained results show that the specific heat, density and thicknesses of metal substrate, bond coat and top coat play important role in the thermal conductivity measurement.
Research limitations/implications: To obtain the correct results in laser-flash technique thickness, density, and cp of the materials are needed to be measured accurately and surface smoothness of samples should be provided sensitively. Errors in these parameters cause high deviations in measurements.
Practical implications: It has been aimed offer an insight into the experimental determination of thermal conductivity of layered TBC system which are used in high technologic applications.
Originality/value: Laser-flash method is the most widely used experimental technique to determine the thermal conductivity of APS TBCs at high temperatures. The research contributes to better understanding and recognition the importance of sample preparation in laser-flash method.
Keywords: Ceramics; Thermal conductivity; TBCs; Laser-flash method

1. Introduction

Oxide ceramic materials feature high melting temperature, relatively low density and low thermal conductivity as well as considerable corrosion resistance to chemically active media in high temperatures. Ceramic coatings, however, seem more effective as thermal barriers TBC deposited upon surfaces of super-alloy surfaces, operating under load in high temperatures [1].

TBCs have been widely used in hot-section metal components in gas turbines either to increase the inlet temperature with a consequent improvement to the efficiency or to reduce the requirements for the cooling air [2-5]. The typical TBC used in gas turbines consists of a bond coat produced by the vacuum or low pressure plasma-sprayed

MCrAlY (M = Ni, Co) and a top coat of yttria partially stabilized zirconia made by the atmospheric plasma spraying or electron beam-physical vapor deposition (EB-PVD) [6-7].

Within the last decade there has been a consistent growth in the use of composite ceramic materials and layer-coated ceramics. Excellent chemical and wear resistance, a wide range of electrical and thermal properties, and high service temperatures have made these materials extremely valuable to industry. Due to their increasing importance, and the wide range of shapes, sizes, and composition in which these materials are produced, it is essential to have reliable methods available to measure their thermal conductivity and diffusivity [8].

There are a variety absolute and comparative methods currently used to measure thermal conductivity or diffusivity, including both transient and steady-state [8-10] techniques. Laser-flash [11-13], hot-wire, and three-omega methods are the most widely used transient techniques [14]. The laser flash method is used commonly and typical of the non-contact transient method. An instantaneous heat pulse is generated by the absorption of the laser energy on the front surface of the sample and it transmits to the rear surface on which the temperature rise is detected by an IR sensor [15]. This method is widely used because of the small sample size required and the ease and rapidity with which measurement can be taken. The disadvantage of this method is that density and heat capacity also need to be known or measured to calculate thermal conductivity. In addition, the use of indirect transient methods may yield questionable results in complex composites or layered ceramics where there are unusual patterns of heat flow within the body of the material [8].

The thermal conductivity of plasma sprayed zirconia (stabilized with 7, 8, and 20 wt % yttria) and of NiAl, NiCr, NiCrAl, NiCrAlY and NiCoCrAlY bond coatings have been measured in the temperature range 27 ºC – 727 Cº with the use of laser-flash method [16].

Plasma sprayed coatings have been investigated between the room temperature and 1200 Cº [17] as an example of Al_2O_3 and ZrO_2 based coatings.

This method was extended to the numerical approach was chosen for the determination of contact resistance, which considers finite pulse time, heat loss, and transparency [18]. Hohenauer and Vozár [19] have been presented measurements of the thermal diffusivity on two- and three-layered copper/alumina composites using the laser-flash method.

In this study the thermal conductivity of two-layered samples which are composed of substrate, ceramic coating and three-layered samples which are composed of substrate, bond coat, ceramic coating have been measured by laser-flash method.

The parameters which will effect the measurement results in determining the thermal conductivity of air plasma sprayed TBC coating (APS) by laser-flash method and will increase the sensitivity of measurement and the reasons of errors in results were disscussed.

2. Material and method

In this research, as type of the coating using yttria stabilized zirconia 8 wt % (8YSZ) air plasma sprayed thermal barrier coating was analyzed.

It is essential to know the thermal diffusivity value of each layer for layered systems in laser-flash method [18-20]. Hence, diffusivity of 321 stainless steel was measured first. Then for the samples composed of substrate and bond coat, thermal diffusivity of the bond coat was recorded. Finally diffusivity of Air Plasma Sprayed (APS) coating was measured. The specific heat of each layer was determined for the purpose of calculating thermal conductivity in view of past literature data.

2.1. Lazer flash technique

The heat balance equation for transient conditions may be written as

$$\nabla\cdot\nabla\lambda T+\left(\text{intrenal source/sink}\right)=C_p\rho\frac{dT}{dt} \tag{1}$$

If there are no internal source:

$$\nabla\cdot\lambda\nabla T=C_p\rho\frac{dT}{dt} \tag{2}$$

For homogeneous materials whose thermal conductivity is nearly independent of temperature, we may treat λ as a constant. Then $\nabla\cdot\lambda\nabla T$ becomes $\lambda\nabla^2 T$, and Eq. (2) can be written as:

$$\lambda\nabla^2 T=C_p\rho\frac{dT}{dt} \tag{3}$$

or

$$\nabla^2 T=\frac{1}{\alpha}\frac{dT}{dt} \tag{4}$$

where $\alpha=\lambda/C_p\rho$ is the thermal diffusivity. For one-dimensional heat flow,

$$\alpha\frac{d^2T}{dx^2}=\frac{dT}{dt}$$

For heterogeneous materials, λ is not independent of position and should not be moved from behind the gradient operator (Eq.(2) and Eq.(3)). In principle, then, the concept of diffusivity is inapplicable to heterogeneous materials. However, in practice, materials are never homogeneous, as point defects, dislocations, grain boundaries, voids and so on are present even in so-called homogeneous materials. Yet diffusivity techniques have been applied to these materials for many years. Successful attemps to extend diffusivity techniques to obviously heterogenous materials have been made for many years. These efforts have been intensified since the 1960s owing to the development of the flash method of measuring diffusivity. This method uses relatively simple sample geometry, permits rapid measurements, and it can handle materials with a large range of diffusivity values over extended temperature intervals with a single apparatus [17].

The laser flash method, ASTM E1461-02 [21], is shown schematically in Figure 1. The sample's front surface recevies a pulse of energy from the laser, which soon raises the back face temperature a degree or two. 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. A solition of a one-dimensional thermal diffusion equation with an initial condition of a heat pulse is,

$$\Delta T(d,t)=\frac{Q}{\rho C_p d\pi r^2}\left[1+2\sum_{n=1}^{\infty}(-1)^n \exp\left(-\frac{n^2\pi^2\alpha t}{d^2}\right)\right] \tag{5}$$

where Q is the absorbed energy at the front surface, and d and r are the thickness and the radius of the sample, respectively. The thermal diffusivity α is deduced from the time to reach one half of the maximum value according to the formula,

$$\alpha=\frac{1.37d^2}{\pi^2 t_{1/2}} \tag{6}$$

where d is the sample thickness and $t_{1/2}$ is the elapsed time needed for the rear face temperature to reach one-half of its maximum rise (Figure1) [17].

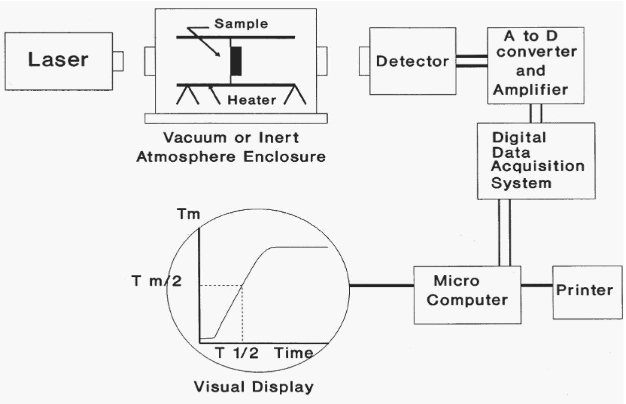

Fig. 1. Schematic of flash diffusivity experimental setup

2.2. Samples

Both two- and three-layered samples were deposited, using the same direct-current 9MB plasma torch (Sulzer Metco) on 321 stainless steel disc substrates (diameter 12.7 mm.)

Two-layered samples are composed of substrate (321 stainless steel) and plasma sprayed zirconia coating (8YSZ), and three-layered samples are composed of substrate, bond coat (NiCrAlY) and plasma sprayed coating.

The measurements were performed with the laser-flash unit LFA 457. Measurements were done between the room temperature and 900 ºC in Nitrogen (N_2) atmosphere and were done at least three times and average values were taken. The laser is a pulsed Nd-YAG type with a wavelenght of 1064 µm and a pulse lenght of 0.2-1.2 ms. The temperature rise of the rear side of the sample is recorded without contact by means of an indium antimonide infrared detector. Before the measurement, the coated surface of the samples were coated with a thin layer of gold. This thin golden layer prevents the direct transition of the laser beams and it helps the energy transfer to the sample. All samples (two and three-layered samples) were graphite coated for absorption and emission.

Furthermore, using the programs that take the radial heat loss into acount, calculations were made.

3. Discussion of the experimental results

The thermal conductivity of samples were calculated from the thermal diffusivity, specific heat and density data with the aid of equation (7).

$$\lambda=C_p.\rho.\alpha \tag{7}$$

where C_p specific heat, ρ density and α thermal diffusivity.

321 Stainless Steel: Small disc-shaped samples of 321 stainless steel which 12.7 mm in diameter with a thickness of 4.21 mm have been used. The density was measured by the Archimedes method and evaluated 7.97 g/cm^3. Specific heat values of steel were obtained from literature [22] and properties of the samples are given in Table 1.

Table 1.
321 Stainless steel sample

Sample thickness (mm)	Density (g/cm^3)	Specific Heat (J/g.K)
4.21	7.970	0.5

For the thermal diffusivity measurements both sides of the samples were coated carbon. Carbon increases the absorption and the emission. This measurements were done in the temperatue range 23 º C – 900 º C and in Nitrogen gas (N_2) atmosphere at a flow rate of 100 mbar/s using the laser-flash method (Netzsch, LFA 457, Selb, Germany). The thermal conductivity was calculated from the thermal diffusivity, density, and specific heat data with the aid of equation (7). Obtained diffusivity data of steel were used in diffusivity measurement of bond coat and 8YSZ coating.

The experimental results of the thermal conductivity of 321 stainless steel is plotted in Figure 2. Thermal conductivity of stainless steel is agreement of metal characteristic. It is observed that thermal conductivity of steel inreases by temperature.

The thermal conductivity of the steel at 100 ºC is about ~ 15.1 W/mK and at 500 ºC is about ~18.3 W/mK as obtained from the laser-falsh method. In this temperature this values are 16.1 W/mK and 22.2 W/mK respectively in literature. A maximum of error 11 % was detected.

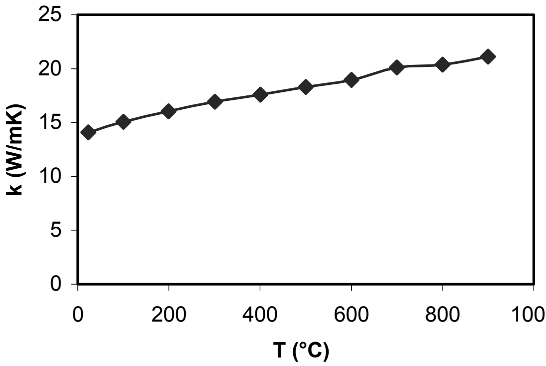

Fig. 2. Thermal conductivity of 321 stainless steel

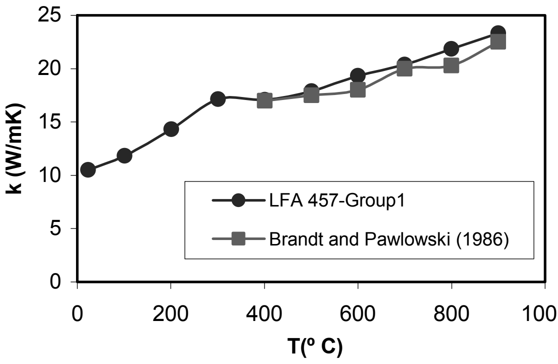

Fig. 3. Thermal conductivity of plasma sprayed NiCrAlY

Nichel-chromium + aluminium, yttrium (NiCrAlY) bond coat: In these measurements three samples which have same properties have been used. The samples were composed of substrate (321 stainless steel) and bond coat (NiCrAlY). The density of the bond coat measurement by the Archimedes method and apparent densitywas found about 3.38 gr/cm^3. The properties of the samples are given in Table 2. Specific heat of bond coat are obtained from MTDATA (version 4.74) source program.

Table 2.
NiCrAlY coatings

	Group 1		
	Sample Z1A	Sample Z1B	Sample Z1C
Steel thickness (mm)	4.27	4.26	4.51
Coating thickness (mm)	No	No	No
NiCrAlY bond coating	0.2	0.21	0.23
Density (g/cm^3)	3.376	3.376	3.376

The thermal diffusivity (α) was determined from equation (6). Obtained values were used in diffusivity measurement of three-layered samples.

The thermal conductivity data of the coatings are plotted in Figure 3. The conductivity of the NiCrAlY sample sprayed measured by Brandt et al. [16] is shown for comparison. A maximum of errors 7% is detected by this figure.

Thermal conductivity of typical bond coat for thermal barrier coatings was measured. The thermal conductivity of NiCrAlY increases from 10.494 to 23.327 W/mK in the temperature range 23-900 ºC. Between 23-300 ºC and 500-900 ºC, the thermal conductivity clearly increases. This values are close to the literature values.

The conductivity of Brandt measurement at 400 ºC is about ~ 16.9 W/mK and 900 ºC is about ~ 22.5 W/mK as obtained from laser-flash method. In experiments at same temperatures 17.1 W/mK and 23.3 W/mK are obtained respectively.

Yttria-stabilized zirconia plasma sprayed coatings (8YSZ): Thermal conductivity of 8YSZ was measured two different form. First, three-layered samples which composed substrate, bond coat and 8YSZ coatings was measured. The coatings have a density of 5.0 gr/cm^3. Specific heat of zirconia are obtained from MTDATA (version 4.74) source program. The properties of three-layered samples are given in Table 3.

Table 3.
Three-layered plasma-sprayed zirconia coatings samples

	Group 3			Group 4			Group 5		
	Z2A	Z3B	Z3C	Z5A	Z5B	Z5C	Z6A	Z6B	Z6C
Steel thickness/mm	4.28	4.19	4.37	4.34	4.24	4.26	4.21	4.33	4.21
Coating thickness/mm	0.5	0.59	0.57	0.72	0.85	0.66	0.46	0.54	0.75
NiCrAlY bond coating/ mm	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Avarege coatings thickness/mm		0.55			0.74			0.58	

Two- and three-layered measurement were performed between RT and 900 ºC using the laser-flash method. Both sides of the samples were coated with gold and carbon. Gold prevents the direct transmission of the beam and improves energy transfer to the samples. Measurements were carried out under a nitrogen gas atmosphere. The thermal conductivity of 8YSZ coatings were calculated according to equation (7).

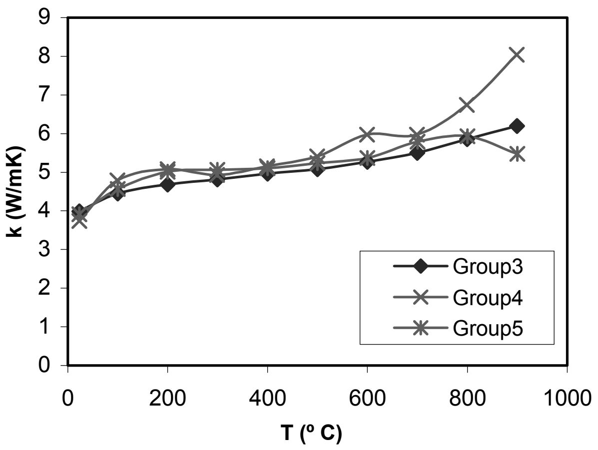

Fig. 4. Thermal conductivity of three-layered 8YSZ coatings

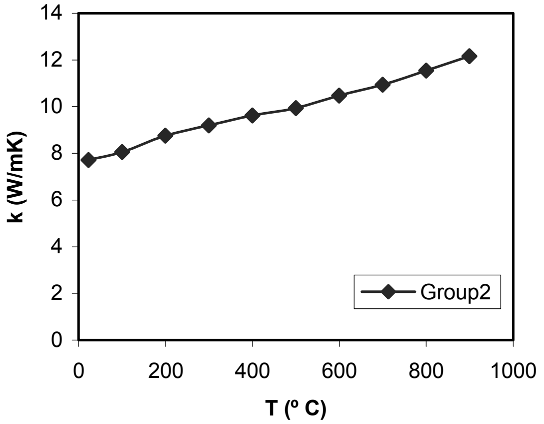

Fig. 5. Thermal conductivity of two-layer 8YSZ coatings

Figure 4. represents the temperature dependence of the thermal conductivity of three-layered samples, containing different coating thicknesses. In this figure, for three group samples with different thicknesses the thermal conductivity was evaluated neglecting the radiation influence. Up to 300 ºC thermal conductivity of all three group measurements are equal. At higher temperature the thicker samples (Group 5) show an apparently higher value of thermal conductivity. The heat pulse due to radiation reaches the sample rear side instantaneously whereas the diffusion takes some time. The time difference is less for thin sample. This means a lower influence on the temperature curve for the thinner samples.

Table 4.
Two-layered plasma-sprayed zirconia coatings samples

	Group 2		
	Sample Z2A	Sample Z2B	Sample Z2C
Steel thickness (mm)	3.18	3.14	3.13
Coating thickness (mm)	0.22	0.46	0.27
NiCrAlY bond coating	NO	NO	NO

Secondly two-layered samples which composed substrate and 8YSZ coatings was measured. The properties of two-layered samples are given Table 4. Specific heat of zirconia for two-layer sample are obtained from literature [16,23]

The experimental results of thermal conductivity for two-layered samples are plotted in Figure 5. This figure is produced by averaging the data obtained for the three samples in Table 4. In this measurement, the experimental thermal conductivity of 8YSZ was obtained at RT about ~7.7 W/mK and 900 ºC about ~ 12.12 W/mK. When these values were compared to the values which in literature it was seen that the values were ten fold bigger. However for three-layer measurements these values were 4 to 8 fold bigger. Cp values used in three-layer measurements provides better results than cp values which in literature.

4. Conclusions

The thermal conductivity of 8YSZ are not strongly temperature dependent. Reliable thermal conductivity values for TBCs can be obtained on two- and three-layer composites by laser-flash technique under specified conditions.

The determination of the thermal conductivity of a two- and three-layered systems is a dependent measurement. An estimation of the thermal conductivity of one layer requires in addition knowledge of other relevant properties (thermal diffusivity, specific heat, density, and thickness of layers) in order to determine the thermal conductivity of the remaining layers. Errors in the measurement of these additional parameters are propagated through the data reduction and results in error in the thermal conductivity determination. Especially the thickness of the coating is very effective on the thermal conductivity (Eq.2). For example a 10% error in coating thickness, causes a 20% error in the calculated conductivity values. Additionally the top and bottom surface of samples should be paralell to each other and being homogeneous in all layer thicknesses play important role in measurement accuracy.

Furthermore, another parameter that affects measurement sensitivity, is surface smoothness of both metal and coating. And another trouble met in measurements is because zirconia partially transparent at high temperatures. It makes difficult the measurement of surface temperature of zirconia. In that reason samples were gold coated for energy transfers to the sample and graphite coated for absorption and emission.

When the results compared to the literature, it was seen that approximately ten fold bigger values were obtained. Thinking that the errors are the results of measurements done as three layer, two layer measurements were done. It is assessed that this error caused from that the coating thickness is not homogeneous, and C_p values are obtained from literature.

Therefore to determine the thermal conductivity of ceramic coating properly, Cp, density and thicknesses of metal substrate and coating are needed to be measured accurately. Additionally it is required that the surface smoothness should be lower than 1% of thickness. Errors in these parameters cause significant deviations for measurement of the thermal conductivity of TBCs.

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