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Evaluation of thermal conductivity of zirconia coating layers deposited by EB-PVD

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Electron beam-physical vapor deposition (EB-PVD) is a widely used technique for depositing thermal barrier coatings (TBCs) on metal substrates for high temperature applications, such as gas turbines, in order to improve thermal efficiency [1]. Characterization of the thermal conductivity of the coating layers is therefore very important for developing superior thermal barrier coatings, but because of the irregular nature of the coated specimens it is difficult to derive the thermal conductivity of the coating layer from measurements of the thermal conductivity of the combined coating and substrate. Two steps are therefore involved in determining the thermal conductivity of a thin coating film: (i) separation of the coating film from the combined coating and substrate specimen, and (ii) measurement of the thermal conductivity of the film. With regards to the first step, it is known that coating layers deposited by EB-PVD have a porous structure so that they are easily damaged because of their poor strength [2, 3]. In other words, in practice it is not easy to physically separate the coating film from the coated substrate by machining or some other method without damaging it. Regarding the second step, even if the coating can be successfully separated from the substrate, it is not a simple matter to measure directly the thermal conductivity of the coating. The laser flash method is generally used to accurately measure the thermal diffusivity and specific heat capacity of materials, from which the thermal conductivity can be calculated. The technique was developed by Parker *et al.* [4], and is usually carried out assuming the specimen to be uniformly dense and opaque. However, coated layers deposited by EB-PVD have a columnar non-uniform structure, making it difficult to measure the thermal conductivity directly. The aim of the present work is therefore to derive a practical method for determining the thermal conductivity of coating layers based on theoretical calculations, and comparing the values obtained with direct experimental measurements. We have therefore adopted the response function method as a means of determining the thermal conductivity of the coating layers. It has been reported that the response function method is a powerful method to analyze one-dimensional heat diffusion across multi-layer materials [5]. We also present the experimental results from thermal conductivity measurements of coated substrates as well as coating layers detached from their substrates as a function of substrate thickness.

In this work, ZrO_2-4 mol% Y_2O_3 coatings have been applied by EB-PVD to zirconia substrates with the same composition as the coating material to minimize interface effects on thermal conductivity. Disc-type zirconia substrates were prepared by pressureless sintering at 1600°C. The sintered substrates were machined to 10.0 mm diameter and 0.1–3 mm thickness. The substrates were first preheated at 900–1000 °C in a heating chamber using a graphite heating element. An electron beam evaporation process was used to deposit the film in a coating chamber under a vacuum level of 10^{-4} Pa using a 45 kW electron gun at a rate of 4 μm/min and substrate rotation speed of 5 rpm. The average coating thickness was about 300 μm. The density of each specimen was determined by measuring its mass on an electronic balance and its volume with a micrometer. All thermal diffusivity and specific heat capacity measurements were carried out three times for each specimen at room temperature by the laser flash method. The microstructure of the coated specimens was observed by SEM.

A typical microstructure of a specimen coated on a zirconia substrate is shown in Fig. 1. The cross-sectional surface of the coated specimen clearly reveals the columnar microstructure, with all columnar grains oriented in the same direction, i.e., perpendicular to the substrate. This columnar structure is very similar to those reported for metal substrates coated by EB-PVD [3]. In other words, the distinctive columnar microstructure can be obtained regardless of whether the substrate being used is metal or ceramic.

The correlation between temperature rise at the rear surface of a specimen and time is shown in Fig. 2 when the front surface of the specimen is uniformly heated using a laser pulse. For bulk materials, the thermal diffusivity (α) is described by the following equation:

$$\alpha = \frac{1.38\,L^2}{\pi^2 t_{1/2}} \tag{1}$$

where L is the thickness of the specimen and $t_{1/2}$ is the time period corresponding to a temperature rise to half of the maximum temperature at the rear surface of the specimen. The value of $t_{1/2}$ can be obtained from a plot of normalized temperature vs. time as shown in Fig. 2. The thermal diffusivity (α), specific heat (C) and density (ρ) can be used to calculate the thermal conductivity (λ) according to

$$\lambda = \alpha \cdot \rho \cdot C \tag{2}$$

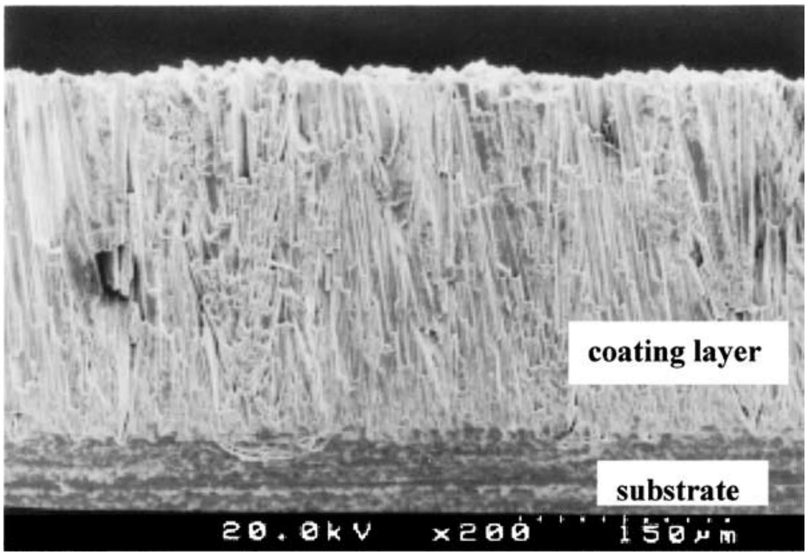

Figure 1 SEM micrograph of a cross-section of a ZrO_2-4 mol% Y_2O_3coating layer deposited onto a ZrO_2-4 mol% Y_2O_3 substrate by EB-PVD.

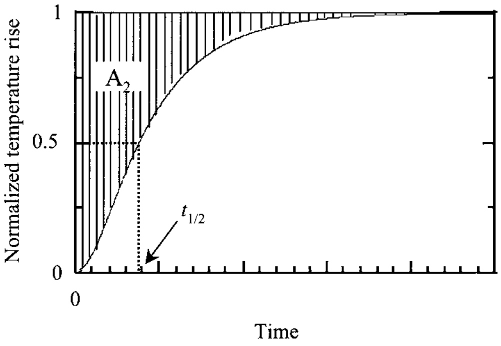

Figure 2 Temperature response as a function of time at the opposite side of a coated specimen after laser pulse heating.

In Fig. 2, the value of $t_{1/2}$ assumes that thermal diffusion occurs across a uniform and isotropic material. However, the specimens used in the present study are non-uniform multi-layer materials that consist of a porous coating layer and a dense substrate. Consequently, using the thermal diffusivity obtained by this method to estimate the thermal conductivity of the coated specimen is not reliable.

Thermal diffusion across multi-layer materials can be systematically analyzed by the response method first suggested by Baba *et al.* [7, 8]. In this study, theoretical calculations based on the response function method are used to derive the thermal conductivity of the coating layer from thermal diffusion measurements of the combined coating and substrate double-layer specimen as follows. For double-layer materials, the area bounded by the temperature rise curve and the maximum temperature line at the rear face of the coated specimen after the laser pulse heating, designated A_2 in Fig. 2, can be obtained by integration. This area is called the "areal thermal diffusion time" and according to the response function method, if boundary thermal resistance is ignored [8], it can be expressed as:

$$A_2 = \frac{b_1\tau_1^{3/2} + 3b_2\tau_1\tau_2^{1/2} + 3b_1\tau_1^{1/2}\tau_2 + b_2\tau_2^{3/2}}{6\cdot(b_1\sqrt{\tau_1} + b_2\sqrt{\tau_2})} \tag{3}$$

where the subscripts 1 and 2 correspond to layers 1 and layers 2, respectively, and b and τ are the thermal effusivity and heat diffusion time, respectively. Also, τ_n can be expressed as

$$\tau_\mathrm{n} = d_\mathrm{n}^2/\alpha_\mathrm{n} \tag{4}$$

where d_n and α_n are the thickness and thermal diffusivity, respectively of materials $n = 1$ and 2. Using Equation 2, τ_n can be rewritten as

$$\begin{aligned}\tau_\mathrm{n} &= d_\mathrm{n}^2/\alpha_\mathrm{n} = d_\mathrm{n}^2/(\lambda_\mathrm{n}/C_\mathrm{n}\rho_\mathrm{n})\\ &= d_\mathrm{n}^2\big/\left\{\left(b_\mathrm{n}^2/C_\mathrm{n}\rho_\mathrm{n}\right)\big/C_\mathrm{n}\rho_\mathrm{n}\right\} = d_\mathrm{n}^2(C_\mathrm{n}\rho_\mathrm{n})\big/b_\mathrm{n}^2\end{aligned} \tag{5}$$

By substituting Equation 5 into Equation 3 for $n = 1$ and $n = 2$, A_2 can be expressed as

$$\begin{aligned}A_2 = {}& \frac{d_1^3(C_1\rho_1)^3\big/b_1^2 + 3d_1^2d_2(C_1\rho_1)^2(C_2\rho_2)\big/b_1^2}{6\cdot(d_1C_1\rho_1 + d_2C_2\rho_2)}\\ &+ \frac{3d_1d_2^2(C_1\rho_1)(C_2\rho_2)^2\big/b_2^2 + d_2^3(C_2\rho_2)^3\big/b_2^2}{6\cdot(d_1C_1\rho_1 + d_2C_2\rho_2)}\end{aligned} \tag{6}$$

Since the thermal effusivity is given by

$$b_\mathrm{n}{}^2 = \lambda_\mathrm{n}C_\mathrm{n}\rho_\mathrm{n} \tag{7}$$

by substituting Equation 7 into Equation 6, A_2 can be rewritten as

$$A_2 = \frac{d_1^2C_1\rho_1/\lambda_1\cdot(d_1C_1\rho_1 + 3d_2C_2\rho_2) + d_2^2C_2\rho_2/\lambda_2\cdot(3d_1C_1\rho_1 + d_2C_2\rho_2)}{6\cdot(d_1C_1\rho_1 + d_2C_2\rho_2)} \tag{8}$$

Thus, the thermal conductivity (λ_2) of layer 2 is given by

$$\lambda_2 = \frac{d_2^2C_2\rho_2(3d_1C_1\rho_1 + d_2C_2\rho_2)}{6A_2(d_1C_1\rho_1 + d_2C_2\rho_2) - d_1^2C_1\rho_1(d_1C_1\rho_1 + 3d_2C_2\rho_2)/\lambda_1} \tag{9}$$

TABLE I Measured values for zirconia substrate and coating layer

	Density (g/cm^3)	Specific heat kJ/(kg · K)	Thermal conductivity W/(m · K)
Substrate	6.0	0.452	2.59
Coating layer	4.8	0.448	1.54

TABLE II Measured values of areal thermal diffusion time for coated specimens

Substrate thickness (mm)	Areal thermal diffusion time (A_2)
0.5	0.125
1	0.302
2	0.921
3	1.884

where d_1, C_1, ρ_1 and d_2, C_2, ρ_2 correspond to the thickness, specific heat and density of layers 1 and layers 2, respectively. λ_1 is the thermal conductivity of layer 1. In the present work, layer 1 and layer 2 correspond to the substrate and coating layer, respectively. Table I summarizes the measured values of density, specific heat and thermal conductivity for each specimen for Equation 9. The coating layer alone (about 300 μm in thickness) was obtained by diamond wheel machining away of the substrate from the combined coating and substrate specimen. The values of areal thermal diffusion time for coated specimens are given in Table II. Fig. 3 shows the correlation between experimental and calculated thermal conductivities for specimens with substrate thicknesses in the range of 0.1–3 mm. The thermal conductivities for each specimen were derived according to Equation 2. The thermal conductivity of the combined coating layer and substrate specimens tend to increase with increase in substrate thickness. The measured thermal conductivity of the zirconia substrate has a constant value regardless of substrate thickness. It may be considered that the lower thermal conductivity of the coating layers compared with that of the sintered zirconia substrates is a result not only of the inherently low thermal diffusivity but also of the low density (porosity 19–22%) of the coating layers. The thermal conductivity of the coating layer from the combined coating and substrate specimens could be successfully calculated using Equation 9 and the calculated thermal conductivities were in range of 1.48–1.52 W/m·K. As shown in Fig. 3, the calculated thermal conductivities of the coating layers are in good agreement with the values obtained by directly measuring the thermal conductivity of the coating layer alone. In summary, these results show that Equation 9 is a useful method for determining the thermal conductivity of coating layers from the combined coating and substrate specimen when it cannot be measured directly from separated coating layers.

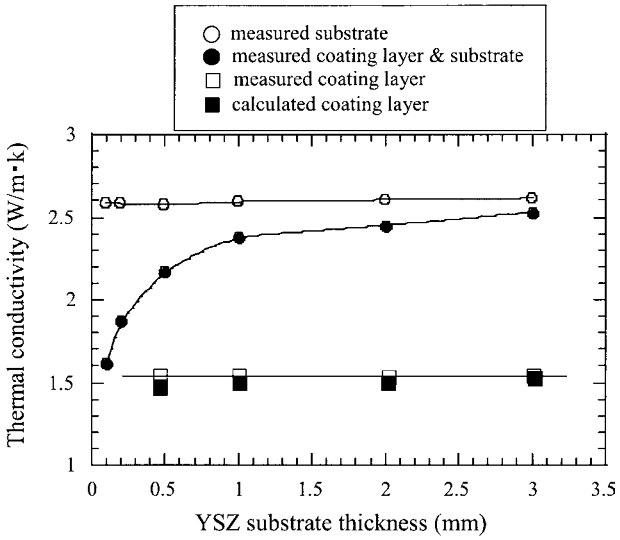

Figure 3 Thermal conductivity as a function of substrate thickness for various specimens.

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References

1. C. LEYENS, U. SCHULZ, K.FRITSCHER, M. BARTSH, M. PETER and W. A. KAYSSER, *Z. Metallkund* **92** (2001) 762.
2. D. D. HASS, P. A. PARRISH and H. N. G. WADLEY, *J. Vac. Sci. Technol.* A **16** (1998) 3396.
3. O. UNAL, T. E. MITCHELL and A. H. HEUER, *J. Amer. Ceram. Soc.* **77** (1994) 984.
4. W. J. PARKER, R. J. JENKINS, C. P. BULTER and G. L. ABBOT, *J. Appl. Phys.* **32** (1961) 1679.
5. T. BABA and N. TAKETOSHI, in Proc. 2000 21th Jpn. Symp. on Thermophysical. Prop. Tokyo, p. 229.
6. S. RAGHAVAN, H. WANG, R. B. DINWIDDIE, W. D. PORTER and M. J. MAYO, *Scripta Materialia* **39** (1998) 1119.
7. T. BABA and N. TAKETOSHI, in Proc. 1998 Eurotherm 57, Poitiers, p. 285.
8. *Idem.*, in Proc. 1999 20th Jpn. Symp. on Thermophysical. Prop. Tokyo, p. 78.

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