Analysis of Thermal Conductivity and
Thermal Diffusivity of EB-PVD Coating Materials

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ZrO_2-4mol% Y_2O_3 (YSZ) coatings have been applied to zirconia substrates with the same composition as the coating material by EB-PVD to minimize the interface effect on thermal conductivity. This work describes the experimental results of thermal conductivity and thermal diffusivity of the YSZ coated sample as a function of substrate thickness. The laser flash method was used for measuring the thermal diffusivity and specific heat capacity of coated samples. The thermal conductivity of the coating layer alone is also calculated based on thermal diffusion results for both substrate and specimens coated onto the substrate. The response function method is employed to obtain an accurate value for the thermal conductivity of the coating layer. These results show that the thermal conductivity of a coating layer can be successfully calculated by the response function method and are in the good agreement with experimental results. The fractured surface of the coated samples reveals a columnar microstructure above the zirconia substrate.
Key Words: EB-PVD, Zirconia, Thermal conductivity, Thermal diffusivity, Laser flash method

1. INTRODUCTION

Among the various coating processes, electron beam physical vapor deposition (EB-PVD) produces coatings with excellent thermal shock resistance behavior of the coatings due to their columnar microstructure. A typical coating material is zirconia doped with 4mol % yttrium oxide (4YSZ), which is an ideal candidate for thermal barrier coatings (TBCs) because of its low density, low thermal conductivity, high melting point and good thermal shock resistant properties [1-3]. Low thermal conductivity is one of the most important properties for superior TBCs. To optimize the TBCs for integration into gas turbine application, a quantitative analysis of thermal conductivity and thermal diffusivity of coated materials is necessary.

It is generally known that coating layers have non-uniform porous structures so that they are easily damaged during measurement of thermal diffusivity due to their poor strength. It is not easy to physically separate the coating layer from the coated substrate by machining without damaging it, as would be required for direct and accurate measurement of the thermal conductivity of thin coating layers.

However, it is difficult to determine the thermal conductivity of the coating layer from the combined coating layer and substrate specimen because of its inhomogeneous structure. For these reasons, measurements of thermal conductivity of dense multi-layer materials have been reported whereas few of porous coated layers have been reported [4-6].

The purpose of the present work is to evaluate the thermal diffusivity of EB-PVD coated specimens using the laser flash method, to derive a practical method for determining the thermal conductivity of thin coating layers based on theoretical calculations, and to compare the values obtained with experimental measurements.

2. EXPERIMENTAL PROCEDURE

Zirconia coatings have been applied to zirconia substrates of the same composition as the coating material to minimize the effect of the interface on thermal conductivity as shown in Fig.1. Zirconia substrates of 4YSZ were prepared by pressureless sintering at 1600°C to form disc shaped substrates 10.0 mm in diameter and 0.1~3 mm thick. A bond coat was not deposited to eliminate the influence of interfaces and bond coat layer on thermal conductivity. The 4YSZ coatings were deposited by EB-PVD using commercially available 4 mol% Y_2O_3 stabilized zirconia targets (Daiichi-kigenso Co.).
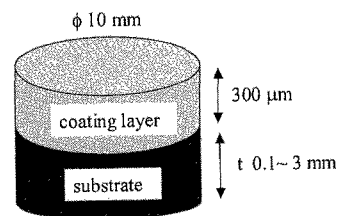

Fig.1 Schematic diagram of sample.

For each operation, zirconia substrates were inserted into a special holder assembly and placed under vacuum. The substrates were first preheated at 900 ~ 1000°C in a preheating chamber using graphite heating elements. The substrates were then moved to the coating chamber for deposition. The electron beam evaporation process was carried out in a coating chamber under a vacuum level of 10^{-4} Pa using a 45 kW electron gun. The target material was heated above its evaporation temperature of 3000°C,

and the resulting vapor was condensed on rotating zirconia substrates. Deposition was generally conducted at a rate of 5 μm/min and substrate rotation of 5 rpm. The obtained coating thicknesses were about 300μm. The density of each coated sample was determined by measuring the mass and volume of the coated samples using an electronic balance and a micrometer, respectively. The microstructures of the coated specimens were observed by SEM.

Thermal diffusivity and specific heat capacity were measured at room temperature by the laser flash method. The laser flash method relies on the generation of a thermal pulse on one face of a thin sample and the observation of the temperature history on the opposite face, as illustrated in Fig. 2. The basic approach for determining the thermal conductivity was originally proposed by Parker et al [7]. They assumed the sample to be a perfectly insulated cylinder, receiving at $t = 0$ a direct thermal pulse uniformly over one face.
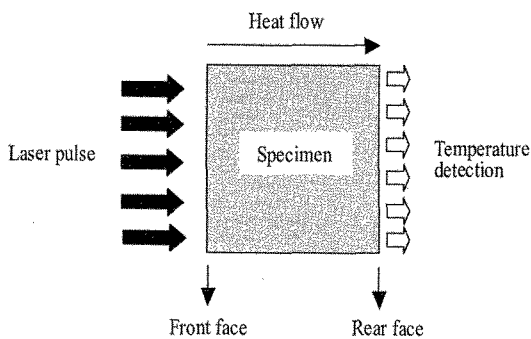
Heat flow

Fig.2 Schematic diagram of the laser pulse technique.

3.   RESULTS AND DISCUSSION

3.1. Characteristics of the coating layer

A typical microstructure of a coated specimen is shown in Fig. 3. The fracture surface of the coating layers deposited on the 4YSZ ceramic substrate clearly reveals a columnar microstructure with all columnar grains oriented in the same direction, i.e., perpendicular to the substrate. This is consistent with the observation that EB-PVD provides distinctive coatings of a unique columnar microstructure on metallic substrates.
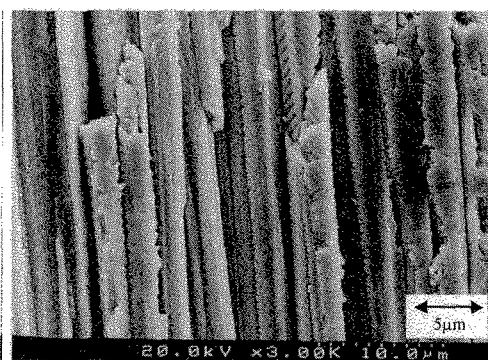
3.2 Thermal diffusivity

By solving the one dimensional thermal conduction equation assuming the ideal conditions in Fig.2, the following temperature response on the rear face of the specimen is obtained [7]:

$$\Delta T = \Delta T_m \left[1 + 2 \sum_{i=1}^{\infty} (-1)^n \exp\left(\frac{-n^2 \pi^2}{L^2} \alpha t\right) \right] \qquad (1)$$

where α and L are the thermal diffusivity and the thickness of the specimen, respectively, and ΔT is the temperature rise of the specimen, ΔT_m is its maximum value, and t is the time after the pulse heating. The representative temperature rise response behavior of coated specimens was obtained as shown in Fig. 4. From Fig. 4, and labeling the time when the temperature reaches $\Delta T/\Delta T_m = 1/2$ as $t_{1/2}$, thermal diffusivity can be calculated from the following equation:

$$\alpha = \frac{0.1388L^2}{t_{1/2}} \qquad (2)$$

where L is the sample thickness 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 sample.
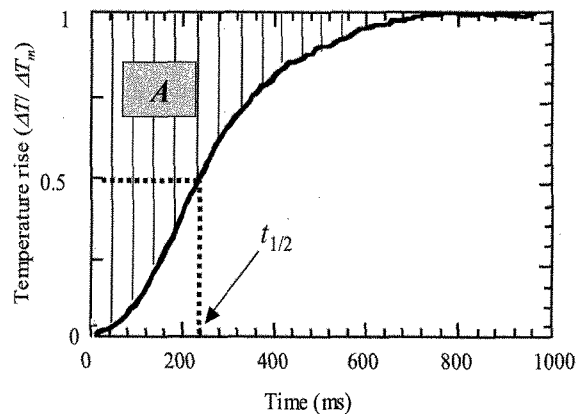

Fig. 4 Temperature response behavior as a function of time at the rear surface of a 300μm coated specimen on a 1mm thick zirconia substrate after laser pulse heating.

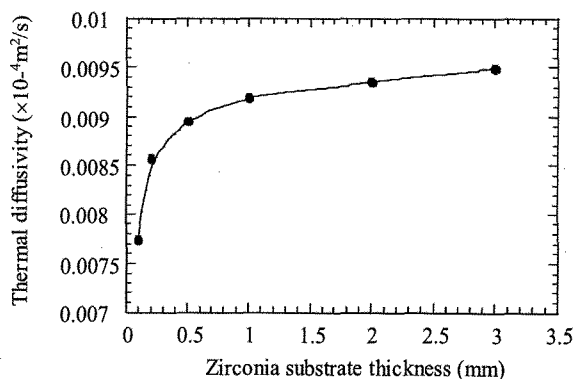Fig.3 SEM micrograph of a zirconia coating layer.

Fig. 5 Thermal diffusivity as a function of substrate thickness for coated specimens.

Fig. 5 shows the relationship between thermal diffusivity and substrate thickness for the combined coating layers and substrate specimens with different coating thicknesses. The thermal diffusivity of the zirconia substrate is almost constant at about $0.0094 \times 10^{-4} \text{m}^2/\text{s}$ regardless of the substrate thickness. In contrast, the thermal diffusivity of the coated samples increases with increasing substrate thickness.

3.3 Thermal conductivity and heat diffusion in the double layer

When calculating the thermal diffusivity using equation 2, the method of determining $t_{1/2}$ values assumes that heat diffusion occurs across a uniform, pure and isotropic material. If this is the case, its value is reliable. However, the present specimens are non-uniform materials that consist of a porous coating layer and dense substrate similar to many multi-layer materials. Consequently, the method of estimating heat diffusion in the coated specimen to calculate the thermal conductivity of the coating layer must be reconsidered.

Baba et al. have suggested that heat diffusion across a multi-layer thin material can be analyzed using the "response function method"[8,9]. 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 in Fig. 4, 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, it can be generally expressed as:

$$A = \int_0^\infty [1 - b\sqrt{\tau} \cdot T_r(t)]dt = \lim_{\xi \to 0}[\frac{1}{\xi} - b\sqrt{\tau} \cdot \widetilde{T}_r(\xi)] \quad (3)$$

where b and τ are thermal effusivity and heat diffusion time, respectively. Equation 3 is a function of time. To solve equation 3, an appropriate model consisting of layer 1 and layer 2 may be visualized as shown in Fig. 6.
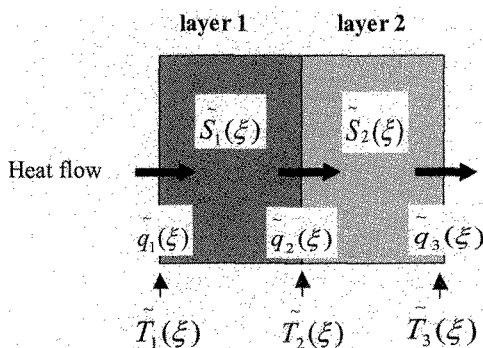

Fig.6 Schematic diagram of four-pole matrices to explain heat diffusion across a two-layer material.

If heat flows ideally from layer 1 to layer 2 in Laplace space, the four-fold matrices ($\widetilde{S}_1(\xi)$) of layer 1 can be expressed as:

$$\begin{bmatrix} \widetilde{q}_2(\xi) \\ \widetilde{T}_2(\xi) \end{bmatrix} = \widetilde{S}_1(\xi) \cdot \begin{bmatrix} \widetilde{q}_2(\xi) \\ \widetilde{T}_2(\xi) \end{bmatrix} \quad (4)$$

where $\widetilde{q}_1(\xi)$, $\widetilde{q}_3(\xi)$ and $\widetilde{q}_2(\xi)$ are heat fluxes at layer 1, layer 2 and the interface, respectively. $T_1(\xi)$, $T_3(\xi)$ and $T_2(\xi)$ are temperature at layer 1, layer 2 and the interface, respectively. Each component can be written as follows:

$$\widetilde{q}_2(\xi) = \cosh(\sqrt{\xi\tau_1}) \cdot \widetilde{q}_1(\xi_1) - b_1(\xi) \cdot \sinh(\sqrt{\xi\tau_1}) \cdot \widetilde{T}_1(\xi) \quad (5)$$

$$\widetilde{T}_2(\xi) = -\frac{1}{b_1(\xi)} \cdot \sinh(\sqrt{\xi\tau_1}) \cdot \widetilde{q}_1(\xi_1) + \cosh(\sqrt{\xi\tau_1}) \cdot \widetilde{T}_1(\xi)(6)$$

The same four-fold matrices ($\widetilde{S}_2(\xi)$) method can be adopted for layer 2 resulting in the following equations:

$$\begin{bmatrix} \widetilde{q}_2(\xi) \\ \widetilde{T}_2(\xi) \end{bmatrix} = \widetilde{S}_2(\xi)^{-1} \cdot \begin{bmatrix} \widetilde{q}_3(\xi) \\ \widetilde{T}_3(\xi) \end{bmatrix} \quad (7)$$

$$\widetilde{q}_2(\xi) = \cosh(\sqrt{\xi\tau_2}) \cdot \widetilde{q}_3(\xi) + b_2(\xi) \cdot \sinh(\sqrt{\xi\tau_2}) \cdot \widetilde{T}_3(\xi) \quad (8)$$

$$\widetilde{T}_2(\xi) = \frac{1}{b_2(\xi)} \cdot \sinh(\sqrt{\xi\tau_2}) \cdot \widetilde{q}_3(\xi) + \cosh(\sqrt{\xi\tau_2}) \cdot \widetilde{T}_3(\xi) \quad (9)$$

By substituting the terms $\widetilde{q}_1(\xi)=1$, $\widetilde{q}_3(\xi)=0$ into equations 5,6,8 and 9, $\widetilde{T}_3(\xi)$ can be obtained from

$$\widetilde{T}_3(\xi) = \frac{1}{\sqrt{\xi}} \cdot \frac{1}{\begin{bmatrix} b_1 \sinh(\sqrt{\xi\tau_1})\cosh(\sqrt{\xi\tau_2}) + \\ b_2 \cosh(\sqrt{\xi\tau_1})\sinh(\sqrt{\xi\tau_2}) \end{bmatrix}} \quad (10)$$

Here, by substituting $\widetilde{T}_r(\xi)=\widetilde{T}_3(\xi)$ into equation 3, equation 3 can be rewritten as:

$$A_2 = \lim_{\xi \to 0}\left[\frac{1}{\xi} - (b_1 \cdot \sqrt{\tau_1} + b_2 \cdot \sqrt{\tau_2}) \cdot \widetilde{T}_3(\xi)\right] \quad (11)$$

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

where subscript 1 and 2 correspond to layer 1 and layer 2, respectively. By rearrangement of equation 11[10], the thermal conductivity (λ_2) of layer 2 is given by:

$$\lambda_2 = \frac{d_2^2 C_2\rho_2(3d_1C_1\rho_1 + d_2C_2\rho_2)}{\begin{bmatrix} 6 A_2(d_1C_1\rho_1 + d_2C_2\rho_2) - \\ d_1^2 C_1\rho_1(d_1C_1\rho_1 + 3d_2C_2\rho_2)/\lambda_1 \end{bmatrix}} \quad (12)$$

where d_1, C_1, ρ_1 and d_2, C_2, ρ_2 correspond to the thickness, specific heat and density of layer 1 and layer 2, respectively. λ_1 is the thermal conductivity of layer 1.

3.4 Evaluation of thermal conductivity

Generally, the thermal conductivity value can be derived by following equation. The thermal diffusivity (α), specific heat (C_p) and density (ρ) are used to

calculate the thermal conductivity (k) according to

$$k = \alpha \cdot \rho \cdot C_p \qquad (13)$$

Using the experimental results of thermal conductivity for both the substrate and specimens coated onto the substrate, the thermal conductivity of the coating layer alone can be calculated according to the following equation.

$$\frac{t_t}{\lambda_t} = \frac{t_1}{\lambda_1} + \frac{t_2}{\lambda_2} \qquad (14)$$

where t_t, t_1, t_2 and λ_t, λ_1, λ_2 correspond to the thickness and thermal conductivity of the total specimen (layer 1 and layer 2), layer 1 only and layer 2 only, respectively. We used two equations, equation 12 and equation 14, to determine the thermal conductivity of the coating layer alone based on thermal diffusion results for both the bare substrate and coated substrate. For equation 12, A_2 can be obtained by integration of the area bounded by the temperature rise curve and the maximum temperature line as shown in Fig.4 for each coated specimen.
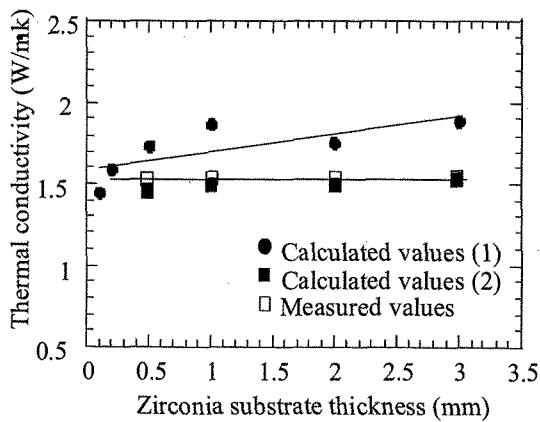

Fig.7 Comparison between calculated and measured values of thermal conductivity of the coating layer.

Figure 7 shows the relation between experimentally measured values and calculated values of thermal conductivities of coating layers for specimens with various substrate thicknesses. Calculated values (1) and calculated values (2) were derived according to equation 14 and equation 12, respectively. Thermal conductivities of 300 μm thick coating layers separated from the substrate by diamond machining were also measured experimentally.

Calculated thermal conductivity values (1) of the coating layers show a large deviation in comparison with the measured values. The calculated and the measured values of thermal conductivity of the coating layers should be constant, because regardless of the substrate thickness, the coating layer thickness is constant. However, calculated values (2) obtained using equation 12 are in good agreement with the values obtained by experimentally measuring the thermal conductivity of

the coating layer alone [10]. This result shows that equation 12 is accurate and reliable. The reason for this difference is that equation 14 does not take into account the thermal diffusion in the double layer even though the whole specimen (coating layer and substrate) constitutes an inhomogeneous double layer.

However, equation 12 takes into account the thermal diffusion in the double layer based on the response function method, as mentioned above. Consequently, equation 12 is a useful means of determining the thermal conductivity of coating layers from a combined coating and substrate specimen when they cannot be measured directly. In summary, we ignored the thermal resistance at the interface in double-layer specimens. However, thermal resistance may occur at the interface. Therefore, a more comprehensive investigation that takes into account thermal resistance at the interface between two-layer materials with different compositions may be necessary.

4. CONCLUSIONS

A ZrO_2-4 mol% Y_2O_3 coating layer was deposited on a ZrO_2-4 mol% Y_2O_3 substrate by EB-PVD and found to consist of columnar grains. Thermal diffusivities of coated specimens were measured experimentally using the laser pulse method. The thermal diffusivity of the combined coating and substrate specimens increased with increasing substrate thickness. The thermal conductivity of the coating layers could be successfully calculated using the response function method applied to a multi-layer specimen. The calculated thermal conductivities of the coating layers were in good agreement with experimental results from the laser flash method.

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