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Thermal Diffusivity Measurement for Thermal Spray Coating Attached to Substrate Using Laser Flash Method

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Ceramic-based thermal barrier coatings are used as heat and wear shields of gas turbine blades. There is a strong need to evaluate the thermal conductivity of coating for thermal design and use. The thermal conductivity of a bulk material is obtained as the product of thermal diffusivity, specific heat capacity, and density above room temperature in many cases. Thermal diffusivity and thermal conductivity are unique for a given material because they are sensitive to the structure of the material. Therefore, it is important to measure them in each sample. However it is difficult to measure the thermal diffusivity and thermal conductivity of coatings because coatings are attached to substrates. In order to evaluate the thermal diffusivity of a coating attached to the substrate, we have examined the laser flash method with the multilayer model on the basis of the response function method. We carried out laser flash measurements in layered samples composed of a CoNiCrAlY bond coating and a 8YSZ top coating by thermal spraying on a Ni-based superalloy substrate. It was found that the procedure using laser flash method with the multilayer model is useful for the thermal diffusivity evaluation of a coating attached to a substrate.

1. Introduction

The use of coating technology is one of the common approaches to enhancing the function of materials. Ceramic-based coatings have been developed for use as heat-resistive and thermal barrier coatings for gas turbines and jet engines. Not only their thermophysical properties, such as thermal conductivity, thermal diffusivity, and specific heat capacity, but also the boundary thermal resistance between the substrate and coating layers is essential information for characterizing their functions. However, there are some difficulties in obtaining this information. A thermal barrier coating (TBC) for gas turbines used in thermal power plants is typically composed of a 500–700-μm-multilayer ceramic layer (top coating) and a 300–500-μm-thick alloy layer (bond coating) on a Ni-based superalloy substrate. TBC fabricated by a thermal spray process is porous to decrease thermal conductivity and thermal diffusivity. Then, the preparation of free-standing TBC removed from its substrate to characterize its thermophysical property is difficult in many cases since it is thin and fragile. Moreover, it is generally difficult to measure the thermophysical properties of a 500–700-μm-thick sample using practical instruments.

Recently, the results of thermophysical property measurements using thick TBC samples specially fabricated for measurement have been reported.[1–5] It was pointed out that the properties of a thick coating may not be the same as those of a thin one of the same material, if we prepare a thick coating specially for measurements using conventional practical instruments. The removal from the substrate may cause some damage to TBC. Measurements by some methods for TBC have also been attempted.[6–9] Some of them need complicated analysis for calculation using complex layered models in the case of TBC with a substrate. Considering these issues, we have studied a measurement method for an as-deposited coating laminated on a substrate without complicated analysis instead of the measurement method for free-standing coatings removed from a substrate.

The flash method[10] is a well-known method for measuring the thermal diffusivity of solid materials above room temperature. We can measure thermal diffusivity across a planar homogeneous solid sample using this method. The front surface of the sample is pulsewise-heated using by a uniform laser beam and the temperature change of the rear-surface is observed using by an infrared radiometer in many cases. Therefore, it is generally called the "laser flash method". Because of its simplicity, the laser flash method is reliable and considered as the standard method for thermal diffusivity measurement.[11] The laser flash method can be used to measure the thermal diffusivity of layered materials as well as homogeneous materials. Analysis in real time space[12,13] and that in Laplace space[14] were proposed for layered materials. Another analysis based on the impulse response method in Laplace transform has also been proposed.[15,16] We have studied thermal diffusivity measurement for two kinds of layered materials using the laser flash method and response function method:[17,18] two-layer ceramic samples that correspond to a porous and a dense ceramic and two-layer metal samples that correspond to a thermally sprayed alloy on SUS 304 substrate.

In this study, we carried out laser flash measurement in three-layer samples composed of a CoNiCrAlY bond coating and an 8 mol % yttria-stabilized zirconia (8YSZ) top coating formed by thermal spraying on a Ni-based superalloy substrate. The samples for this study were made from materials similar to an actual gas turbines. We estimated thermal diffusivities of the bond coating and top coating attached to a substrate from measured data of these layered samples.

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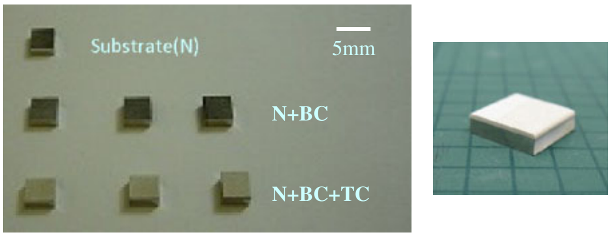

Fig. 1. (Color online) Samples for thermal diffusivity measurement. The left photo shows all kinds of samples with an area of $5 \times 5\,\mathrm{mm}^2$ and the right one shows an example of N + BC + TC with an area of $10 \times 10\,\mathrm{mm}^2$.

2. Experimental of Thermal Diffusivity

2.1 Samples

A Ni-based superalloy (IN 738LC) for use as a substrate was prepared by Hitachi. The layered samples for measurements consisted of a CoNiCrAlY bond coating (BC) and a 8YSZ top coating (TC) were thermally sprayed on the substrate (N) by TOCALO. The sprayed powders were commercial CoNiCrAlY powder (Sulzer Metco AMDRY 9954) and ZrO_2–8% Y_2O_3 (Sulzer Metco METCO 204NS). These powders are deposited by the atmospheric plasma spraying method. Figure 1 shows some examples of the samples used for this study.

We prepared samples of different thicknesses to investigate the thickness range in which the procedure using laser flash method with the multilayer model can be used. Table I shows sizes and thicknesses of the samples. The thickness of each layer was estimated from a scanning electron microscope (SEM) cross-sectional photograph of each sample. Total thickness was measured using a linear gauge.

The samples were spray-coated with graphite on both sides for laser flash thermal diffusivity measurement.

2.2 Measurement facilities

The thermal diffusivity of TBC attached to the substrate was estimated from the measurement results of the laser flash method. The laser flash instruments, LFA-502N (Kyoto Electronics Manufacturing) in the National Institute of Advanced Industry Science and Technology (AIST), and TC-7000 (Ulvac-Riko) in Sumitomo Metal Technology (SMT), and Ulvac-Riko (ULVAC) were used in this study. The measured temperature rise curves were analyzed by the half-rise-time method ($t_{1/2}$)[10] and curve fitting method (CF).[19]

2.3 Measurement procedure

The flash method is observation of one-dimensional heat diffusion phenomena from the surface to the rear-surface of a plate-shaped specimen. It is a very convenient method that involves no contact and requires only a short time. This method is known as a reliable method because it is very simple. Thermal diffusivity in the case of a homogeneous material is ideally determined as follows (half-rise-time method):[10]

$$\alpha = \frac{d^2}{\tau} = 0.1388 \times \frac{d^2}{t_{1/2}}. \qquad (1)$$

Table I. Samples for this study. Thicknesses of substrate in case of two- and three-layer samples described with parentheses, and estimated from total thickness and thicknesses of BC and/or TC thickness.

Sample	Lab.	Shape (mm)	Thickness (mm)			
			Total	N	BC	TC
N	AIST	10 × 10	2.018	2.018	—	—
	AIST	5 × 5	2.054	2.054	—	—
	SMT	ϕ10	2.052	2.052	—	—
	ULVAC	10 × 10	2.041	2.041	—	—
BC	AIST	10 × 10	2.041	—	2.041	—
	SMT	ϕ10	2.097	—	2.097	—
TC	AIST	10 × 10	1.436	—	—	1.436
	SMT	ϕ10	1.462	—	—	1.462
N + BC01	AIST	10 × 10	2.125	(2.065)	0.06	—
	AIST	5 × 5	2.122	(2.062)	0.06	—
	SMT	ϕ10	2.108	(2.048)	0.06	—
	ULVAC	10 × 10	2.121	(2.061)	0.06	—
N + BC03	AIST	10 × 10	2.282	(2.032)	0.25	—
	SMT	ϕ10	2.288	(2.038)	0.25	—
	ULVAC	10 × 10	2.285	(2.035)	0.25	—
N + BC05	AIST	10 × 10	2.441	(2.031)	0.41	—
	SMT	ϕ10	2.471	(2.061)	0.41	—
	ULVAC	10 × 10	2.478	(2.068)	0.41	—
N + BC01 + TC03	AIST	10 × 10	2.425	(2.065)	0.07	0.29
	AIST	5 × 5	2.358	(1.998)	0.07	0.29
	SMT	ϕ10	2.403	(2.043)	0.07	0.29
	ULVAC	10 × 10	2.371	(2.011)	0.07	0.29
N + BC01 + TC05	AIST	10 × 10	2.549	(2.019)	0.07	0.46
	SMT	ϕ10	2.604	(2.074)	0.07	0.46
	ULVAC	10 × 10	2.573	(2.043)	0.07	0.46
N + BC01 + TC07	AIST	10 × 10	2.830	(2.080)	0.07	0.68
	ULVAC	10 × 10	2.784	(2.034)	0.07	0.68

Here, α is the thermal diffusivity, d is the specimen thickness, τ is the heat diffusion time, and $t_{1/2}$ is the half-rise-time. Equation (1) is an approximate solution of temperature rise curve equation.

In practical measurement, there are some uncertainty factors, for example, heat loss effect. Equations considering the heat loss effect are proposed to analyze the temperature rise curve.[20–23] We used Cape and Lehman's equation[20,21] in the CF analysis. The equal area heat diffusion time method was also adopted in CF analysis.[19]

According to the multilayer model based on the response function method[16] shown in Fig. 2, real heat diffusion time is defined as the area surrounded by the horizontal line at the height of the maximum temperature rise and the temperature rise curve on the rear surface after pulsed heating as shown in Fig. 3. The areal heat diffusion time A is expressed as

$$A = \int_0^\infty [1 - b\sqrt{\tau}\cdot T_r(t)]\,dt = \lim_{\xi\to 0}\left[\frac{1}{\xi} - b\sqrt{\tau}\cdot \tilde{T}_r(\xi)\right], \qquad (2)$$

where τ is the heat diffusion time, ξ is the Laplace parameter and $\tilde{T}_r(\xi)$ is the Laplace transform of $T_r(t)$ defined by $\tilde{T}_r(\xi) = \int_0^\infty T_r(t)\exp(-\xi t)\,dt$. The thermal effusivity b is defined as follows:

$$b = \sqrt{\lambda c\rho} = \sqrt{\alpha c\rho c\rho} = c\rho\sqrt{\alpha} = c\rho\frac{d}{\sqrt{\tau}}, \qquad (3)$$

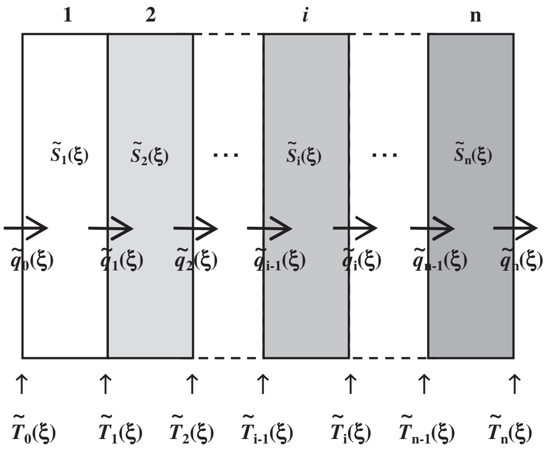

Fig. 2. Multilayer model based on response function method in case of an *n*-layer material.

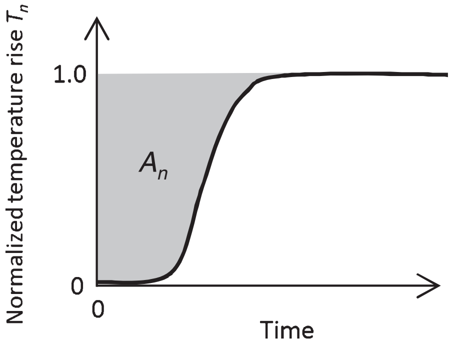

Fig. 3. Temperature rise curve and areal heat diffusion time “A_n” in multilayer model based on response function method.

where λ is the thermal conductivity, c is the specific heat capacity, ρ is the density and α is the thermal diffusivity.

Heat diffusion across an *n*-layered material is systematically analyzed by the response function method.[16] In the Laplace transformed space, the heat flux $\tilde{q}_i(\xi)$ and the temperature $\tilde{T}_i(\xi)$ on the rear surface of the *i*-th layer are shown by the following equation ($i = 1, 2, \ldots, n$):

$$\begin{bmatrix} \tilde{q}_i(\xi) \\ \tilde{T}_i(\xi) \end{bmatrix} = S_i \cdot S_{i-1} \cdots S_2 \cdot S_1 \cdot \begin{bmatrix} \tilde{q}_0(\xi) \\ \tilde{T}_0(\xi) \end{bmatrix}, \tag{4}$$

$$S_i = \begin{bmatrix} \cosh\sqrt{\xi\tau_i} & b_i\sqrt{\xi}\cdot\sinh\sqrt{\xi\tau_i} \\ -\dfrac{1}{b_i\sqrt{\xi}}\sinh\sqrt{\xi\tau_i} & \cosh\sqrt{\xi\tau_i} \end{bmatrix}_i, \tag{5}$$

where $\tilde{q}_0(\xi)$ is the heat flux into the first layer from the outside and $\tilde{T}_0(\xi)$ is the temperature of the surface of the first layer. τ_i is the heat diffusion time and b_i is the thermal effusivity of the *i*-th layer.

In the case of the two-layer model, the Laplace transformed temperature change at the 2nd layer ($i = 2$) is

$$\tilde{T}_2 = \frac{1}{\sqrt{\xi}(b_1\sinh\sqrt{\xi\tau_i}\cosh\sqrt{\xi\tau_2} + b_2\cosh\sqrt{\xi\tau_1}\sinh\sqrt{\xi\tau_2})}. \tag{6}$$

From eqs. (2) and (6), the areal heat diffusion time $A_{n=2}$ obtained from the temperature rise curve measured for the two-layer sample is

$$A_{n=2} = \frac{b_1\tau_1^{3/2} + 3b_2\tau_1\tau_2^{1/2} + 3b_1\tau_1^{1/2}\tau_2 + b_2\tau_2^{3/2}}{6\cdot(b_1\sqrt{\tau_1} + b_2\sqrt{\tau_2})}. \tag{7}$$

From eqs. (3) and (7), the heat diffusion time of the 2nd layer is

$$\tau_2 = \frac{6A_{n=2}(c_1\rho_1 d_1 + c_2\rho_2 d_2) - (c_1\rho_1 d_1 + 3c_2\rho_2 d_2)\tau_1}{3c_1\rho_1 d_1 + c_2\rho_2 d_2}, \tag{8}$$

since thermal diffusivity of each layer is defined as

$$\alpha_i = \frac{d_i^2}{\tau_i}. \tag{9}$$

τ_2 is calculated using eqs. (1) and (8) when α_1, c_1, ρ_1, d_1, c_2, ρ_2, and d_2 are known.

Similarly, the heat diffusion time of the 3rd layer is shown as

$$\begin{aligned} \tau_3 &= \frac{X + Y + Z}{3c_1\rho_1 d_1 + 3c_2\rho_2 d_2 + c_3\rho_3 d_3} \\ X &= 6A_3(c_1\rho_1 d_1 + c_2\rho_2 d_2 + c_3\rho_3 d_3) \\ Y &= -(c_1\rho_1 d_1 + 3c_2\rho_2 d_2 + c_3\rho_3 d_3)\tau_1 \\ Z &= -\Bigg(3c_1\rho_1 d_1 + c_2\rho_2 d_2 + 3c_3\rho_3 d_3 \\ &\qquad + \frac{6c_1\rho_1 d_1 c_3\rho_3 d_3}{c_2\rho_2 d_2}\Bigg)\tau_2. \end{aligned} \tag{10}$$

Then the thermal diffusivity of a layer in the layered sample can be obtained using this multilayer model on the basis of the response function method.[16]

We have to estimate the areal heat diffusion time “A_n” from the observed temperature rise curve when we calculate thermal diffusivity using this multilayer model. There are two ways to estimate A_n. One is direct estimation by calculating the area surrounding the vertical line at $t = 0$, the time when the sample is pulse-heated, the horizontal line at the height of the maximum of T_2, $t = 0$ axis, and the temperature rise curve using raw data of the observed temperature rise curve (as shown in Fig. 3). It may be difficult to estimate A_n by this direct calculation when the temperature rise curve shows deviations from ideal conditions.

The other is estimation using an approximation assuming a homogeneous single layer. There is a relation of what in the case of single layer ($n = 1$) according to the multilayer model based on the response function method:

$$A_{n=1} = \frac{\tau}{6} = \frac{d^2}{6\alpha}. \tag{11}$$

If the apparent temperature rise curve of the two-layer sample is approximately explained by the equation of the temperature rise curve for the single-layer sample, it is assumed that

$$A_n \approx A_{n=1} = \frac{\tau_{\text{apparent}}}{6} = \frac{d^2}{6\alpha_{\text{apparent}}}, \tag{12}$$

where τ_{apparent} is the apparent heat diffusion time, α_{apparent} is the apparent thermal diffusivity, and d is the total thickness of the *n*-layer sample. τ_{apparent} is obtained by conventional analysis, for example, by the half time method and CF method. This estimation using apparent heat diffusion time has advantages as a practical procedure because of its simplicity and ease of implementation, however it remains

Table II. Measured thermal diffusivities of single-layer samples at room temperature.

Sample	Lab.	Analysis	Thermal diffusivity α ($10^{-6}\,m^2\,s^{-1}$)		
			Result	Average	Standard deviation
N	AIST	CF	2.72	2.82	0.10
	AIST	$t_{1/2}$	2.82		
	SMT	$t_{1/2}$	2.78		
	ULVAC	$t_{1/2}$	2.84		
BC	AIST	CF	1.32	1.35	0.07
	AIST	$t_{1/2}$	1.39		
	SMT	$t_{1/2}$	1.42		
TC	AIST	CF	0.508	0.521	0.03
	AIST	$t_{1/2}$	0.534		
	SMT	$t_{1/2}$	0.557		

only as an approximation. It is also expected that some corrections will be applied, for example, heat loss correction in calculating apparent heat diffusion time.

We attempted to estimate A_n using both methods in a previous study.[17] We confirmed that both methods performed at room temperature gave reasonable results. However, we found that there are some difficulties in these estimations at high temperatures because of a strong heat loss effect.

3. Results and Discussion

3.1 Thermal diffusivity of single-layer samples

Table II shows the measurement results of the single layer of the Ni supperalloy substrate (IN 738LC) (N), CoNiCrAlY bond coating (BC), and 8YSZ top coating (TC) at room temperature. The thermal diffusivities reported by the three participant laboratories show good agreement independent of the analysis method.

3.2 Thermal diffusivity of two-layer sample

Figure 4 shows the temperature rise curves for the two-layer samples with various thicknesses of the BC layer attached to the Ni-based superalloy substrate. No difference between the two-layer sample with the 0.1-mm-thick BC layer and the single-layer consisting of only the substrate. The temperature rise curve becomes broader increasing the thickness of the BC layer in the case of two-layer samples with the 0.3- and 0.5-mm-thick BC layers. In this procedure, we estimated the thermal diffusivity of the BC layer attached to the substrate. Expectedly, we can estimate the thermal diffusivity of the BC layer when the difference between the temperature rise curve of the substrate and that of the two-layer sample is clear. There is very little heat loss effect in temperature rise curves, as shown in the inset of Fig. 4. We were able to estimate area heat diffusion time from these curves by ignoring the heat loss effect.

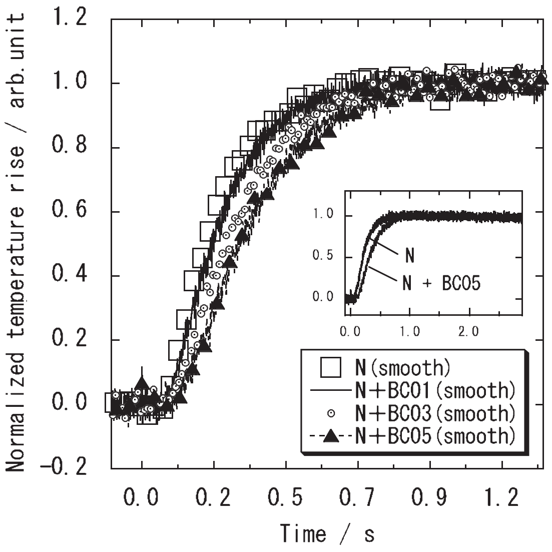

Fig. 4. Temperature rise curves of two-layer samples with BC layers of various thicknesses attached to Ni-based superalloy substrate at room temperature. The inset shows the temperature rise curves with a wider range of time scale.

Table III. Estimated thermal diffusivities of BC layer in two-layer samples at room temperature.

Sample	Lab.	Analysis	Thermal diffusivity α ($10^{-6}\,m^2\,s^{-1}$)		
			Apparent	BC	Average
N + BC01	AIST	CF	2.83	(−0.20)	—
	AIST	$t_{1/2}$	2.87	(−0.50)	
	SMT	$t_{1/2}$	2.86	(−0.29)	
	ULVAC	$t_{1/2}$	2.75	(−0.0067)	
N + BC03	AIST	CF	2.66	1.4	1.35
	AIST	$t_{1/2}$	2.73	1.3	
	SMT	$t_{1/2}$	2.72	1.4	
	ULVAC	$t_{1/2}$	2.75	1.3	
N + BC05	AIST	CF	2.55	1.3	1.35
	AIST	$t_{1/2}$	2.64	1.4	
	SMT	$t_{1/2}$	2.60	1.3	
	ULVAC	$t_{1/2}$	2.68	1.5	

Table III shows the estimated apparent thermal diffusivities of the two-layer samples and thermal diffusivities of the BC layer calculated using eqs. (8) and (9). We used the specific heat capacity and bulk density obtained in §3.5 and §3.6 for the calculation. The apparent thermal diffusivities of the two-layer sample agree with each other. In the case of the 0.1-mm-thick BC layer attached to the substrate, the estimated thermal diffusivity of the BC layer shows anomalous negative value. It is indicated that the 0.1-mm-thick BC layer is too thin for the approximetrly 2.0-mm-thick Ni-based supperalloy substrate to detect whether BC is attached to the substrate.

We found a clear difference between the temperature rise curves of the substrate and those of the 0.3- and 0.5-mm-thick BC layers with the substrate, as shown in Fig. 4. The calculated thermal diffusivities of the 0.3- and 0.5-mm-thick BC layers show good agreement in terms of independent thickness and the laboratories who measured them, as shown in Table III. The average of these result is concluded as $1.35 \times 10^{-6}\,m^2\,s^{-1}$. The value agrees with that obtained from the single-layer measurement, as shown in Table II. According to these results, the estimation using the above procedure based on the multilayer model is effective for the two-layer samples. Then, the procedure has sensitivity for detecting the thermal barrier effect using a CoNiCrAlY BC layer that is more than 0.3 mm thick for a Ni-based supperalloy substrate of about 2.0 mm thickness. We considered that the interfacial thermal resistance between

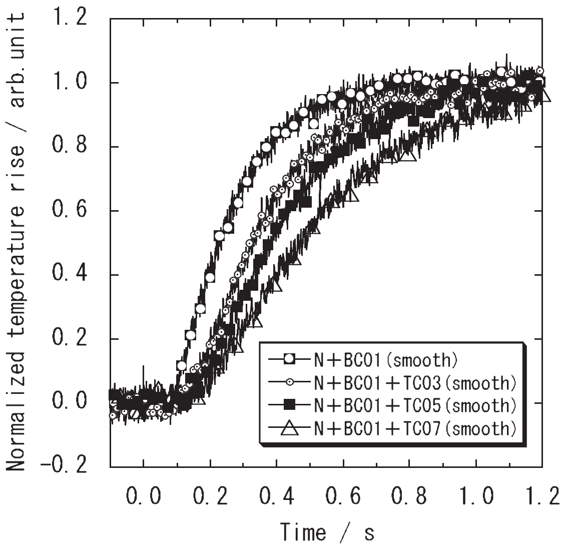

Fig. 5. Temperature rise curves of three-layer samples with TC layers various thickness attached to about a 0.1-mm-thick BC layer and Ni-based superalloy substrate at room temperature.

the BC layer and the substrate has no contribution to that because both materials are metals.

3.3 Thermal diffusivity of three-layer sample

Figure 5 shows the temperature rise curves of the three-layer samples with the TC layers of various thickness attached to an approximately 0.1-mm-thick BC layer and a Ni-based superalloy substrate. It was found that the temperature rise curve becomes broader with increasing thickness of the TC layer.

The apparent thermal diffusivities and calculated thermal diffusivities of the TC layer are shown in Table IV. The apparent thermal diffusivities of the three-layer sample almost agree independently of the analysis method and laboratory. The thermal diffusivity of the TC layer calculated on the basis of the three-layer model varied in the range from 0.33×10^{-6} to $0.47 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$. From these calculated values, the thermal diffusivity of the TC layer is $0.40 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$ on the average with a standard deviation of $0.05 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$. This result is about 30% smaller than the measured result of the single layer. We considered two possible reasons for this approximately 30% difference: interfacial thermal resistance and calculation error due to rounding off. The interfacial thermal resistance between BC and TC is expected to be significant since it is a junction of different materials, alloy and ceramic.

It is not sufficient to measure the thermal diffusivity of the samples prepared for this study to investigate the interfacial thermal resistance effect. Thus, we have plan to prepare two- and/or three-layer samples with various thicknesses by changing the interfacial conditions after this study.

We checked the calculation several times and found no significant calculation errors. Thus, calculation error seems an improbable reason. Moreover, some physical properties may not be the same between thin and thick TC layers prepared by thermal spraying although we prepared the layers under the same conditions. This point is one of our future research subjects.

Table IV. Estimated thermal diffusivities of TC layer in three-layer samples at room temperature.

Sample	Lab.	Analysis	Thermal diffusivity α ($10^{-6}\,\mathrm{m^2\,s^{-1}}$)		
			Apparent	BC	TC
N + BC01 + TC03	AIST	CF	2.32	1.35	0.45
	AIST	$t_{1/2}$	2.21		0.47
	SMT	$t_{1/2}$	2.19		0.33
	ULVAC	$t_{1/2}$	2.32		0.40
N + BC01 + TC05	AIST	CF	1.80	1.35	0.38
	AIST	$t_{1/2}$	1.90		0.40
	SMT	$t_{1/2}$	1.86		0.38
N + BC01 + TC07	AIST	CF	1.33	1.35	0.33
	AIST	$t_{1/2}$	1.52		0.41

Note that thermal diffusivity is a function of thickness and heat diffusion time according to eq. (1). We easily determined total thickness of a sample to three decimal places in mm using a linear gauge. On the other hand, it was difficult to estimate the thickness of each layer from the SEM cross-sectional image of the sample since the interface is very rough in the case of the thermally sprayed samples. The third decimal place on the mm scale of thickness of the BC and TC layers is sometimes unreliable. Heat diffusion time is analytically determined from a temperature rise curve. We empirically consider that heat diffusion time can be calculated up to three significant digits in this study. Then the number of significant digits of certain reliable thermal diffusivities of the BC and TC layers is considered to be two.

Therefore, it was found that the multilayer model based on the response function method is useful to estimate the thermal diffusivity of an unknown layer attached to the substrate for the laser flash method as practical use. We can estimate the thermal diffusivities of the thick BC and TC layers more than 0.3 mm attached to the 2.0-mm-thick Ni-based supperalloy substrate. This procedure is practically useful if we need a rough estimation of the thermal diffusivity of layered samples.

3.4 Thermal diffusivity above room temperature

The temperature dependence of the apparent thermal diffusivity of the layered samples is measured as shown in Fig. 6. The difference in thermal diffusivity between the substrate single-layer sample and the two-layer sample consisting of a BC layer and a substrate is small, because the thermal diffusivity of the BC layer is similar to that of the substrate, being about half that of the substrate. The apparent thermal diffusivity of the three-layer samples is significantly smaller than those of the substrate and two-layer samples. It was found that the TC of 8YSZ shows a significant thermal barrier effect.

We also measured the thermal diffusivity of the Ni-based superalloy, BC(CoNiCrAlY) and TC(8YSZ) from room temperature to about 800–1000 °C in vacuum. Figure 7 shows the temperature dependence of the thermal diffusivity of these single-layer samples. We also measured the thermal diffusivity of these samples at room temperature after the heating measurement to confirm their stability.

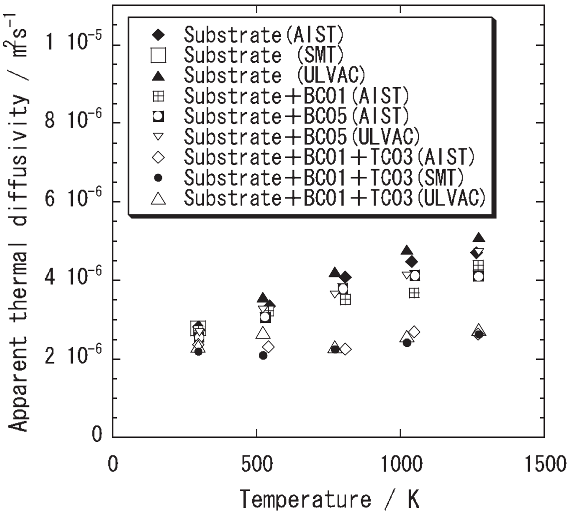

Fig. 6. Apparent thermal diffusivities of substrate and thermally sprayed samples from room temperature to about 1000 °C.

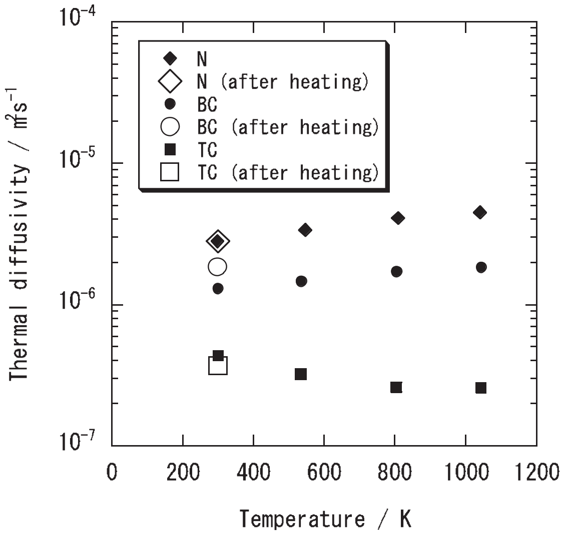

Fig. 7. Temperature dependence of thermal diffusivity of each single-layer sample from room temperature to 800–1000 °C in vacuum: Ni-base supperalloy substrate (◇, ◆), CoNiCrAlY bond coating (○, ●), and 8YSZ top coating (□, ■).

The thermal diffusivity of the Ni-based supperalloy shows no change in thermal diffusivity after heating to 1000 °C. Also, the Ni-based substrate is very stable in the temperature range from room temperature to 1000 °C.

The thermal diffusivity of CoNiCrAlY increased after heating up to 1000 °C. It is expected that thermally sprayed CoNiCrAlY was sintered owing to heating. In general, the thermally sprayed porous material is known that it was sintered by annealing. The thermal diffusivity of the 8YSZ single-layer sample before and after heating to about 800 °C. It was found that thermal diffusivity shows no significant changes after heating since the deviations are large. We did not heat 8YSZ up to 1000 °C because we expected that 8YSZ was sintered at a temperature higher than about 800 °C according to the example of porous 3YSZ.[24)]

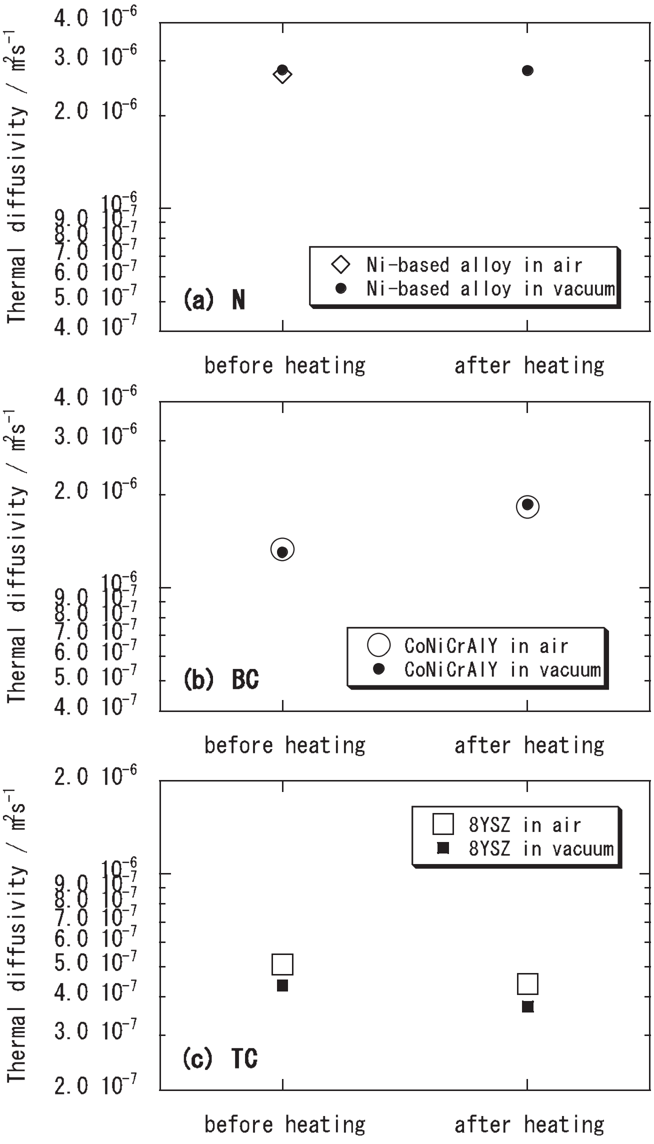

Fig. 8. Thermal diffusivity of each single-layer sample at room temperature in air or vacuum before and after heating to 800–1000 °C: (a) Ni-based superalloy substrate, (b) CoNiCrAlY bond coating, and (c) 8YSZ top coating.

Therefore, the thermal diffusivity of the thermally sprayed coating may be dependent on heating history. The measured thermal diffusivity in Fig. 6 may be affected by heating up to 1000 °C although the temperature dependence is qualitatively reasonable. Thermal diffusivity measurement by heating to high temperatures is interesting for investigating the physical properties of the TBC layer. However, it is difficult to confirm thermal diffusivity again after the change caused by heating. We have to carefully plan the thermal diffusivity measurement before starting our study.

3.5 Effect of measurement conditions

We also check the contribution of atmosphere during the measurement by comparing the result in air and in vacuum because thermally sprayed TBC is porous. Here, "vacuum" means atmospheric conditions at about 10^{-3} Pa. As shown in Fig. 8(a), the thermal diffusivity of the Ni-based supperalloy did not depend on atmosphere. This is reasonable because the alloy is a dense material.

Table V. Specific heat capacities of each layer at room temperature.

Sample		Method	Specific heat capacity c ($\mathrm{kJ\,kg^{-1}\,K^{-1}}$)
N	Bulk	Catalog	0.420
	Bulk	LF	0.424
BC	Thermally sprayed	DSC	0.492
	Powder	DSC	0.487
TC	Thermally sprayed	DSC	0.467
	Powder	DSC	0.472

Table VI. Bulk densities of all layers at room temperature.

Sample	Lab.	Bulk density ρ ($10^3\,\mathrm{kg\,m^{-3}}$)			
		Apparent	N	BC	TC
N		8.11	8.11	—	—
BC	SMT	6.61	—	6.61	—
TC		5.37	—	—	5.37
N + BC01		8.06	(8.11)	6.2	—
N + BC03		7.90	(8.11)	6.3	—
N + BC05	SMT	7.83	(8.11)	6.4	—
N + BC01 + TC03		7.70	(8.11)	6.2	5.2
N + BC01 + TC05		7.54	(8.11)	6.2	5.2
Average		—	8.11	6.3	5.2

Table VII. Estimated thermal conductivities of all layers at room temperature.

Sample	α ($10^{-6}\,\mathrm{m^2\,s^{-1}}$)	c ($\mathrm{kJ\,kg^{-1}\,K^{-1}}$)	ρ ($10^3\,\mathrm{kg\,m^{-3}}$)	λ ($\mathrm{W\,m^{-1}\,K^{-1}}$)
N	2.82	0.422	8.11	9.6
BC	1.35	0.490	6.61	4.4
BC-layer	1.35	0.490	6.3	4.2
TC	0.52	0.470	5.37	1.3
TC-layer	0.40	0.470	5.2	1.0

In Fig. 8(b), there is no difference between the thermal diffusivity of thermally sprayed CoNiCrAlY measured in air and that measured in vacuum before and after heating. In Fig. 8(c), the thermal diffusivity in air is larger than that in vacuum before and after heating. The thermal diffusivity of thermally sprayed 8YSZ is small compared with those of the Ni-based supperalloy and thermally sprayed CoNiCrAlY, and is on the same order as the thermal diffusivity of air. It is considered that the thermal diffusivity depends on the atmosphere, for example, the type of gas and gas pressure, since effect of the heat loss to air is large in the case of porous 8YSZ. Then, the thermal diffusivity of the thermally sprayed coating may be dependent on atmosphere during measurement.

TBC is used in air or in pressurized atmosphere. It seems that the thermal diffusivity measured in air is useful for the thermal design of TBC. We may have to choose the atmosphere for measuring the condition for TBC considering the environment where TBC is to be used.

3.6 Specific heat capacity of samples

The specific heat capacities used in thermal diffusivity estimation using a multilayer model were measured by the laser flash (LF) method and differential scanning calorimetry (DSC) method by SMT. The results are shown in Table V.

In the case of the BC and TC layers, we measured the specific heat capacities of the thermally sprayed samples removed from the substrate and of the raw powders. The deviation between specific heat capacities measured by DSC using the raw powder and the removed layer is about 1%. This is within the limit of error. We found that specific heat capacity measurements using the raw powder and removed layer are both effective.

We used the average of the specific heat capacities of the BC and TC layers measured by DSC using a thermally sprayed sample removed from its substrate and raw powder for thermal diffusivity calculation according to the multilayer model.

3.7 Bulk density of samples

The bulk density used in the thermal diffusivity estimation using the multilayer model was calculated from the sample mass and the sample size by SMT. The thickness of each layer was estimated from a cross-sectional image by SEM.

Table VI shows the obtained bulk densities of the substrate, BC, and TC. The bulk density of BC layer measured using the two-layer and the three-layer sample shows good agreement. However, the value is smaller than that of the single-layer BC. It was similar to the bulk density of TC obtained from three-layer samples. The estimation of the thicknesses of BC and TC from the cross-sectional images limits resolution to a 0.01 mm order. Moreover, this estimation was carried out for disk samples 10 mm in diameter and 2 mm–3 mm in thickness. Since the sample is small, we determined bulk density from a layered sample up to two significant figures.

In the thermal diffusivity calculation using the multilayer model, we use the following bulk densities: $8.11 \times 10^3\,\mathrm{kg\,m^{-3}}$ for the substrate, $6.61 \times 10^3\,\mathrm{kg\,m^{-3}}$ for BC, and $5.37 \times 10^3\,\mathrm{kg\,m^{-3}}$ for TC, estimated from single-layer samples. Although we also calculated thermal diffusivity using bulk densities of $6.3 \times 10^3\,\mathrm{kg\,m^{-3}}$ for BC, and $5.2 \times 10^3\,\mathrm{kg\,m^{-3}}$ for TC, there was no significant difference due to the difference in bulk density.

3.8 Thermal conductivity of samples

We estimated the thermal conductivity of the samples using the thermal diffusivities, specific heat capacities, and bulk densities shown in Table VII. Thermal conductivity is expressed as

$$\lambda = \alpha c \rho. \tag{13}$$

In the calculation, we use averages in this study. There is a tendency for the thermal diffusivity, bulk density, and thermal conductivity obtained from the layered TBC samples to be smaller than those of the bulk single-layer samples.

The thermal conductivity of TBC consisting of a 0.1-mm-thick BC layer and a 0.7-mm-thick TC layer is calculated as $1.1\,\mathrm{W\,m^{-1}\,K^{-1}}$ using

$$\lambda_{\mathrm{TBC}} = \frac{(d_{\mathrm{BC}} + d_{\mathrm{TC}}) \cdot \lambda_{\mathrm{BC}} \cdot \lambda_{\mathrm{TC}}}{d_{\mathrm{BC}} \cdot \lambda_{\mathrm{TC}} + d_{\mathrm{TC}} \cdot \lambda_{\mathrm{BC}}}. \tag{14}$$

4. Conclusions

The thermal diffusivity of the layered samples composed of CoNiCrAlY bond coating and 8YSZ top coating prepared by thermal spraying on a Ni-based superalloy substrate was investigated using the laser flash method according to the multilayer model on the basis of the response function method at room temperature. We proposed a simple estimation using the apparent thermal diffusivity of a layered sample and the areal heat diffusion time.

The calculated thermal diffusivities agree with that obtained by single-layer measurement in the case of a two-layer sample consisting of a BC layer and a substrate. In the case of a three-layer consisting of TC, BC, and a substrate, the calculated thermal diffusivity of TC is smaller than the value measured using an 8YSZ single-layer sample. This might have been contributed to the interfacial thermal resistance between the BC layer and the TC layer.

We checked the stability of the Ni-based superalloy substrate, BC, and TC above room temperature. Slight changes were observed depending on the heat cycle and atmosphere in the case of BC and TC. It was found that we have to carefully select the conditions during measurement of thermally sprayed samples.

It is found that the estimation using the procedure according to the multilayer model is effective for layered samples and very practically useful.

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