Determination of Thermal Diffusivity of Ceramics Coating by Flash Method†

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Abstract

The laser flash method is extended for measuring the thermal diffusivity of sprayed coatings. A flash pulse is absorbed in the front surface of a thermally insulated spacemen, which is composed of a ceramics coating layer and the substrate. The resulting temperature history of the rear face, or the surface of the ceramics coating is measured by a radiation thermometer and recorded with a transient memory and a pen-recorder. The time required for the temperature to rise 30 and 70 percents, for example, of the maximum temperature rise is read from the temperature versus time curve. These results are used for the numerical computation based on the theoretical equation of the normalized temperature increase on the rear face and the method of bisection. The thermal resistance at the interlayer surface can be also obtained easily as well as the thermal diffusivity. The present method is applied to five kinds of thermal sprayed ceramics coatings, and the effectiveness of this method is confirmed.

KEY WORDS : (Thermophysical Property)(Thermal Diffusivity)(Laser Flash Method)(Ceramics Coating)(Thermal Spraying)

1. Introduction

Recently, thermal spraying has been drawn attention as a surface coating technique for improving the properties of metal surfaces such as wear-, corrosion- and thermal-resistance. Especially, ceramics coating by plasma spraying and rod spraying has been widely used for the materials in aerospace industry, ocean development, and so on. At present, mechanical properties of sprayed coatings such as tensile strength and hardness are mainly investigated for various spraying conditions, but the measuring methods of thermophysical properties of sprayed coatings are not established. If the thermophysical properties can be also measured easily, the thermal sprayed coatings may be improved by obtaining the optimum spraying conditions.

In this paper, an extension of the laser flash method for measuring the thermal diffusivity of sprayed coatings is proposed, and the present method is applied to some thermal sprayed ceramics coatings.

2. Specimens and Experimental Procedures

2.1 Specimens

Five kinds of ceramics materials were used for coating. Their chemical compositions are shown in **Table 1**, where the names of materials such as OAT-F and GAT-40 are used for commerce. These ceramics materials were sprayed by plasma spraying except R-C, which was sprayed by rod spraying. The ceramics coatings of 600 to 800 μm thick were obtained on the SUS 304 stainless steel disks of 10 mm in diameter and 5 mm thick. One side of each disk was blasted with Al_2O_3 powder just before thermal spraying.

Plasma spraying equipment used was METCO 3MB type, and the spraying conditions are shown in **Table 2**. Ceramics rod spraying equipment used was Mogul Rokide Ceramic Spray Gun, and was operated using acetylene fuel gas (pressure; 15 psi and flow; 13 *l*/min) and oxygen gas (pressure; 90 psi and flow; 18 *l*/min). Compressed air pressure was 80 psi and spraying distance was 200 mm. The flat surfaces of these sprayed coatings were polished and decreased to about 350 μm thick. Then the opposite SUS 304 surfaces were polished. The final thickness of the specimens was about 1 mm. The specimens were sectioned at the plane which contains the centerline of the disk after the experiments of measuring the thermal diffusivity of the ceramics coatings. The thickness of both sprayed coating and substrate was measuered through a Nomarski microscope. The degree of the parallelism between both surfaces and the interlayer surface was fairly good. An example of the cross section of the specimen is shown in **Fig. 1**. The coating is made of flattened ceramics particles, and small porosity of high density can be observed in the sprayed coating.

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2.2 Experiment

The experiments were carried out with a flash type thermal constant analyzer, TC3000HNC, developed by Sinku-Riko Inc. The pulse width of the ruby laser used was about 0.7 millisecond, and the laser was irradiated on the surface of SUS 304 base metal.

The temperature detector used was a radiation thermometer (InSb sensor) and the temperature history on the rear surface of the specimen, that is, the surface of the ceramics coating was recorded by a transient memory and a pen-recorder. The laser pulse was irradiated thirty times in total for each specimen. This experiment was carried out in the air at the room temperature. The time required for the temperature to rise 30 and 70 pcts. of the maximum temperature increase was read from the temperature versus time curve.

The thermal diffusivity of SUS 304 stainless steel used was determined by the same apparatus using conventional half-time method[1] for a homogeneous layer. The specific heat of both SUS 304 and specimens was measured using the laser-flash calorimetric method[2], then the specific heat of the sprayed coatings were determined as the difference in the measured results between each specimen and SUS 304.

3. Determination of Thermal Diffusivity

The schematic diagram of the geometry of a two-layer composite is shown in **Fig. 2**. In the flash method, the front surface of the sample is subjected to a short radiant energy pulse and the resulting temperature history of the rear surface is recorded. If we set up the following assumptions;

(1) one dimensional heat flow,
(2) no heat loss from the sample surfaces,
(3) each layer is homogeneous,
(4) thermal resistance between layers is uniform,
and (5) heat pulse is uniformly absorbed on the front surface, the normalized temperature of the rear surface is represented as Eq.(1)[3,4].

$$\Theta(\gamma, R^*; t^*) = 1+4\gamma[(c\rho)^* d^* +1] \sum_{n=1}^{\infty} \exp(-\beta_n^2 \gamma^2 t^*) / C_n \qquad (1)$$

where

$$\Theta = (c_1\rho_1 d_1 + c_2\rho_2 d_2)T_1(d_1, t) / Q, \qquad (2)$$

$$\gamma^2 = a_1/a_2, \quad (c\rho)^* = c_1\rho_1/(c_2\rho_2), \quad d^* = d_1/d_2,$$

$$R^* = c_2\rho_2 a_2 R / d_2, \quad t^* = a_2 t / d_2^2, \qquad (3)$$

$$C_n = (d^*+\gamma)[(c\rho)^*\gamma+1]\cos\beta_n(d^*+\gamma) + (d^*-\gamma)[(c\rho)^*\gamma-1]\cos\beta_n(d^*-\gamma) - (c\rho)^*\gamma^2 R^* \{\beta_n[(d^*+\gamma)\sin\beta_n(d^*+\gamma) - (d^*-\gamma)\sin\beta_n(d^*-\gamma)] - [\cos\beta_n(d^*+\gamma) - \cos\beta_n(d^*-\gamma)]\}, \qquad (4)$$

and a, c, ρ, R and Q and the thermal diffusivity, specific heat, density, thermal resistance at the interlayer surface

Table 1 Chemical compositions of powders used for spraying.

Material	OAT-F	GAT-40	OZRY	C-73SF·NS	R-C
composition %	Al_2O_3 95.0	Al_2O_3 60	ZrO_2 92	WC 83	Cr_2O_3 90.1
	TiO_2 2.6	TiO_2 40	Y_2O_3 8	Co 17	SiO_2 6.0
	SiO_2 1.3				MgO 1.6
	Fe_2O_3 0.7				Al_2O_3 1.6
	CaO 0.2				Fe_2O_3 0.5
	MgO 0.1				CaO 0.2

Table 2 Plasma spraying conditions.

Specimen		OAT-F	GAT-40	OZRY	C-73SF·NS
Main arc gas		Ar	Ar	Ar	Ar
Pressure	psi	100	100	100	100
Flow	ℓ/m	84.0	67.2	44.8	84.0
Auxiliary gas		H_2	H_2	H_2	H_2
Pressure	psi	50	50	50	50
Flow	ℓ/m	26.5	26.5	26.5	26.5
Arc current	A	500	500	500	500
Arc voltage	V	72	70	63	72
Powder feed gas		Ar	Ar	Ar	Ar
Spraying distance	mm	120	120	120	150
Powder size range	μm	5~25	5~45	10~60	5~38

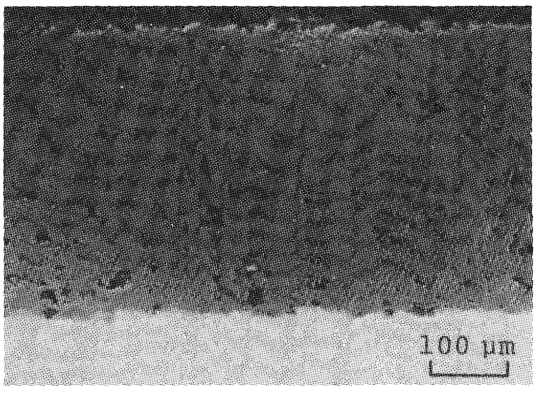

Fig. 1 Cross-section of GAT- sprayed coating.

and the heat input per uint area on the front surface, respectively. The subscripts 1 and 2 mean the properties of each layer. The β_n is the n-th positive root of

$$[(c\rho)^*\gamma+1]\sin\beta(d^*+\gamma)+[(c\rho)^*\gamma-1]\times\sin\beta(d^*-\gamma)+\beta(c\rho)\gamma^{*2}R^*[\cos\beta(d^*+\gamma)-\cos\beta(d^*-\gamma)]=0. \quad (5)$$

Figure 3 shows some examples of normalized temperature versus dimensionless time curves at the rear surface obtained by calculating Eq.(1). We introduce a new parameter $t_\alpha{}^*$ defined by the following equation:

$$\Theta(\gamma, R^*; t_\alpha{}^*)=\alpha, \quad (6)$$

where $0<\alpha<1$.

Let the temperature versus time curve of $\gamma=0.1$ and $R^*=10$, that is, the curve P in Fig. 3 be obtained by temperature measurement, then $t_{0.3}{}^*$ and $t_{0.7}{}^*$, for example, can be read as 7.715 and 16.74 from the figure when α is set at 0.3 and 0.7, respectively. When t_α is known and γ and R^* are variables, the combinations of γ and R^* which satisfy Eq.(6) are expressed as the γ - R^* curves, as shown in **Fig. 4**, and these curves crossed at a point P, which shows the values of γ and R^* to be obtained. Therefore, if we express R^* which satisfys Eq.(6) for any γ like as $R^*(\gamma; t_\alpha)$, both γ and R^* can be determined by solving the equation

$$R^*(\gamma; t_{\alpha_1})-R^*(\gamma; t_{\alpha_2})=0, \quad (7)$$

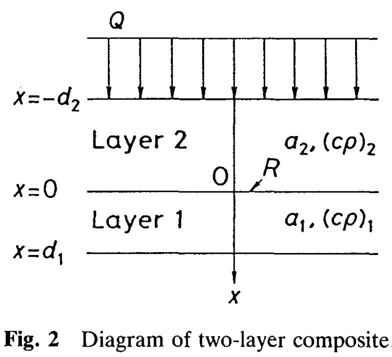

Fig. 2 Diagram of two-layer composite.

which holds for two α-values, α_1 and α_2. The solution can be obtained easily through the numerical calculation. In this study, the method of bisection algorithm was addopted, and the numerical calculations were carried out on a mini-computer, HITAC E-800. The iteration was stopped when γ at the (n+1)th step satisfied the following condition:

$$(\gamma^{(n+1)}-\gamma^{(n)})/\gamma^{(n)}<0.5\times10^{-4}, \quad (8)$$

where the superscript (n) denote the value which is obtained at the n-th iteration. For many numerical examples, the solution were obtained within about 35 second, and the iteration time was less than twenty times at most.

4. Results and Discussion

4.1 Experimental results

Table 3 shows the 30 pct. and 70 pct. time measured and the results of both thermal diffusivity of the ceramics coating and thermal resistance at the interlayer surface obtained by the present method. The thermal diffusivity and the specific heat of SUS 304 used was 3.60×10^{-6} m²/s

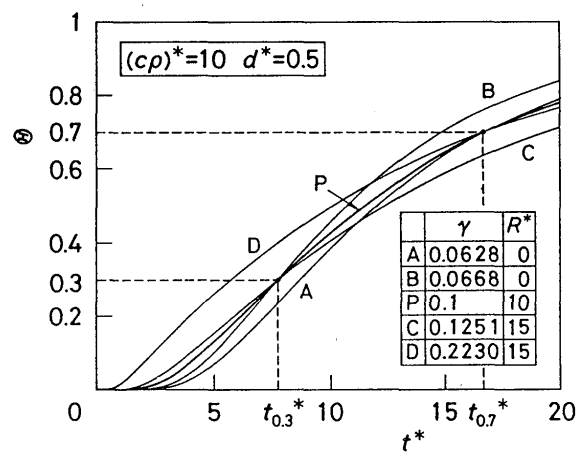

Fig. 3 Normalized temperature versus dimensionless time curves at the rear surface.

Table 3 Measured results.

		OAT-F	GAT-40	OZRY	C-73SF·NS	R-C
d_1	mm	0.354	0.374	0.372	0.333	0.334
d_2	mm	0.719	0.702	0.594	0.703	0.727
$t_{0.3}$	ms	91.2	61.7	88.8	37.6	60.2
$t_{0.7}$	ms	247.5	121.3	182.0	66.8	112.3
$(c\rho)_1$	J/m³K	1.25×10^6	1.13×10^6	1.20×10^6	2.87×10^6	2.68×10^6
a_1	m²/s	3.79×10^{-6}	1.19×10^{-6}	4.51×10^{-7}	1.85×10^{-6}	7.50×10^{-7}
R	m²K/W	3.61×10^{-4}	6.14×10^{-5}	——	——	——

and 466 J/(kg·K), respectively.

The precision of the measured results of thermal diffusivity was in ±5 pct. except OAT-F. The precision in the case of OAT-F was about ±25 pct. OAT-F-sprayed coating was separated from substrate when the specimen was sectioned to measure the thickness of each layer. Therefore, the thermal resistance of OAT-F is relatively large and the precision of thermal diffusivity is also large, comparing with the results of the other specimens. The thermal diffusivity of the bulk of Al_2O_3 and ZrO_2 is about $(6.8\sim8.3)\times10^{-6}$ and $(6.6\sim6.9)\times10^{-7}$ m^2/s, respectively[5]. Therefore, the results of OAT-F and OZRY coatings are about 50 and 60 pct. of thermal diffusivity of bulk, respectively. These differences may be caused by bonding strength between the flattened ceramics particles and porosity.

As above mentioned, thermal resistance of OAT-F was relatively large, and this is nearly equal to the value in the case of sillicon linking of two metal disks[6]. Thermal contact resistance of other specimens were not recognized. These results show that the minimum value of thermal resistance which can be determined by the present method may be the order of 10^{-5} m^2K/W.

4.2 Theoretical estimation on accuracy

Since the present method is an indirect measurement method, it is important to investigate the influence of the error of each parameter, that is, thickness of each layer, measuring time and thermophysical properties on the measured results. If the values used for calculation, which are denoted by the superscript " ' ", have relative errors ε for the true values, d_i, $(c\rho)_j$, a_2 and $t_{\alpha k}$ $(i, j, k=1,2)$, we can express these parameters as

$$d_i'=(1+\varepsilon_{di})d_i, \quad i=1,2 \tag{9}$$
$$(c\rho)_j'=(1+\varepsilon_{(c\rho)_j})(c\rho), \quad j=1,2 \tag{10}$$
$$a_2'=(1+\varepsilon_{a2})a_2 \tag{11}$$
$$t_{\alpha k}'=(1+\varepsilon_{t\alpha k})t_{\alpha k}, \quad k=1,2 \tag{12}$$

Substituting Eqs.(9) to (12) into Eq.(3), the dimensionless value of parameters can be written as

$$(c\rho)^{*\prime}=[(1+\varepsilon_{(c\rho)_1})/(1+\varepsilon_{(c\rho)_2})](c\rho)^*, \tag{13}$$
$$d^{*\prime}=[(1+\varepsilon_{d1})/(1+\varepsilon_{d2})]d^*, \tag{14}$$
$$t_{\alpha k}^{*\prime}=[(1+\varepsilon_{a2})(1+\varepsilon_{t\alpha k})/(1+\varepsilon_{d2})^2]t_{\alpha k}^*, \quad k=1,2 \tag{15}$$

The value of γ obtained through the present measuring method using the above values has relative error ε_γ, and it is written as follows:

$$\gamma'=(1+\varepsilon_\gamma)\gamma. \tag{16}$$

Therefore, a_1' is expressed by

$$a_1'=(1+\varepsilon_\gamma)\gamma^2(1+\varepsilon_{a2}) \tag{17}$$

from Eq.(3), and the relative error of a_1' can be estimated by

$$\varepsilon_{a1}=(1+\varepsilon_\gamma)^2(1+\varepsilon_{a2})-1, \tag{18}$$

after all.

The estimated results of errors are shown in **Fig. 5** for the same numrical example as the previous section. The values of α_1 and α_2 are set to 0.3 and 0.7, respectively. The abscissa means the absolute value of the relative errors in Eqs. (9) to (12), and the influence of each error of these parameters on ε_{a1} is shown in this figure. Either ε^+ or ε^- mean that the error of each parameter is positive or negative, respectively, and the absolute values are equal each other, when other parameters have no error. It is clear that the value of ε_{a1} increases as each

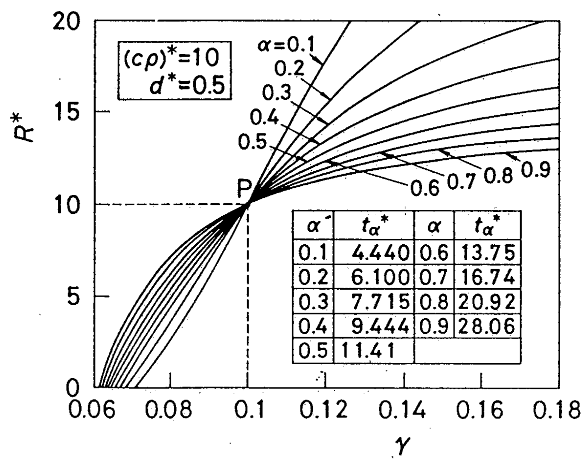

Fig. 4 γ-R* curves.

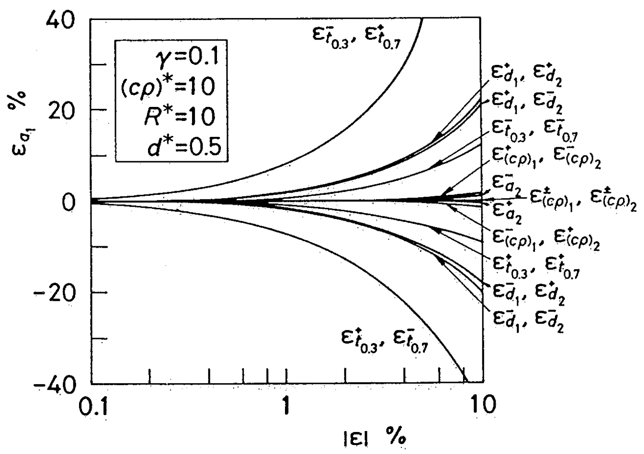

Fig. 5 Influence of each relative error of d_i, $(c\rho)_i$ (i=1, 2), a, $t_{0.3}$ and $t_{0.7}$ on accuracy of a

relative error increase. Especially, when $\varepsilon_{t_{0.3}}$ and $\varepsilon_{t_{0.7}}$ have different sign, the measured error becomes largest, and the errors of thickness are followed. The errors of specific heat $(c\rho)_i$ $(i=1,2)$ and thermal diffusivity a_2 do not affect the final accuracy so much.

5. Conclusions

An extension of the laser flash method for measuring the thermal diffusivity of sprayed coatings is proposed. A flash pulse is absorbed in the front surface, which is the substrate, of a thermally insulated spacemen. The resulting temperature history of the rear face, or the surface of the ceramics coating is measured by a radiation thermometer and recorded with a transient memory and a pen-recorder. The time required for the temperature to rise 30 and 70 percents, for example, of the maximum temperature rise is read from the temperature versus time curve. These results are used for the numerical computation based on the theoretical equation of the normarized temperature increase on the rear face and the method of bisection. The thermal resistance at the interlayer surface can be also obtained easily as well as the thermal diffusivity. The present method is applied to five kinds of thermal sprayed ceramics coatings, and the effectiveness of this method is confirmed.

This method will be effective to compare the difference of the thermophysical properties depend on the coating materials, coating method, coating conditions, and so on. Furthermore, it will be also effective to investigate the effect of the heat treatment for the coatings by lasers, for example.

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References

1) Parker, W. J., Jenkins, R. J., Butler, C. P. and Abott, G.L.: Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity, *J. Appl. Phys.*, Vol.32, No.9, p.1679 (1961).
2) Takahasi, Y.: Measurement of Thermophysical Properties by Laser-Flash Method, *Jpn J. Thermophysical Properties*, Vol.1, No.1, p.3 (1987). (in Japanese)
3) Inoue, K. and Ohmura E.: Measurement by Laser Flash Method of Thermal Diffusivity of Two-Layer Composites, *J. Jpn Welding Soc.*, Vol.6, No.3, p.442 (1988). (in Japanese)
4) Inoue, K. and Ohmura E.: Determination of Thermal Diffusivity of Two-Layer Composites by Flash Method, *Trans. JWRI*, Vol.17, No.2, p.49 (1988).
5) Touloukian, Y. S., et al., *Thermophysical Properties of Matter, Thermal Diffusivity*, p.378, 409 (1973), IFI/Plenum.
6) Inoue, K. and Ohmura E.: Determination of Thermal Contact Resistance in Two-Layer Composites by Flash Method, *Trans. JWRI*, Vol.15, No.2, p.21 (1986).