

Development of Reference Materials for Thermal-Diffusivity Measurements by the Flash Method

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Abstract The thermal conductivity of solid materials used for thermal simulations and thermal designs can be obtained as the product of thermal diffusivity, specific heat capacity, and bulk density in many cases. The thermal diffusivity is usually measured by the flash method, and the specific heat capacity is usually measured by differential scanning calorimetry. In order to obtain reliable thermal conductivities for strict thermal design, it is necessary to measure the thermal diffusivity using the flash method, a well-validated apparatus. Reference materials are an effective means for validation of most practical measurement apparatus. For the flash method, isotropic graphite was selected as a candidate reference material. A batch of isotropic graphite samples was prepared and characterized in detail in order to be a certified reference material for thermal-diffusivity measurement. The detailed characterization ensures the traceability of the measurement results to the international system of units (SI). A convenient reference material for thermal conductivity was also obtained by using the known thermal-diffusivity measurements, specific heat capacity, and density of the material.

Keywords Certified reference materials · Flash method · Graphite · Specific heat capacity · Thermal conductivity · Thermal diffusivity

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1 Introduction

Thermal design has an impact on efficient energy use and energy conservation. In order to make strict thermal simulations in the design process, reliable thermophysical property data are essential. In particular, well-verified thermal-conductivity data are required because they are used in almost all simulations.

For most solid materials in the temperature range from room temperature to over 1000 K, the thermal conductivity is obtained as the product of the thermal diffusivity, specific heat capacity, and bulk density. The thermal diffusivity is typically measured by the flash method [1]. The specific heat capacity is often measured by differential scanning calorimetry (DSC) or it is sometimes quoted from data books. Density is easily calculated dividing the mass by volume of the specimen. Note that thermal conductivity and thermal diffusivity are transport properties that are sensitive to material structure. It is known that materials with the same composition and the same purity show different transport properties dependent on such structural factors as follows: crystal structure, grain size, defects, porosity, and density. In order to obtain well-verified values of thermal conductivity, the most used path is to measure the thermal diffusivity with a well-validated apparatus employing the flash technique.

Reference materials are effective tools for validation of measurement apparatus. Since the 1960s, some reference materials of thermal conductivity for dense solid materials have been supplied by the National Institute of Standards and Technology (NIST) [2]. Unfortunately, many of them are currently out of stock. Reference materials supplied from the Institute for Reference Materials and Measurements (IRMM) [3] and Japan Fine Ceramics Center (JFCC) [4] are available. However, the reference materials for validation of practical apparatus using the flash method do not cover a sufficiently wide thermal-diffusivity range.

Considering the background, we have studied the thermal diffusivity of solid materials for the purpose of developing reference materials for the flash method. In the National Metrology Institute of Japan (NMIJ), the intrinsic thermal diffusivity of materials can be determined with traceability to the international system of units (SI) according to ISO/IEC 17025 [5].

Isotropic graphite was selected as a candidate material. The thermal diffusivity of a batch of isotropic graphite was determined by detailed measurements of sample specimens from the batch. The reference material was named as NMIJ RM 1201a, and has been supplied as a reference material since 2006. In order to encourage wider use, it was renamed as NMIJ CRM 5804a [6] in 2010 following a re-check of the thermal-diffusivity values and stability according to ISO Guide 34 [7].

Some practical flash apparatus not only measure thermal diffusivity but also measure the specific heat capacity in order to provide measurements of the thermal conductivity at the same time. Considering users' convenience, a thermal-conductivity reference material named NMIJ RM 1401a was developed. The thermal conductivity of RM 1401a was provided with the thermal diffusivity measured by the flash method, the specific heat capacity measured by DSC, and the density estimated from sizes and masses. In this paper, we describe how to produce these reference materials for validation of practical apparatus using the flash method. The requirements for reference materials in the field of thermophysical properties are also discussed.

2 Experimental Apparatus and Procedures

2.1 Specimens

Isotropic graphite was chosen as a candidate reference material because it is stable, homogeneous, and easy to handle. It is also opaque to near-infrared light. With the flash method, the specimen is heated by a pulse of light absorbed at the surface and the temperature change at the rear surface is observed by infrared radiometry. Therefore, it is required that the specimen is opaque and the surface has a high emissivity. Specimens sometimes need to be coated with graphite spray for practical measurements in order to satisfy these conditions. However, the coating becomes one of the large uncertainty factors. A material that can be measured without a coating is preferable for a reference material.

When we prepared a batch of thermal-diffusivity reference materials, we selected IG-110, a grade of isotropic graphite manufactured by Toyo Tanso Co. Ltd. It was known from a recent study [8,9] that it showed good homogeneity and stability. Sixty sets of IG-110 specimens were prepared as a batch of a thermal-diffusivity certified reference material named NMIJ CRM 5804a. Each set is composed of four disks of 10 mm diameter with 1.4 mm, 2.0 mm, 2.8 mm, and 4.0 mm thicknesses. All specimens were cut from a block by machining. Six sets were sampled randomly from the sixty sets in order to determine the thermal diffusivity and to investigate the homogeneity.

The specimens for thermal-conductivity reference material NMIJ RM 1401a were prepared as a different batch from CRM 5804a. The batch of RM 1401a consists of 10 rods of ϕ 10 mm \times 100 mm made by IG-110, machined from a single block. The specimens for characterization and supply were cut from these rods.

2.2 Apparatus

The thermal diffusivity of these reference materials was measured by the laser-flash measurement system in NMIJ [8] at temperatures from 297 K to 1500 K. The system was optimized using advanced techniques [10]. The specific heat capacity to calculate the thermal conductivity was measured by using a power-compensated DSC at temperatures from 300 K to 900 K.

2.3 Procedure to Determine Thermal Diffusivity

The thermal diffusivity α is calculated from the thermal diffusion time τ_0 and thickness of the specimen d in the flash measurement [1],

$$\alpha = \frac{d^2}{\tau_0}. \quad (1)$$

The time, τ_0 , was estimated by analysis of the temperature-rise curve using Cape and Lehman's function [11,12] and the equiareal method [10]. The intrinsic thermal diffusivity was determined using an extrapolation procedure [13].

The uncertainty of the thermal diffusivity of a reference material is evaluated as a combination of the uncertainty attributed to thermal-diffusivity measurements and the uncertainty caused by inhomogeneity and stability of the material. The uncertainties were all calculated in accordance with the “Guide to the expression of uncertainty in measurement” (GUM) [14]. The uncertainty of homogeneity of the material is estimated by analysis of the variance. The thermal diffusivity is a derived quantity of length and time according to Eq. 1 and its unit is expressed as “ $\text{m}^2 \cdot \text{s}^{-1}$.” On the other hand, the thermal diffusivity is a physical property that depends on temperature. The laser-flash measurement system is also composed of three parts related to the measurements of length, time, and temperature. By uncertainty evaluation of each part, SI traceability of the thermal diffusivity can be established. The uncertainty factors of thermal-diffusivity measurements in this study are as follows [8, 15];

- (1) Uncertainty of specimen thickness
- (2) Uncertainty of sampling time
- (3) Uncertainty of response time of infrared radiation thermometer
- (4) Uncertainty of pulse width
- (5) Uncertainty due to non-uniform heating effect
- (6) Uncertainty due to heat loss effect
- (7) Uncertainty due to distortion of data by drift of specimen temperature
- (8) Uncertainty of data analysis
- (9) Uncertainty of extrapolation analysis
- (10) Uncertainty of specimen temperature.

Here, factors (3) to (9) are characteristic uncertainty factors for the flash method. The typical uncertainty attributed to thermal-diffusivity measurements around room temperature is about 4 % with a coverage factor $k = 2$.

3 Results

3.1 Certified Reference Material of Thermal Diffusivity

3.1.1 Determination of Thermal Diffusivity

Figure 1 shows the apparent thermal diffusivity at room temperature for the six sets sampled from the 60 sets. Here, an apparent thermal diffusivity was estimated from a temperature-rise curve that includes change of the thermal diffusivity during temperature rise. The thermal diffusivity was determined as the intercept of the extrapolation in these plots. The slope of extrapolation was expected to be usually a negative value reflecting the temperature dependence of the thermal diffusivity. However, Fig. 1d shows a positive slope. The difference is due to the large variation of the apparent thermal diffusivity with a small amplitude of the output signal from thick specimens. It is not considered to be an anomaly since the slope is extremely small. Figure 2 summarizes thermal diffusivities of these 24 specimens, as determined from Fig. 1. It seems that there was no significant dependence on set number and specimen thickness. The numerical data are also shown in Table 1.

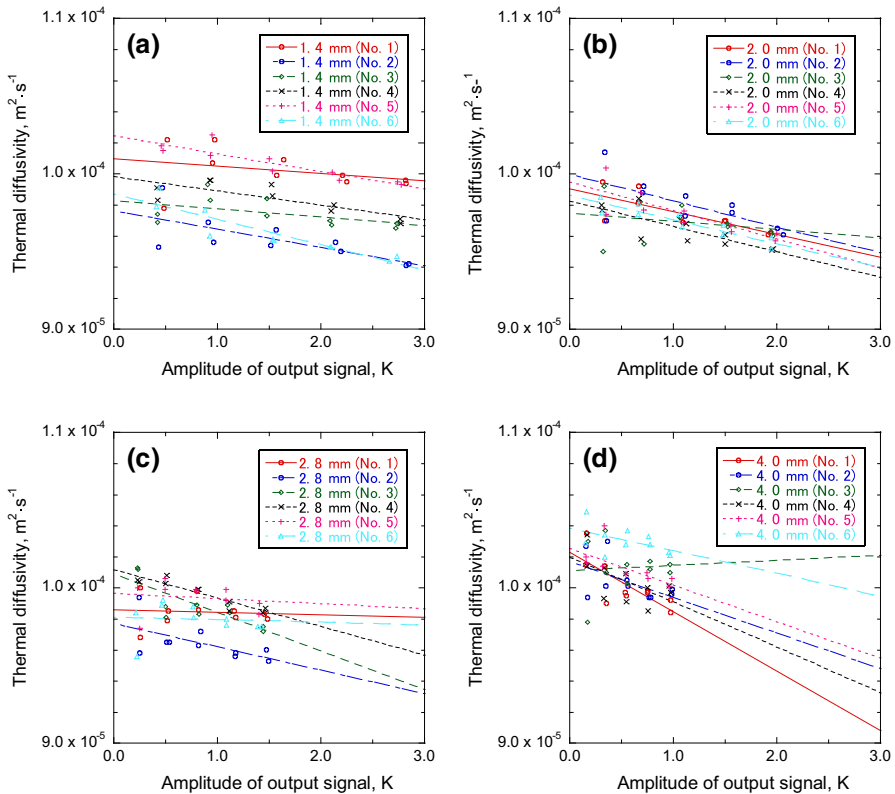


Fig. 1 Amplitude of output signal dependence of apparent thermal diffusivity calculated from each temperature-rise curve measured at room temperature changing pulsed heating energy for (a) 1.4 mm thickness specimens, (b) 2.0 mm thickness specimens, (c) 2.8 mm thickness specimens, and (d) 4.0 mm thickness specimens. Here, the amplitude of output signal was converted into temperature because the infrared radiometer was calibrated from 293 K to 473 K to decrease nonlinearity effect of output

Fig. 2 Thermal diffusivity at room temperature determined as intercept of the extrapolation as shown in Fig. 1. Error bar shows standard deviation caused by the extrapolation procedure

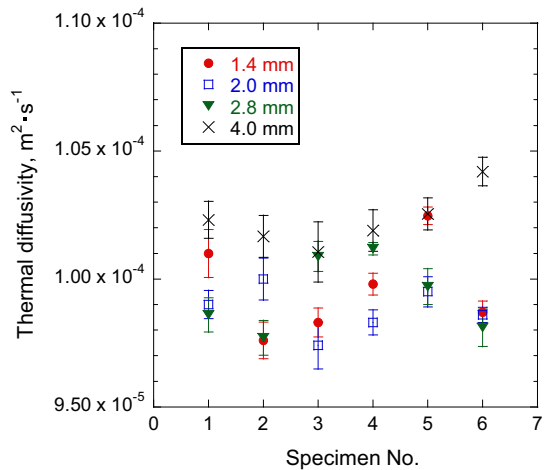
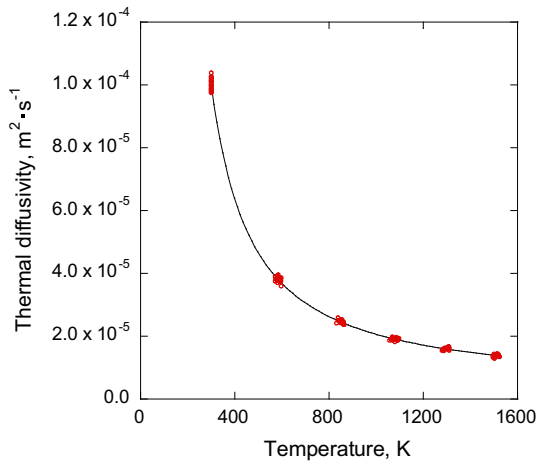


Table 1 Data for analysis of variance (thermal-diffusivity values of 24 specimens at room temperature) of NMIJ CRM 5804a

Thickness	Set number					
	Thermal diffusivity ($10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$)					
	P1 (No.1)	P2 (No.2)	P3 (No.3)	P4 (No.4)	P5 (No.5)	P6 (No.6)
t1 (1.4 mm)	10.1	9.76	9.83	9.80	10.3	9.87
t2 (2.0 mm)	9.90	10.0	9.74	9.83	9.95	9.86
t3 (2.8 mm)	9.86	9.77	10.0	10.1	9.97	9.81
t4 (4.0 mm)	10.2	10.7	10.1	10.2	10.3	10.4

Fig. 3 Temperature dependence of thermal diffusivity of NMIJ CRM 5804a. The *symbol* shows thermal diffusivity determined by the extrapolation procedure of 24 specimens. The *solid line* represents Eq. 5



The measured thermal diffusivities of the 24 specimens, from room temperature to 1500 K, are plotted in Fig. 3. The thermal-diffusivity values of the 24 specimens agree well with each other. It was found that the thermal diffusivity decreases from $1.0 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$ to $1.3 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ with increasing temperature. From the measured result, we determined the thermal diffusivity of this reference material as a function of temperature. Generally, the Debye temperature Θ_D of graphite is about 2000 K [16]. It is known that thermal conduction by phonon heat transfer is dominant below the Debye temperature [17]. In this temperature region, the thermal conductivity λ is known to be proportional to an exponential function as follows [17]:

$$\lambda(T) \propto \left(\frac{T}{\theta_D}\right)^n \times \exp\left(\frac{\theta_D}{bT}\right). \tag{2}$$

Here, T is the temperature, n is an integer, and b is a constant. The specific heat capacity c of graphite at temperatures from 300 K to 1500 K is reported as [16]

$$c = -5.293 + 58.998 \times 10^{-9} T - 43.225 \times 10^{-6} T^2 + 11.51 \times 10^{-9} T^3 \text{ [J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\text{]}. \tag{3}$$

Since the third term, which is proportional to T^2 , is the most dominant term in Eq. 3, it is supposed that the specific heat capacity is roughly approximated as $c \propto T^2$. The density ρ is a constant independent of temperature when the thermal expansion is small enough to be ignored. It follows that the thermal diffusivity is able to be assumed as

$$\alpha(T) = \frac{\lambda(T)}{c(T) \cdot \rho} \propto \left(\frac{T}{\theta_D}\right)^{n-2} \times \exp\left(\frac{\theta_D}{bT}\right). \quad (4)$$

Here, we make the approximation $\left(\frac{T}{\theta_D}\right)^{n-2} = \left(\frac{T}{\theta_D}\right)^{0.05} \approx 1$, which was obtained by the least-squares fit of thermal-diffusivity values using Eq. 4 with $\theta_D = 2000$ K. According to these results, we propose a temperature dependence of the thermal diffusivity α with an approximation as follows:

$$\alpha(T) = M_1 + M_2 \times \exp\left(\frac{M_3}{T}\right), \quad (5)$$

Here, M_1 , M_2 , and M_3 are constants. They are determined by the least-squares method as $M_1 = -3.692 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$, $M_2 = 3.964 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$, and $M_3 = 3.719 \times 10^{-2} \text{ K}$ for CRM 5804a, as shown in Fig. 3. Note that the thermal diffusivity was calculated using specimen thicknesses measured at room temperature in this study. The necessity for a thermal-expansion correction is sometimes pointed out. This subject is discussed in Sect. 3.3.

3.1.2 Evaluation of Inhomogeneity of the Material

The inhomogeneity was evaluated from the distribution of thermal diffusivities at room temperature. The reasons are as follows: specimens can be compared easily at the same conditions at room temperature. The distribution of thermal diffusivity seems to be relatively sensitive to measurement uncertainty and inhomogeneity at room temperature, since the temperature dependence of the thermal diffusivity shows a heavy slope around room temperature. The thermal diffusivities of the 24 specimens were identified by thickness (factor- t) and set number (factor- P) as shown in Table 1 for analysis of the variance in order to estimate the distribution of them. The analysis of the variance was carried out using a program “AIST-ANOVA” [18].

Table 2 is an analysis of the variance table for CRM 5804a. The F -distributions were estimated for the F -test. $F(x, y)_z$ is an F -distribution cumulative distribution function with x degrees of freedom in the numerator and y degrees of freedom in the denominator the $(z \times 100) \%$ significance level. $F(x, y)_z$ is given as the F -distribution table in a text book on statistics. F_t which is a F value estimated for the factor- t as shown in Table 2a is larger than $F(3, 20)_{0.05} = 3.098$. It was found that the distribution attributed to thickness is judged as 5 % of the significant level. F_P which is an F -value estimated for the factor- P as shown in Table 2b is sufficiently smaller than $F(5, 18)_{0.05} = 4.956$. It indicates that there is no significant difference on set number.

Table 2 Analysis of variance table on thermal diffusivity for (a) thickness (factor-*t*) and (b) set number (factor-*P*) of NMIJ CRM 5804a

(a) factor- <i>t</i>				
Source	Sum of squares	Degrees of freedom	Mean square	$F_t = V_t/V_E$
Between group	$S_t = 4.31 \times 10^{-3}$	3	$V_t = 1.44 \times 10^{-3}$	7.72
Within group	$S_E = 3.72 \times 10^{-3}$	20	$V_E = 1.86 \times 10^{-4}$	
(b) factor- <i>P</i>				
Source	Sum of squares	Degrees of freedom	Mean square	$F_P = V_P/V_E$
Between group	$S_P = 8.50 \times 10^{-4}$	5	$V_P = 1.70 \times 10^{-4}$	0.42
Within group	$S_E = 7.18 \times 10^{-3}$	18	$V_E = 3.98 \times 10^{-4}$	

The expectation values for factor-*t* and factor-*P* were obtained:

$$E(V_t)^2 = \sigma_e^2 + 6\sigma_t t^2 = 2.38 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}, \tag{6}$$

$$E(V_P)^2 = \sigma_e^2 + 6\sigma_P P^2 = 1.28 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}, \tag{7}$$

$$\sigma_e^2 = 3.19 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}. \tag{8}$$

Here, σ_e^2 is the variance of the error. These expected values can be pooled to a variance of error because they are very small. The standard deviation σ_t and error of σ_s^2 on factor-*t* are obtained as follows:

$$\sigma_T = \left[\left(E(V_t)^2 - \sigma_e^2 \right) / 6 \right]^{1/2} = 1.88 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}, \tag{9}$$

$$\sigma_s^2 = 1.65 \times 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}. \tag{10}$$

Since the factor-*t* shows a 5 % significant level and the factor-*P* is not significant, the inhomogeneity was evaluated as σ_t . The thermal diffusivity at room temperature α_{RT} is calculated by Eq. 2. The relative uncertainty caused by inhomogeneity is estimated as $(\sigma_t / \alpha_{RT}) \times 100 = 1.9\%$ with coverage factor $k = 1$. The deviation of the thermal diffusivity attributable to inhomogeneity was about 1.9 % among specimens, independent of specimen thickness.

3.1.3 Examination of Stability

The reference material is used repeatedly at temperatures from 300 K to 1500 K. The stability of the reference material during repeated use with a heat cycle should be examined. The specimen was heated from room temperature to 1500 K with a heating rate of $200 \text{ K} \cdot \text{h}^{-1}$ and cooled at a rate of $200 \text{ K} \cdot \text{h}^{-1}$ from 1500 K to 1000 K, and then naturally cooled to room temperature in vacuum as a series of heat treatments. The thermal-diffusivity measurements were carried out at six temperature levels during the first heat treatment and during the 10th heat treatment.

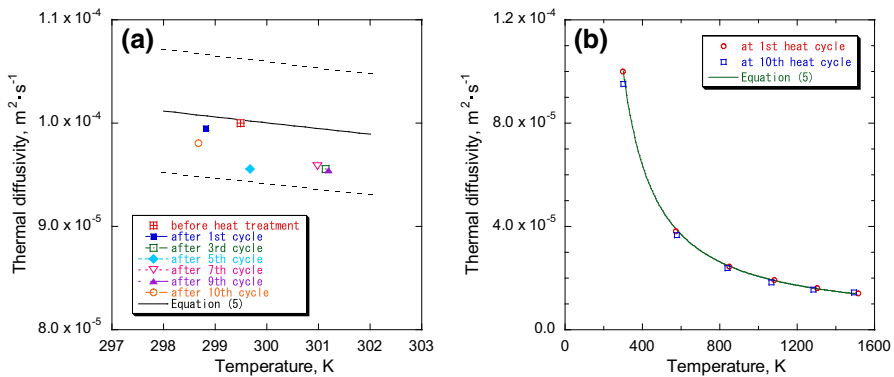


Fig. 4 Stability for heat cycles; (a) thermal diffusivity of an IG-110 specimen at room temperature before and after 1st, 3rd, 5th, 7th, 9th, and 10th heat treatments. *Solid line* shows thermal diffusivity as a function of temperature as shown as Eq. 5. *Dashed line* shows expanded uncertainty. (b) Temperature dependence of thermal diffusivity of an IG-110 specimen measured during 1st and 10th heat treatments. *Solid line* shows thermal diffusivity shown as Eq. 5

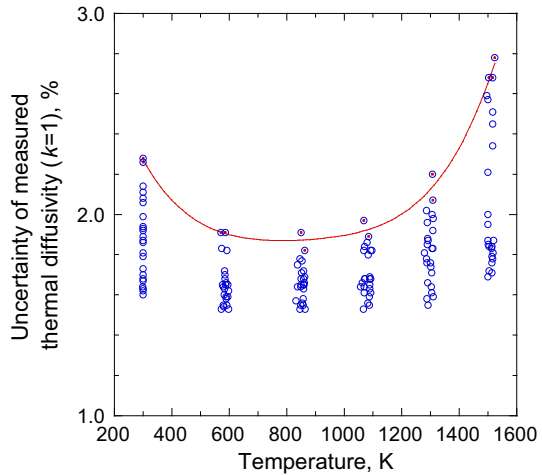
Figure 4a shows the thermal diffusivity of an IG-110 specimen at room temperature after each heat treatment. Thermal diffusivities before and after 1st, 3rd, 5th, 7th, 9th, and 10th heat treatments varied unsystematically within the uncertainty for the laser-flash measurements. We considered that there is no significant change during 10 heat treatments. The total exposure time above 1500 K corresponds to about 40 h after the 10th heat treatment. The temperature dependences of the thermal diffusivity for an IG-110 specimen during the 1st heat treatment and 10th heat treatment from room temperature to 1500 K in vacuum are shown in Fig. 4b. There is no change between the 1st and 10th heat treatments. It, therefore, was confirmed that the isotropic specimen was stable above 1500 K for 40 h or for 10 heat treatments from room temperature to 1500 K.

According to ISO Guide 34, it is necessary to check storage stability. The certified reference material is stored in an environment at $(23 \pm 5) ^\circ C$ and at a relative humidity less than 50 % at NMIJ. We checked the thermal diffusivity of some IG-110 specimens kept in the environment at room temperature every year. When it was certified as a certified reference material in 2010, the thermal diffusivity at room temperature shows no significant change compared with the value when it was produced as NMIJ RM 1201a in 2006. According to this, the certification of CRM 5804a is valid until March 31, 2015. Moreover, there is no significant change of thermal diffusivity of the other IG-110 specimens prepared in 2004 when we checked in 2013. It indicates that this isotropic graphite is very stable for storage in the environment.

3.1.4 Estimation of Uncertainties

Figure 5 shows uncertainties of the measured thermal diffusivity of the 24 specimens. It consists of the uncertainty of measurement by our system. It is found that the measurement uncertainty depends on temperature. The uncertainty becomes smaller at temperatures between 500 K and 800 K than in the other temperature regions. In this

Fig. 5 Temperature dependence of uncertainty of the thermal diffusivity by the flash measurement of 24 specimens with coverage factor $k = 1$



temperature region, an infrared radiometer becomes more sensitive and the specimen temperature before pulse heating seems to be more stable rather than for the other region. At around room temperature (300 K), the distribution of measurement results tends to be large since the temperature dependence of the thermal diffusivity shows a steep slope. The uncertainty above 1000 K tends to become larger due to instability of the specimen temperature and the effects of heat loss by radiation. We evaluated the uncertainty attributed to the measurement as a function of temperature by the least-squares method for two selected values from the maximum in descending order at each temperature as shown in Fig. 5. The residual standard deviation of the temperature dependence was also estimated.


The uncertainty of Eq. 5, which is the temperature dependence of the thermal diffusivity, was evaluated as the standard deviation of residuals between the measured thermal diffusivities and Eq. 5. The inhomogeneity of 1.9 % with $k = 1$ was obtained by variance analysis described in Sect. 3.1.2.

Combining these contributions, the expanded uncertainties with a coverage factor $k = 2$ of the thermal diffusivity of NMIJ CRM 5804a were evaluated as 6 % at 300 K to 400 K, 5 % at 500 K to 1200 K, 6 % at 1300 K to 1400 K, and 7 % at 1500 K.

3.1.5 Certified Reference Material “NMIJ CRM 5804-a”

We have established a certified reference material for validation of the thermal-diffusivity measurement apparatus. The specification of the reference material is as shown in Table 3. It was developed according to ISO Guide 34 [7]. NMIJ CRM 5804a which consists of 60 sets for this batch was sold out in 2014. We are currently preparing the next batch of NMIJ CRM 5804b.

Table 3 Specification of the reference material “NMIJ CRM 5804a”

Name	NMIJ CRM-5804a	
Configuration	φ 10 mm × 1.4 mm, 2.0 mm, 2.8 mm, 4.0 mm (4 specimen set)	
Value (α , Thermal diffusivity)	$1.00 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1} \geq \alpha > 1.39 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ Temperature dependence as a function is given. Table of values every 100 K is given.	
Temperature region	300 K $\leq T \leq$ 1500 K	
Uncertainty ($k = 2$)	5 % to 7 %	
Note	Atmosphere: in vacuum or in non-oxidized gas flow Stability: until 40 h above 800 °C or until 10 times heat treatment from room temperature to 1500 K Expiration of Certification: March 2020	

3.2 Reference Material of Thermal Conductivity

It is known that the specific heat capacity is theoretically able to be measured by the flash method. Thermal conductivity is sometimes obtained by the flash method when the thermal diffusivity and specific heat capacity are measured at the same time. In order to validate thermal-conductivity measurements by the flash method, we also developed a thermal-conductivity reference material named NMIJ RM 1401a. It was produced by the following process.

We kept 10 rods with 10 mm diameter and 100 mm length of IG-110 as a batch for the thermal-conductivity reference material. The specimens for determination of the thermal diffusivity, specific heat capacity, and density were cut from these rods. The specimens for supply were also prepared from these rods.

Each of the 12 sets of specimens, composed of five disks of 10 mm diameter with 1.0 mm, 1.4 mm, 2.0 mm, 2.8 mm, and 4.0 mm thicknesses, were prepared in order to determine the thermal diffusivity and evaluate the homogeneity similarly to NMIJ CRM 5804a. Thermal diffusivities of 12 specimens of 2.0 mm thickness were measured at temperatures from 300 K to 900 K. Figure 6a shows the measured data and determined thermal diffusivities as a function of temperature by Eq. 5. Here, $M_1 = -3.795 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$, $M_2 = 4.091 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$, and $M_3 = 3.5716 \times 10^2 \text{ K}$. Note that M_i ($i = 1, 2, 3$) of RM1401a is different from that of CRM 5804a because RM 1401a was prepared from a different batch of IG-110. We confirmed that the thermal diffusivity was independent of specimen thickness from the measurements of a specimen set in this temperature range. The uncertainty of the thermal-diffusivity measurement ($k = 1$) is shown in Fig. 6b. The inhomogeneity was estimated by analysis of the variance for thermal diffusivities at room temperature of all 60 spec-

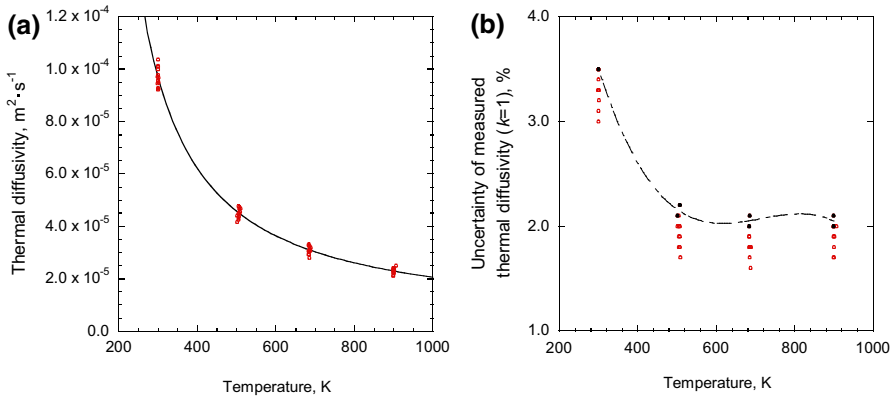


Fig. 6 Temperature dependence of (a) thermal diffusivity and (b) uncertainty of measured thermal diffusivity with coverage factor $k = 1$ of NMIJ RM 1401a

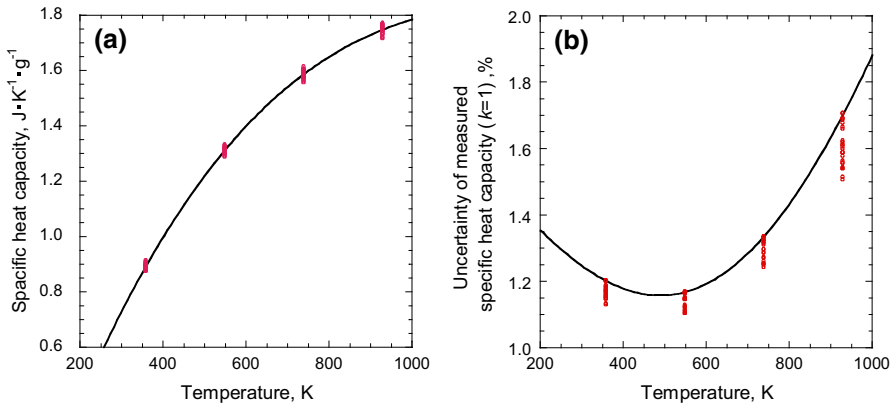


Fig. 7 Temperature dependence of (a) specific heat capacity and (b) uncertainty of measured specific heat capacity with coverage factor $k = 1$ of NMIJ RM 1401a

imens of 12 sets. The F -value for (11, 48) degrees of freedom was estimated as $F(11, 48) = 5.065$. A significant difference of more than 5 % was indicated since it is larger than $F(3, 2)_{0.05} = 1.994$. the inhomogeneity was evaluated as 2.7 % ($k = 1$) for the standard deviation for the factor- P .

The specific heat capacity was measured by a power-compensated DSC for 13 specimens prepared from the three different positions in one rod and the same positions in 10 rods. The disk specimens are 5.0 mm in diameter and 1.0 mm in thickness. NMIJ established the specific-heat-capacity measurements using the adiabatic calorimeter below 350 K and DSC at temperatures from 300 K to 1600 K. A certified reference material was produced [19]. The specific heat capacity c_t [$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$] of RM 1401a was determined at temperatures from 300 K to 900 K (Fig. 7a) as a function of temperature T using DSC,

$$c_t = -0.39119 + 4.6281 \times 10^{-3} T - 3.1676 \times 10^{-6} T^2 + 7.1481 \times 10^{-10} T^3 \quad (11)$$

A sapphire specimen, which is traceable to NIST SRM720 [20], was used as the reference sample for the DSC measurement. We measured the specific heat capacity of NIST SRM720 and the sapphire specimen. The uncertainty of the measurement is shown as an error bar in Fig. 7b. An uncertainty related to deviation of the reference sample was included in the whole uncertainty to ensure the traceability of the specific heat capacity measurement of isotropic graphite [21]. The inhomogeneity, measured as the dispersion of the specific heat capacity of 13 specimens at 360 K, was also investigated by analysis of the variance. The analysis was carried out for specimens prepared from three different positions in one isotropic graphite rod. The difference was also estimated for specimens from the same position in ten isotropic graphite rods. The F -values for (2,3) and (9,10) degrees of freedom are $F(3, 2) = 1.276$ and $F(9, 10) = 1.184$, respectively. They are much smaller than the critical values of F for the 5 % significance level, $F(3, 2)_{0.05} = 9.552$ and $F(9, 10)_{0.05} = 3.020$. We made a judgment that a significant difference does not appear. Therefore, the uncertainty for inhomogeneity with respect to the specific heat capacity can be ignored.

The density was estimated from the mass and size at room temperature. We prepared 10 cylinder specimens whose sizes are 10 mm diameter and 10 mm height. The diameter and height were measured carefully by a linear gage calibrated by gage blocks. The mass of the specimen is measured by a balance. The density of the RM 1401a was determined as $1.78 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$ with the uncertainty as $13 \text{ kg}\cdot\text{m}^{-3}$ ($k = 2$).

The stability of the reference material was investigated with respect to both the thermal diffusivity and specific heat capacity. It was clear that the stability during storage in the laboratory is no problem according to the case of CRM 5804a. This reference material will be used repeatedly at temperatures from 300 K to 900 K. Then we investigated the stability against heat cycles. The thermal diffusivity and specific heat capacity were measured before and after 10 heat cycles from room temperature to about 1000 K in an Ar gas flow. These properties did not show a significant change after the heat cycles.

Figure 8 shows the thermal conductivity of NMIJ RM 1401a. The thermal conductivity changes from $70.6 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $126 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ dependent on the temperature cycle. The thermal-conductivity value of this reference material is traceable to the SI unit. The specification of the reference material is summarized in Table 4.

3.3 Discussion on Requirements for These Reference Materials

In order to guarantee reliability of the thermal diffusivity and thermal conductivity of these reference materials, we considered that the values should be traceable to SI units as the standard and they should be intrinsic as a physical property of solid materials. The issues related to measurement of material properties had been discussed by the ad hoc Working Group on Material Metrology (WGMM) of Comité International des poids et Mesures (CIPM) collaborating with the Versailles Project on Advanced Materials and Standards (VAMAS) [22]. According to the report by WGMM [22], the thermal diffusivity is one of the intrinsic material properties that are independent of measurement methods and procedures, in contrast to procedural material properties which are dependent on measurement methods and procedures [23]. This means that the absolute

Fig. 8 Temperature dependence of thermal conductivity of NMIJ RM 1401a. *Error bar* shows the uncertainty of thermal conductivity with coverage factor $k = 2$

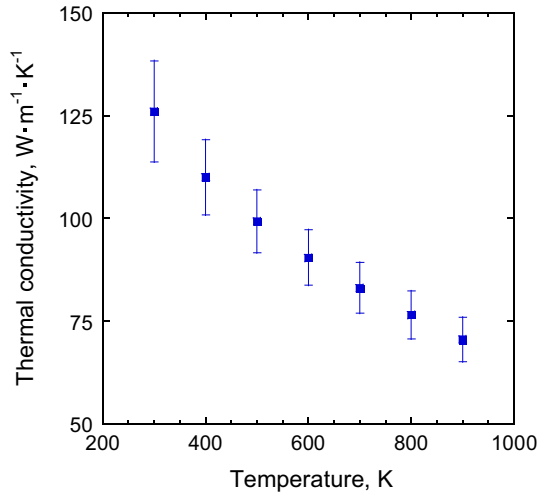



Table 4 Specification of the reference material “NMIJ RM-1401a”

Name	NMIJ RM-1401a 
Configuration	$\phi 10 \text{ mm} \times 1.0 \text{ mm}, 2.0 \text{ mm}$ (2 specimen set)
Value (λ , Thermal conductivity)	$126 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \geq \lambda > 70.6 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ Table of values every 100 K is given Temperature-dependence functions of thermal diffusivity and specific heat capacity are given as reference data There is information on the density at room temperature which is used for thermal-conductivity calculation
Temperature region	$300 \text{ K} \leq T \leq 900 \text{ K}$
Uncertainty ($k = 2$)	7.2 % to 9.8 %
Note	Atmosphere: in vacuum or in non-oxidized gas flow Stability: until 40 h above 800 °C or until 10 times heat treatment from room temperature to 1500 K Expiration of Certification: March 2020

value of the thermal diffusivity can be defined independent of the measurement conditions, and the thermal-diffusivity value can be traceable to SI units. Therefore, the thermal-diffusivity standard can be established based on intrinsic, absolute, and SI traceability.

It is important that these reference materials should be user friendly because they are used for validation of practical apparatus in laboratories. Strictly speaking, the value

should be corrected to become the absolute value considering the thermal expansion of the specimen. However, we determined certified values using the specimen thickness measured at room temperature, giving priority to usability. When the users of the flash apparatus carried out thermal-diffusivity measurements, the results are usually semi-automatically calculated from the heat diffusion time and specimen thickness. The specimen thickness, which is measured by a micrometer caliper at room temperature, is put into the apparatus before the flash measurement in many cases. It is convenient that the thermal-diffusivity without a thermal-expansion correction is expressed in the certification sheets of the reference materials for use at the laboratory. Moreover, when it is clear that the thermal-diffusivity values are calculated with the specimen thickness at room temperature, users can make the thermal-expansion correction if it is needed. Note that the thermal-expansion effect is about 0.3 % of this isotropic graphite. It is not large compared with the uncertainty of the thermal-diffusivity measurement of about 4 % to 7 %.

Reference materials are sometimes supplied as a small block before machining. However, our reference materials are prepared as disks to fit the apparatus. We are concerned that there may be a risk of damage given by machining, since the thermal diffusivity is sensitive to the microstructure of the material. A set of specimens with different thicknesses is expected to be effective to check a wide range of the time response of the apparatus. This supplying style is new and useful.

The stability for storage according to Guide 34 was checked in this study. In the case of thermophysical property reference materials, the stability during repeated measurements of the heat cycles is more important. Moreover, they are used repeatedly. Unfortunately, there are no details on the stability investigation for repeated use with temperature change in Guide 34. We carried out original accelerated tests with considered conditions in this study.

4 Conclusions

Reference materials for validation of a practical apparatus for thermal-diffusivity measurement using the flash method were established. They are made of isotropic graphite because it can be measured by the flash method without a surface coating. The stability for storage and repeated use with heat cycles was investigated.

One certified reference material for thermal-diffusivity measurements was named NMIJ CRM 5804a produced according to ISO Guide 34. This is supplied as a set of four disks with 10 mm in diameter and 1.4 mm, 2.0 mm, 2.8 mm, and 4.0 mm thicknesses. The intrinsic thermal diffusivity with SI- traceability was provided from $1.39 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$ to $1.00 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$, dependent on temperature from 300 K to 1500 K, and the expanded uncertainty of the thermal diffusivity was 5 % to 7 % with a coverage factor $k = 2$.

The other certified reference material is a thermal-conductivity reference material named NMIJ RM 1401a. The thermal conductivity from $126 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $70.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, dependent on temperature from 300 K to 900 K, was determined from values of the thermal diffusivity, specific heat capacity, and density. The expanded

uncertainty is 7.2 % to 9.8 % with a coverage factor $k = 2$. This is supplied as a set of two disks with 10 mm in diameter and 1.0 mm and 2.0 mm thicknesses.

We expected that these reference materials are helpful to validate measurement apparatus for thermal diffusivity and thermal conductivity.

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