

# SHINAGAWA TECHNICAL REPORT

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# 品川技報

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### 要 旨

非酸化物系耐火物の熱伝導率測定に使用されるJIS R 2251-3熱流法の代替を意図して、LF法の検討を行った。多くの種類の非酸化物系耐火物を検討した結果、LF法は熱流法を代替できることが示唆できた。今後はさらにいろいろな非酸化物系耐火物の熱伝導率をLF法によって測定し、LF法の適用範囲を決めることで規格化を図っていきたい。

### Abstract

Application of the laser flash (LF) method in place of the stationary heat flow method which was standardized in JIS R 2251-3 for measuring the thermal conductivity of non-oxide refractory materials was studied. Evaluation of many types of non-oxide refractory materials confirmed that the LF method could replace the stationary heat flow method. In the future, the scope of the LF method for measuring the thermal conductivity of non-oxide refractory materials should be researched for standardization.

## 1. はじめに

日本では、耐火物の熱伝導率は2007年に制定されたJIS R 2251-1, -2, -3の3つの規格にしたがって測定される。JIS R 2251-1は熱線法(直交法)と言われる規格であり、熱伝導率 $10\text{W}/(\text{m}\cdot\text{K})$ 以下の耐火物、JIS R 2251-2は熱線法(平行法)であり、 $25\text{W}/(\text{m}\cdot\text{K})$ 以下の耐火物が適用範囲であり、いずれも電気伝導性を示さない酸化物系耐火物が主な対象になっている。建設用耐火物には規格が定められているものもあり、これら2つのJISが有効な試験方法として役に立っている。

## 1. Introduction

In Japan, the thermal conductivity of refractory materials is determined in accordance with the standards of JIS R 2251-1, -2 and -3. JIS R 2251-1, based on the cross-array hot-wire method, is applicable to refractory materials with thermal conductivities of  $10\text{W}/(\text{m}\cdot\text{K})$  or less. JIS R 2251-2, which is based on the parallel hot-wire method, is applicable to refractory materials with conductivities of  $25\text{W}/(\text{m}\cdot\text{K})$  or less. Each standard is applicable to refractory materials which do not exhibit electrical conductivity. Since the thermal conductivity of

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一方、電気伝導性を有する炭素系、炭化珪素系などの非酸化物系耐火物にはJIS R 2251-3の熱流法が適用されている。本規格が制定された当時、当該材料を対象にした市販の熱伝導率試験装置が複数の企業で使用されていた状況を踏まえ、本測定装置の構成を骨子とした規格が立案された<sup>1)</sup>。

2007年の規格制定から10年ほどが経過しているが、本測定装置自体の稼働期間は長く、当社では30年を超えている。現在、メーカーは本測定装置の製造から撤退し、また、修理部品の供給も行っていない。装置の故障は当該JISによる熱伝導率測定が不可能な状態に陥ることを意味する。このような状況は、当社だけでなく、多くの日本の耐火物メーカーに関係する事態である。さらに、JIS R 2251-3の熱流法には前記以外に技術的な課題がいくつかある<sup>2)</sup>。そのうち大きな課題と考えられるのは、測定温度範囲がおおよそ300～700℃と限定されること、および測定温度が一定間隔で離れた2点の平均温度であることである。これらの課題を解決することは熱流法ではほぼ不可能であると考えられる。

そこで、当社では、測定温度範囲が広く、任意温度での測定が可能なレーザーフラッシュ法（以下、LF法と記載する）を熱流法の代替として検討することにした。従来、LF法は、試料サイズが小さいために、大きな粒径を有した不均質な組織を示す耐火物のような試料には不向きとされてきた。しかし、近年は、比較的サイズの大きな試料も測定できるようになっている。本検討でも、サイズの大きい試料が使用できる装置を用いた。本報告では、各種非酸化物系耐火物へのLF法の適用結果を示すとともに、測定によって明らかになってきた課題を情報として提供する。

## 2. LF法の測定原理

MgO-Cれんが、浸漬ノズルに代表される非酸化物系耐火物は電気伝導性、高熱伝導性の特性を示す。このような特性を考慮して制定されたのが

oxide refractory materials is often specified in the case of construction of iron making facilities, measurements based on the above two standards are carried out.

On the other hand, JIS R 2251-3, which is based on the stationary heat flow method, is applied for non-oxide refractory materials such as carbon and silicon carbide which exhibit electrical conductivity. The standard was created based on the configuration of a commercial measuring apparatus that is available for those materials, because several companies had used the apparatus of the same type at the time of the enactment<sup>1)</sup>.

It has been about a decade since the enactment of the standard in 2007. The measuring apparatus has been in use for a long period of time, for example, over 30 years in our company. At present, there are no manufacturers producing a measuring apparatus and there are not any suppliers for the repair-parts. If the measuring apparatus has a problem, thermal conductivity cannot be determined in accordance with this standard. The current situation is as true at our company as any other company in Japan. In addition to the above-mentioned fact<sup>2)</sup>, JIS R 2251-3, based on the stationary heat flow method, has some technical problems. The two major issues are that the measurement temperature is limited to the range of about 300℃ to 700℃, and that the measuring temperature of the thermal conductivity is indicated by the average of two temperature data, which are measured in each pair of thermocouples located at a fixed interval in a test specimen. It is thought that the stationary heat flow method cannot solve those issues.

Accordingly, we have studied the Laser flash method-hereafter, referred to as the LF method-which can measure at any temperature in a wide temperature range as an alternative to the stationary heat flow method. The previous LF method could not be applied to refractory materials containing large particles and inhomogeneous texture because of the small size of the

定常熱伝導方程式に基づいたJIS R2251-3の熱流法である。一方、LF法は非定常熱伝導方程式に基づいている。本検討では、ファインセラミックスに適用される規格JIS R 1611を参考にした<sup>3)</sup>。使用装置はNETZSCH社LFA457である。本装置は、 $\phi 25.4\text{mm}$ の全域に熱源であるフラッシュ光を照射でき、熱流法の $\phi 20\text{mm}$ と遜色のない加熱範囲になっている。すなわち、現在のLF法装置は粗粒のある耐火物にも適用可能になってきたと言える。以下にLF法の原理を概説する。

熱拡散率 $\alpha$ を(1)式のハーフタイム法によって求め、同時に得られる(2)式の熱容量 $C$ とJIS R 2205に準拠して得られた試料の密度 $\rho$ から(3)式にしたがい熱伝導率 $\lambda$ を求めた。

$$\alpha = 0.1388 \cdot k \cdot d^2 / t_{0.5} \dots\dots\dots (1)$$

$$C = (\Delta T_{\text{ext}}^{\text{ref}} / \Delta T_{\text{ext}}^{\text{sam}}) \cdot F(Q, \rho, d, D_{\text{orifice}}) \cdot C^{\text{ref}} \dots\dots (2)$$

$$\lambda = \alpha \cdot \rho \cdot C \dots\dots\dots (3)$$

ここで、 $k$ ：熱損失の補正係数、 $d$ ：試料厚み、 $t_{0.5}$ ：ハーフタイム、 $\Delta T_{\text{ext}}$ ：試料をパルス加熱したときの断熱温度上昇 (Fig.1の外挿値)、 $Q$ ：試料表面で吸収されたフラッシュ光のエネルギー、 $D_{\text{orifice}}$ ：オリフィス内径、 $F(\ )$ ： $Q, \rho, d, D_{\text{orifice}}$ の関数、 $\text{sam}$ ：測定試料、 $\text{ref}$ ：参照試料 (黒鉛, アルミナ)、 $C^{\text{ref}}$ ：参照試料の熱容量である。

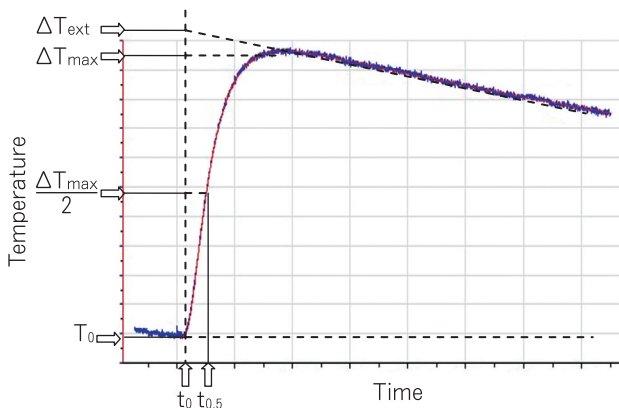


Fig.1 Temperature elevation curve measured by laser flash method.

test specimens measured. However, the recent apparatus, which is based on the LF method, can measure a test specimen of comparatively large size. Therefore, in the present study, we used an apparatus which could measure a test specimen of large size. This report provides the results for the LF method, which was applied to various types of non-oxide refractory materials, and explains new problems which were revealed by the measuring.

## 2. Principal of the LF Method

Non-oxide refractory materials which are exemplified by MgO-C bricks and submerged entry nozzles have a highly electro-conductive property and a highly thermo-conductive property. JIS R 2251-3, based on the stationary heat flow method, depends on the equation of steady state heat conduction while taking such properties into consideration. However, the LF method depends on the equation of non-steady state heat conduction. In the present study, we used JIS R 2205 which was applied to fine ceramics as reference<sup>3)</sup>. The apparatus used was a product of the model number LFA457 made by NETZSCH GmbH. The heating area of the apparatus, in which the laser flash, a short energy pulse of the heat source, is radiated on the whole area of a 25.4mm diameter test specimen, can reach levels comparable to that of the stationary heat flow method using a 20mm diameter test specimen. Accordingly, the current LF method apparatus may be applicable to refractory materials containing coarse grains. The principal of the LF method is summarized as follows. Thermal conductivity  $\lambda$  is obtained by substituting thermal diffusivity  $\alpha$  of equation (1) using the half time method, specific heat capacity  $C$  of equation (2) measured at the same time and sample density  $\rho$  conforming to JIS R 2205 into equation (3).

$$\alpha = 0.1388 \cdot k \cdot d^2 / t_{0.5} \dots\dots\dots (1)$$

$$C = (\Delta T_{\text{ext}}^{\text{ref}} / \Delta T_{\text{ext}}^{\text{sam}}) \cdot F(Q, \rho, d, D_{\text{orifice}}) \cdot C^{\text{ref}} \dots\dots (2)$$

$$\lambda = \alpha \cdot \rho \cdot C \dots\dots\dots (3)$$

Fig.1は今回の測定で得られた温度上昇曲線の一例である。試料の表面にフラッシュ光を照射したときの背面で観測される上昇温度を表している。今回の一連の測定で得られた温度上昇曲線はいずれも熱損失を考慮したCowanの理論曲線によくフィットしていた。したがって、(1)式の熱損失補正係数は、Cowanモデルにもとづいて得られる数値を用いた。

Where,  $k$  is the correction coefficient to correct the heat loss,  $d$  is the thickness of the test specimen,  $t_{0.5}$  is time value at the half temperature height,  $\Delta T_{\text{ext}}$  is the adiabatic temperature rise value at the time of pulse heating which is the extrapolated value shown in Fig.1,  $Q$  is the energy of the laser flash beam which is absorbed on the surface of the test specimen,  $D_{\text{orifice}}$  is the internal diameter of the orifice,  $F()$  is a function of  $Q$ ,  $\rho$ ,  $d$  and  $D_{\text{orifice}}$ ,  $\text{sam}$  is the

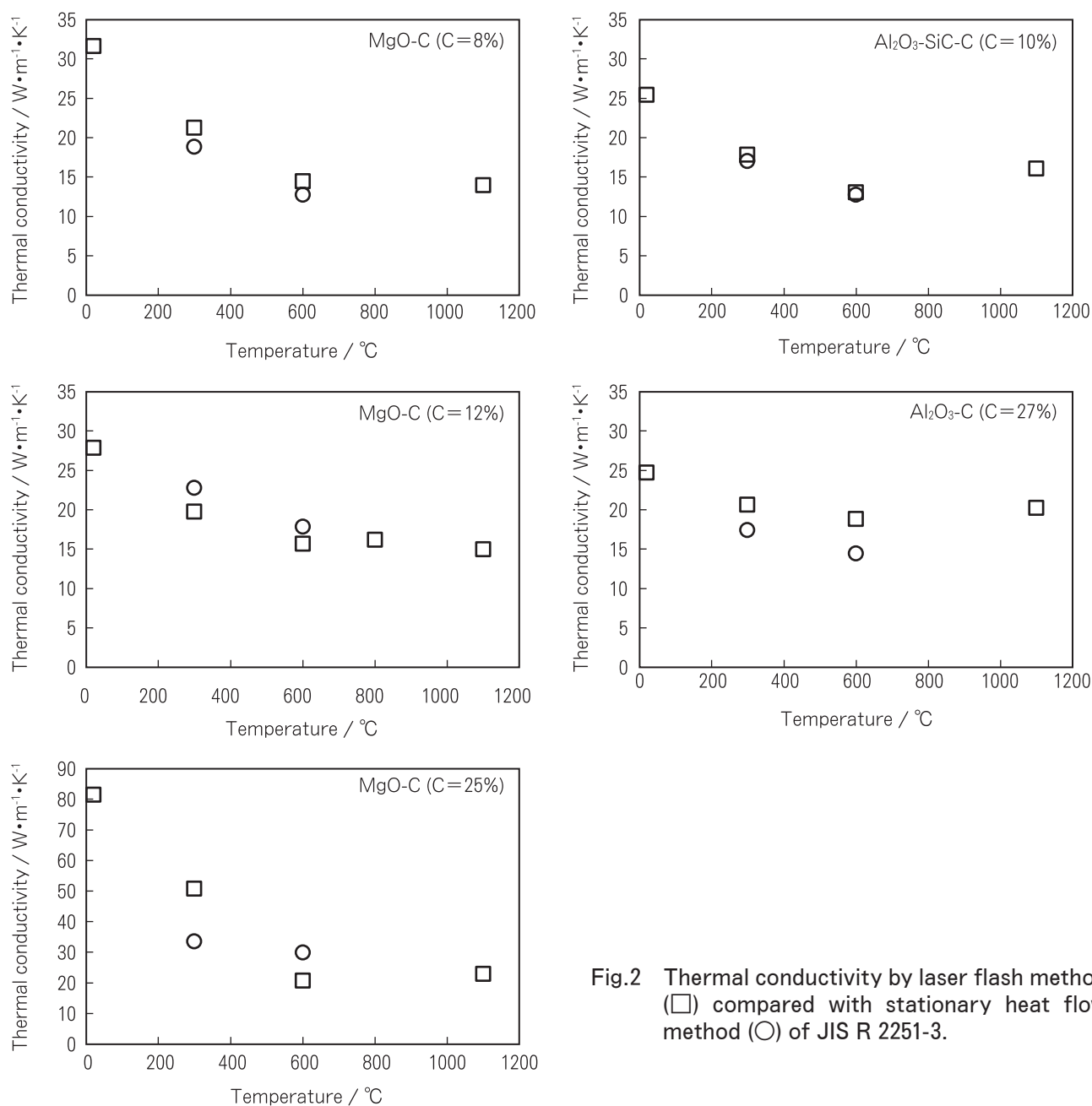


Fig.2 Thermal conductivity by laser flash method (□) compared with stationary heat flow method (○) of JIS R 2251-3.

### 3. LF法の評価結果

#### 3. 1 LF法と熱流法の比較

LF法を用いた非酸化物系耐火物の測定例は数少ないが、C=15%のMgO-Cれんがの測定で、熱流法と遜色ない結果を示した例がある<sup>4)</sup>。そこで、両方法から得られる結果を、非酸化物系耐火物の種類（Fig.2参照）を広く変えて比較してみた。

熱流法では $\phi 20 \times H150$ mm、LF法では $\phi 25.4 \times H5$ mmの試料を用いて測定を行った。Fig.2に示すように、両者が大きく異なることはなく、ほぼ同等になった。

#### 3. 2 LF法における試料厚みの影響

熱流法とLF法の試料の径方向サイズはほぼ同等になったが、厚み方向には依然として違いが生じている。熱流法に比べLF法に用いる試料の厚みは薄い。また、(1),(3)式から分かるように、厚みの2乗で熱伝導率に効いているので、厚みの影響が出やすいと考えられる。そこで、LF法での試料厚みの影響を調べることにした。試料数Nを5、試料厚みを3mmと5mmにした場合のLF法による測定を行った。用いた試料の特徴をTable 1に、また、測定に供した試験片の外観の一例をFig.3に示す。材質および粒度構成の異なる5種の試料である。測定はTable 2に示す条件で行った。測定温度は300, 500, 700, 900, 1100℃の5水準である。比熱のデータを得るための標準物質に黒鉛とアルミナを選定した。

Table 1 Outline of samples applied for measurement shown in Figs.3 and 4

| Sample name                                         | Quantity of main component                                       | Bulk density /g・cm <sup>-3</sup> |
|-----------------------------------------------------|------------------------------------------------------------------|----------------------------------|
| Al <sub>2</sub> O <sub>3</sub> -SiC-C               | Al <sub>2</sub> O <sub>3</sub> =80%, SiC=5%, C=15%               | 3.35                             |
| MgO-C No.1                                          | MgO=85%, C=5%                                                    | 3.35                             |
| MgO-C No.2                                          | MgO=80%, C=15%                                                   | 3.19                             |
| ZrO <sub>2</sub> -C                                 | ZrO <sub>2</sub> =80%, C=15%                                     | 4.63                             |
| Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> -C | Al <sub>2</sub> O <sub>3</sub> =80%, ZrO <sub>2</sub> =10%, C=5% | 3.54                             |

measured sample, ref is the reference sample such as carbon and alumina, and  $C^{\text{ref}}$  is the specific heat capacity of the reference sample.

An example of temperature elevation curves obtained in this study is shown in Fig.1. It represents a rising temperature observed on the back surface of a test specimen, when the front surface of the test specimen was irradiated with the laser flash. Each temperature elevation curve which was obtained by a series of our measurements was fitted well to Cowan's theoretical curve taking heat loss into consideration. Accordingly, the correction coefficient of heat loss in equation (1) was a numerical value which was obtained based on Cowan's model.

### 3. Evaluation of LF Method

#### 3. 1 Comparison of thermal conductivity by LF method and stationary heat flow method

There isn't much literature in which non-oxide refractory materials have been measured by the LF method. However, it was reported that the 15% carbon containing MgO-C bricks of which the thermal conductivities were obtained by the LF method were almost the same as those obtained by the stationary heat flow method<sup>4)</sup>. Thus, in this study, results of both methods were compared by evaluating many types of non-oxide refractory materials, as shown in Fig.2.

The test specimen size provided for measurement by the stationary heat flow method was  $\phi 20 \times H150$ mm and that for the LF method was  $\phi 25.4 \times H5$ mm. As shown in Fig.2, the results of both methods were not greatly different from each other and almost the same.

#### 3. 2 Influence of thickness of the test specimen in the LF method

The radial direction size in the LF method came to almost the same as that in the stationary heat flow method. However, a difference of size in the thickness direction remained. The thickness of the LF method test specimen was thinner than that of the stationary heat flow

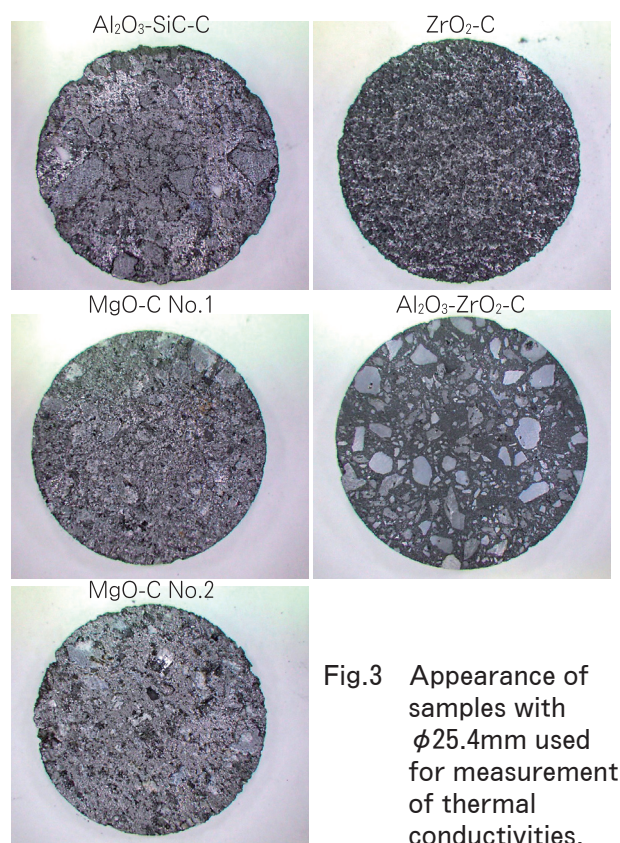


Fig.3 Appearance of samples with  $\phi 25.4\text{mm}$  used for measurement of thermal conductivities.

Table 2 Measurement conditions

|                                                           |                                                   |
|-----------------------------------------------------------|---------------------------------------------------|
| Measurement temperature/ $^{\circ}\text{C}$               | 300, 500, 700, 900 and 1100                       |
| Number of repeating measurement                           | 6                                                 |
| Heating-up speed / $^{\circ}\text{C}\cdot\text{min}^{-1}$ | 10                                                |
| Atmosphere                                                | Argon                                             |
| Standard materials                                        | Graphite, Alumina                                 |
| Sample size                                               | $\phi 25.4 \times 3 \text{ mm}$ or $5 \text{ mm}$ |

Fig.4に熱伝導率の測定結果を示す。得られた結果をもとに、試料厚みの違いに関する統計的な有意差検定を行った。Table 3に示すように、いくつかの試料、測定温度で有意差が認められたが、多くのケースで有意差はないことがわかった。

#### 4. LF法の適用と課題

近年、低熱伝導性炭素含有耐火物などが開発され、実炉で実績をあげている<sup>5),6)</sup>。一方、開発した低熱伝導性炭素含有耐火物を事前に評価するには、熱伝導率のデータが必要である。しかし、前

method test specimen. In addition, thermal conductivity data obtained by the LF method is susceptible to the thickness of the test specimen, because they are affected by the second power of thickness, as shown in equation (1) and (3). Thus, the influence of the thickness of the test specimen in the LF method was studied. 5 samples, having the thickness of 3mm or 5mm, were subjected to the thermal conductivity measurement at various temperatures by the LF method. The features of the samples are shown in Table 1 and the appearances of samples used for measurement are shown in Fig.3. 5 types of samples which were different from each other in materials and grain size configurations were used. The measurements were conducted under the condition shown in Table 2. The samples were measured at a temperature of 300, 500, 700, 900 and 1000 $^{\circ}\text{C}$ . Graphite and alumina were selected as standard materials to obtain the specific heat capacity of the measured samples.

The results of thermal conductivity measurements are shown in Fig.4. The verification of whether there was a significant difference between test specimen thickness results was statistically performed using acquired data. As shown in Table 3, no significant difference was recognized in many cases, although it was recognized for several samples and at several temperatures.

#### 4. Applications and Issues of the LF Method

In recent years, low-thermal-conductive carbon-containing refractory materials which were developed have shown good results in the actual furnace<sup>5),6)</sup>. On the other hand, thermal conductivity data was needed to previously evaluate the effect of low-thermal-conductive carbon-containing refractory materials before actual use. However, as mentioned above, data by the stationary heat flow method of JIS R 2251-3 were obtained at temperatures of no more than about 700 $^{\circ}\text{C}$ . Therefore, developed products must be evaluated by using thermal

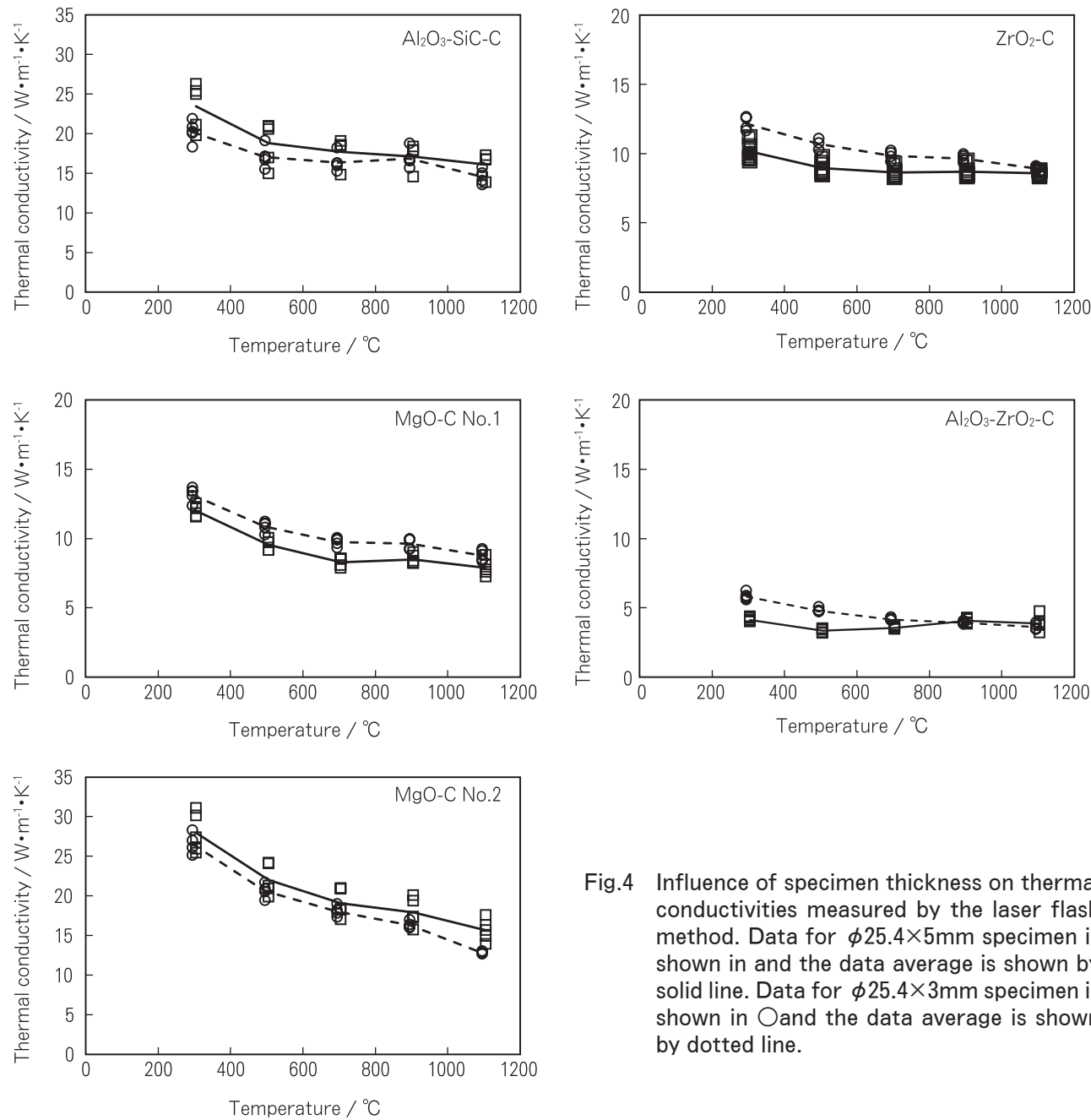


Fig.4 Influence of specimen thickness on thermal conductivities measured by the laser flash method. Data for  $\phi 25.4 \times 5 \text{ mm}$  specimen is shown in  $\square$  and the data average is shown by solid line. Data for  $\phi 25.4 \times 3 \text{ mm}$  specimen is shown in  $\bigcirc$  and the data average is shown by dotted line.

Table 3 Statistical verification of whether the test specimen of  $\phi 25.4 \times 3 \text{ mm}$  is significantly different from that of  $\phi 25.4 \times 5 \text{ mm}$

|                                                     | 300℃ | 500℃ | 700℃ | 900℃ | 1100℃ |
|-----------------------------------------------------|------|------|------|------|-------|
| Al <sub>2</sub> O <sub>3</sub> -SiC-C               | ○    | ○    | ○    | ○    | ○     |
| MgO-C No.1                                          | ×    | ×    | ×    | ×    | ×     |
| MgO-C No.2                                          | ○    | ○    | ○    | ○    | ○     |
| ZrO <sub>2</sub> -C                                 | ×    | ○    | ○    | ○    | ○     |
| Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> -C | ×    | ×    | ×    | ○    | ○     |

× : Significant difference, ○ : Not significant difference

conductivity data measured at a low temperature, or by using values at high temperatures extrapolated from a curve fitted to data points in the low temperature range for heat transfer analysis. That was why the LF method is becoming increasingly important.

As shown in Fig.2, results by the LF method were not greatly different from those by the stationary heat flow method while little deviations were recognized. On this issue, it should be noted that results obtained by the stationary

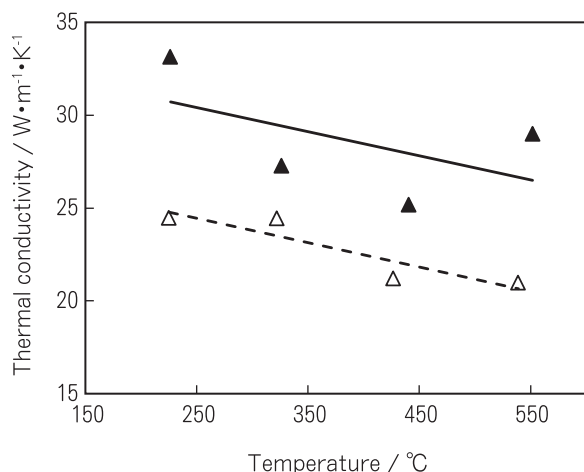


Fig.5 Thermal conductivity of MgO-C bricks measured by stationary heat flow method based on JIS R 2251-3.

Solid line is simple expression obtained from data shown in ▲ for samples with 25% carbon content. The dotted line is simple expression obtained from data shown in △ for samples with 12% carbon content.

述したように、JIS R 2251-3熱流法では、せいぜい700℃までのデータしか得られないので、開発品は低温度における熱伝導率を用いて評価されるか、または、伝熱解析を行う場合には、高温域に外挿した推定データを用いて評価されるしかなかった。そのような点でも、LF法の適用は重要性を増していると言える。

Fig.2に示したように、LF法の結果と熱流法の結果には多少の差はあるものの大差はなかった。ここで、熱流法の結果が真の値として正しい結果を示しているとは言い切れないことに注意したい。JIS R 2251-3には制定の経緯が記されているが、ステンレスを用いた共同実験によって熱流法を評価している。しかし、現実の耐火物を用いた結果については報告されていない。この点から見ると、現段階では、どちらがより正しい結果とは言えないようだ。

いずれの測定においても試料の厚み方向に1次元に熱を流すことがポイントになるが、熱流法ではH150mmの長さに渡って1次元熱流にする

heat flow method are not necessarily the true value. According to the explanation on how the standard of JIS R 2251-3 was established, the stationary heat flow method was evaluated by round robin test using a sample of stainless steel. However, results about refractory materials have not been reported. For this reason, currently, we cannot explain which method provides data closer to a true value.

It is important for both methods that the one-dimensional heat flow is made along the thickness direction of a test specimen. The heat flow by the stationary heat flow method must be one-dimensional along the entire length of the H150mm thickness. Hence, the stationary heat flow method requires sophisticated measuring techniques. In addition, as a temperature gradient is produced along the thickness direction in the stationary heat flow method, the thermal conductivity data is reported at mean temperatures between each pair of thermocouples located at 18mm intervals on the test specimen. Therefore, strictly speaking, the thermal conductivity of the  $\phi 20 \times H18$ mm test specimen is measured. When those measurement conditions are taken into consideration, the stationary heat flow method is not necessarily suitable. An example of the measurement result which was obtained by the stationary heat flow method is shown in Fig.5. In JIS R 2251-3, as the measurement result –thermal conductivity– is recommended to be defined by a linear expression of temperature, the result at an arbitrary temperature which is in the temperature measuring range is calculated from the linear expression. As shown in Fig. 5, it was found that data for the 12% carbon content sample almost fit the linear expression and those for the 25% carbon content sample, of which the accuracy was questionable, did not fit it. In consideration of this, the LF method can be effective, because it can measure at temperatures ranging from low-temperature regions such as room temperature to high-temperature regions by simple operation. Thermal conductivity measurement

必要がある。熱流法には高度な測定技術が求められる。また、熱流法では、試料の厚み方向に温度差を生じさせ、その途中に18mm間隔で熱電対を設置し、熱電対間の平均熱伝導率を測定する。したがって、実質的には $\phi 20 \times H18\text{mm}$ の試料の測定になっている。これらの測定条件を考慮したとき、必ずしも熱流法が良いとも言い切れない。Fig.5は熱流法による測定結果例である。JIS R 2251-3では、測定結果を温度に対して1次式で表すことが推奨され、得られた1次式から測定温度範囲内の任意温度での結果を算出している。Fig.5に示すように、ほぼ1次式で表してよいケースもあるが、1次式で表すことの妥当性が疑われるケースもあることが分かる。このような点を考慮すると、簡便でしかも高温まで測定できるLF法によってN数を増やして測定することも一つの方法と考えられる。

次に、LF法における試料厚みの影響については、今回の検討範囲では、ほとんどの試料で有意差が無い結果になった。ここで、さらに詳しく調べて見た。3mm厚みの試料と5mm厚みの試料で得られた結果についてのばらつきを調べた。

Table 4に示すように、全体的にばらつきは小さいことがわかった。Fig.3に見られるように、粗粒が散見されるが、このような試料においてもばらつきが小さいことから、LF法はある程度の確度を持って非酸化物系耐火物の熱伝導率測定に使用できると言える。

ところで、Table 4から、測定温度が高くなるほどばらつきが大きくなる傾向を示し、また、5mm厚み試料の方が3mm厚み試料よりもばらつきが大きくなっていることもわかった。厚みが厚いほど1次元的な熱流が得られにくくなるものと推定されるので、それだけばらつきも大きくなるのだろう。一方、試料厚みを薄くすると、組織の不均質性の影響を受けやすくなるとともに、そもそも厚みを薄くした試験片は加工が難しく作り難い。したがって、供試試料の厚みにはある程度適切な

by increasing the number of samples further improves reliability of the LF method.

Whether or not the thickness of test specimens affected the thermal conductivity data obtained with the LF method was studied. As a result, a significant difference was not recognized in many cases within the scope of this study. However, the variability of results for samples with the thickness of 3mm and 5mm was examined in detail.

As shown in Table 4, the degree of thermal conductivity data variation was small. Though coarse grains often appeared in Fig.3, it can be said that the LF method was applicable to the thermal conductivity measurement of non-oxide refractory materials within a certain degree of accuracy.

As shown in Table 4, it was found that the thermal conductivity had a tendency of a higher degree of variation with elevating temperature, and that the degree of variation of samples with a thickness of 5mm became higher than that of samples with a thickness of 3mm. The latter is explainable as follows; the thicker the thickness of test specimens is, the more difficult the achievement of the one-dimensional heat flow becomes and the higher the degree of variation of data may be. However, when the thickness of the test specimen is made thinner, results are easily affected by the inhomogeneous texture of the samples. In addition, machining of the test specimen of which the thickness is made thin is difficult. In other words, the appropriate thickness of test specimens may be in a certain range. In light of the data, the test specimen with the thickness of 5mm is applied for the LF method as the standard in our company. A further study should be conducted on various non-oxide refractory materials in this regard.

## 5. Conclusion

The thermal conductivity of non-oxide refractory materials was studied in order to substitute the LF method for the stationary heat flow method.

**Table 4 Standard deviation ( $2\sigma$ ) of thermal conductivity obtained by 6 measuring times for a sample at each temperature**

| Materials                                           | Specimen size   | $\phi$ 25.4 and 3mm in thickness                                 |   |           | $\phi$ 25.4 and 5mm in thickness                                 |   |           |
|-----------------------------------------------------|-----------------|------------------------------------------------------------------|---|-----------|------------------------------------------------------------------|---|-----------|
|                                                     | Temperature /°C | Average thermal conductivity /W·m <sup>-1</sup> ·K <sup>-1</sup> |   | $2\sigma$ | Average thermal conductivity /W·m <sup>-1</sup> ·K <sup>-1</sup> |   | $2\sigma$ |
| Al <sub>2</sub> O <sub>3</sub> -SiC-C               | 300             | 20.23                                                            | ± | 0.14      | 23.47                                                            | ± | 0.20      |
|                                                     | 500             | 17.06                                                            | ± | 0.16      | 18.83                                                            | ± | 0.34      |
|                                                     | 700             | 16.36                                                            | ± | 0.18      | 17.69                                                            | ± | 0.30      |
|                                                     | 900             | 16.88                                                            | ± | 0.37      | 17.13                                                            | ± | 0.85      |
|                                                     | 1100            | 14.57                                                            | ± | 1.02      | 16.12                                                            | ± | 2.20      |
| MgO-C No.1                                          | 300             | 13.15                                                            | ± | 0.09      | 12.00                                                            | ± | 0.21      |
|                                                     | 500             | 10.85                                                            | ± | 0.06      | 9.54                                                             | ± | 0.40      |
|                                                     | 700             | 9.74                                                             | ± | 0.13      | 8.28                                                             | ± | 0.26      |
|                                                     | 900             | 9.63                                                             | ± | 0.28      | 8.49                                                             | ± | 0.60      |
|                                                     | 1100            | 8.78                                                             | ± | 0.74      | 7.89                                                             | ± | 1.42      |
| MgO-C No.2                                          | 300             | 27.96                                                            | ± | 0.31      | 27.95                                                            | ± | 0.23      |
|                                                     | 500             | 21.65                                                            | ± | 0.28      | 22.02                                                            | ± | 0.18      |
|                                                     | 700             | 18.98                                                            | ± | 0.37      | 19.06                                                            | ± | 0.33      |
|                                                     | 900             | 17.28                                                            | ± | 0.55      | 17.92                                                            | ± | 0.79      |
|                                                     | 1100            | 13.53                                                            | ± | 0.91      | 15.63                                                            | ± | 2.26      |
| ZrO <sub>2</sub> -C                                 | 300             | 11.84                                                            | ± | 0.05      | 10.16                                                            | ± | 0.27      |
|                                                     | 500             | 10.10                                                            | ± | 0.07      | 8.96                                                             | ± | 0.29      |
|                                                     | 700             | 9.83                                                             | ± | 0.11      | 8.62                                                             | ± | 0.15      |
|                                                     | 900             | 9.63                                                             | ± | 0.12      | 8.68                                                             | ± | 0.38      |
|                                                     | 1100            | 8.92                                                             | ± | 0.27      | 8.59                                                             | ± | 0.78      |
| Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> -C | 300             | 5.80                                                             | ± | 0.17      | 4.13                                                             | ± | 0.33      |
|                                                     | 500             | 4.80                                                             | ± | 0.19      | 3.35                                                             | ± | 0.32      |
|                                                     | 700             | 4.16                                                             | ± | 0.13      | 3.57                                                             | ± | 0.28      |
|                                                     | 900             | 3.92                                                             | ± | 0.15      | 4.08                                                             | ± | 1.10      |
|                                                     | 1100            | 3.60                                                             | ± | 0.47      | 3.87                                                             | ± | 2.05      |

範囲があるものと考えられる。今回の結果から、当社では5 mm厚みを標準としている。ただし、今後種々の非酸化物系耐火物について、さらに検討していく必要があると考えられる。

## 5. おわりに

非酸化物系耐火物の熱伝導率測定に用いられる熱流法の代替を意図して、LF法による熱伝導率測定を検討した。

熱流法は真の値として正しい結果を与えるものではないが、LF法によって熱流法を代替できる可能性が得られた。LF法には、熱流法では測定できない高温での測定が可能であり、熱流法が平均

Results obtained by the stationary heat flow method were not necessarily true value. However the LF method is a capable of replacing the stationary heat flow method. The LF method has the following merits. Measurements at high temperature can be conducted by the LF method, while it is impossible by the stationary heat flow method. The LF method gives the thermal conductivity measured at an optional temperature, although the stationary heat flow method provides that at mean temperatures between each pair of thermocouples.

In the future, a further study should be conducted by the LF method on the thermal conductivity of various non-oxide refractory

温度で測定するのに対して任意の指定温度での測定ができるなど、特長があることもわかった。

今後はさらにいろいろな非酸化物系耐火物の熱伝導率をLF法によって測定し、LF法の適用範囲を決め、JIS化を図ることが課題になると考えられた。

materials. The scope of the LF method for non-oxide refractory materials should be researched for the purpose of standardization.

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