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Thermal Diffusivity Measurements of Refractory Metals as Candidate Reference Materials by the Laser Flash Method[1]

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A working group for standardization has organized to establish the Japanese Industrial Standard (JIS) for thermal diffusivity measurements of metals in the temperature range of 300–1700 K by the laser flash method. As candidate reference materials with high purity, high-temperature stability, and easy-to-get on a commercial basis, tantalum, niobium, and molybdenum have been selected. Thermal diffusivity values of the specimens, cut out of these materials, have been measured independently by members of the working group. Comparisons of results have been performed for different high-temperature stabilities, repeatabilities, and manufacturers, as well as by different members. Comparisons show that the measured values agree within 10% for different specimens by different institutions, and no systematic differences have been observed for materials from different manufacturers. The measured results for molybdenum specimens agree well with the recommended values of thermal

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diffusivity of matter from the TPRC data series, and the high-temperature stability is found to be the best. The results for tantalum and niobium, however, show significant differences with those of the TPRC data series in the high-temperature range, and some further study on the stability of these materials is needed for recommending these values. As a result, molybdenum can be recommended as a reference material for practical use of the laser flash method.

KEY WORDS: candidate reference materials; laser flash method; molybdenum; niobium; refractory metals; tantalum; thermal diffusivity.

1. INTRODUCTION

The thermal diffusivity of metals in the room- to high-temperature range is usually measured by the laser flash method. A working group for standardization has been organized since 1998 to establish the Japanese Industrial Standard (JIS) for thermal diffusivity measurements of metals by the laser flash method [1].

The laser flash method can be used to determine the absolute value of thermal diffusivity. For establishing the first standard of thermal diffusivity, the National Metrology Institute of Japan has improved some key techniques in the measurement, and developed a standard instrument for the laser flash method [2]. On the other hand, some industrial standards such as the JIS have given recommendations on specifications and performance of practical instruments for general users [3].

The standard and practical instruments can generally be classified as shown in Fig. 1. The standard one can provide accurate absolute values but is difficult to handle because the candidate specimen is restricted, while the practical one can only provide relative measurement values but is easy to handle for different candidates. The aim of the industrial standard is to provide a standard reference material of thermal diffusivity and a recommended material, by which the standard instrument and the practical one can be connected. Then the practical instrument will maintain its advantages while providing traceability to absolute values and an evaluation of the uncertainty.

In this work, the thermal diffusivities of selected candidate reference materials (tantalum, niobium, and molybdenum) using the laser flash method have been measured independently by members of the working group. Comparisons of the results are performed for different high-temperature stabilities, repeatabilities, and manufacturers. Comparisons are also made with the recommended values of the Thermophysical Properties of Matter from the TPRC data series, to assist with selecting candidates for thermal diffusivity reference materials [7].

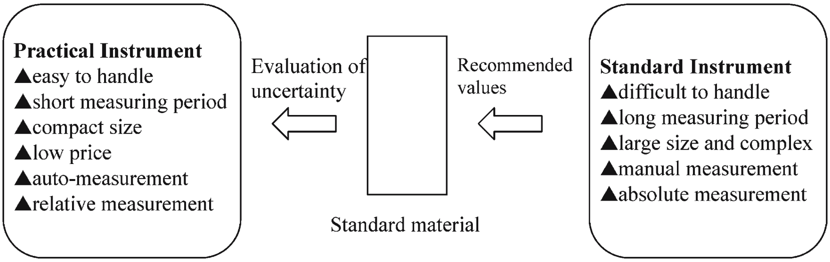

Fig. 1. Relationship of the standard and practical instruments.

2. EXISTING STANDARD REFERENCE MATERIALS

Until now, the standard reference material of thermal diffusivity provided by Japanese public organizations is only one kind, which is Alumina TD-AL from the Japan Fine Ceramics Center [4]. As standard reference metallic materials, the National Institute of Standards and Technology of USA provides electrolysis iron RM 8420 and 8421, with only thermal conductivity, but no reference data for the thermal diffusivity are provided [5]. The Committee on Data for Science and Technology has published recommended standard data of pure metals, such as Cu and Al, which are independent of manufacturer [6]. The National Metrology Institute of Japan has been working on the evaluation of carbon, which does not need a coated black layer on the surface during measurements.

The current working group has selected three kinds of metals, tantalum, niobium, and molybdenum, as candidate standard reference materials of thermal diffusivity, and measurements of thermal diffusivity have been carried out independently by the members of the group.

3. CANDIDATE STANDARD REFERENCE MATERIALS OF THERMAL DIFFUSIVITY

Following the development of measuring techniques for the thermal diffusivity of metals, we have been attempting to develop standard reference materials of thermal diffusivity. Three kinds of high-temperature metals, tantalum, niobium, and molybdenum, are selected and obtained from the Nilaco Co. and Good Fellow Co., Ltd. The specimens are in the shape of disks with a diameter of 10 mm. For determining the system error, three kinds of materials are divided into four kinds of specimens with thicknesses of 1.0, 1.4, 2.0, and 2.8 mm; this is defined as one specimen group. Eight groups, named A-, B-, C-, D-, E-, F-, G-, and H-Lab, have been assembled and distributed to the member institutions of the working group. Six institutes carried out the measurements; (1) Ibaraki University; B-Lab, (2) Japan Fine Ceramics Center; C-Lab, (3) Kyote Electronic Industry; D-Lab, (4) Ulvac-Riko Inc.; E-Lab, (5) Japan Ultra-high Temperature Materials Research Institute; G-Lab, and (6) Toray Research Center Inc.; H-Lab.

4. STABILITY OF THE SPECIMENS

For measuring the thermal diffusivity at high temperature, the stability of the specimens has to be taken into account. Especially for the standard reference materials, it is necessary that their thermal diffusivity is stable at high temperature. Two members of the working groups (B- and C-Lab) have tested the stability of the selected standard reference metals, tantalum, niobium, and molybdenum, by comparing the specimens' masses, thicknesses, and thermal diffusivity before and after a temperature rise up to 1700 K. The experimental results of both institutions are almost the same. The results measured by C-Lab are shown in Table I for mass, Table II for thickness, and Table III for thermal diffusivity at room temperature.

These experiments were combined with the thermal diffusivity measurements, so the histories of temperature changes of the stability test in the vacuum furnace were the same as the measuring process of the thermal diffusivity measurements. The thermal diffusivities were measured at four temperatures (300, 1100, 1400, and 1700 K) between room temperature and 1700 K. The heating rate from one temperature to the next was 8 K per minute, and at the measured temperature, the temperature was kept constant for 1.5–2.0 h. The cooling rate from 1700 K to room temperature was about 10 K per minute. So it took about 12 h for measurements for one specimen.

Table I. Measured Masses Before and After Temperature Rise

		Mass (g)		Difference	
Provider	Material	Before temperature rise	After temperature rise	(g)	(%)
Nilaco	Ta	2.5637	2.5638	0.0001	0.00
	Nb	1.2936	1.2949	0.0013	0.10
	Mo	1.6201	1.6204	0.0003	0.02
GF	Ta	2.5259	2.5261	0.0002	0.01
	Mo	1.5995	1.5997	0.0002	0.01

Table II. Measured Thicknesses Before and After Temperature Rise

		Thickness (mm)		Difference	
Provider	Material	Before temperature rise	After temperature rise	(mm)	(%)
Nilaco	Ta	1.965	1.966	0.001	0.05
	Nb	1.929	1.933	0.004	0.21
	Mo	2.006	2.011	0.005	0.25
GF	Ta	1.934	1.933	−0.001	−0.05
	Mo	2.005	2.010	0.005	0.25

Table III. Measured Thermal Diffusivities Before and After Temperature Rise

		Thermal diffusivity ($10^{-4}m^2 \cdot s^{-1}$)		Difference	
Provider	Material	Before temperature rise	After temperature rise	($10^{-5}m^2 \cdot s^{-1}$)	(%)
Nilaco	Ta	0.241	0.237	−0.04	−1.66
	Nb	0.228	0.215	−0.13	−5.70
	Mo	0.536	0.543	0.07	1.31
GF	Ta	0.247	0.237	−0.10	−4.05
	Mo	0.543	0.538	−0.05	−0.92

From the results for mass and thickness, it was observed that the mass of niobium increases, and the thicknesses of both niobium and molybdenum increase after the temperature rise. For niobium, the specimen does not show metallic luster on the surface after the high temperature rise, which indicates that a film formed on the surface. The increases of both mass and thickness are caused by this film. But for molybdenum, no film has been found on the surface, the reasons for the differences are not yet clear.

From the results for thermal diffusivity, it was observed that those of tantalum and niobium decrease after a high temperature rise. The change of the thermal diffusivity of tantalum after heating could be caused by the change in the orientation of the crystal. The differences in changes in thermal diffusivity after the high temperature rise for different suppliers resulted from differences in the manufacturing and processing methods. For niobium, the differences must be evaluated further with consideration of the reason for the film formation on the surface.

According to the above results, changes in the mass, thickness, and thermal diffusivity may occur because of heating to high temperatures. Therefore, the measured results were checked by comparing the values before and after the temperature rise. In addition, it is necessary to determine the temperature range over which the standard reference materials are stable.

5. COLLABORATIVE MEASUREMENTS FOR THERMAL DIFFUSIVITY

For evaluating the development of measuring instruments and techniques for thermal diffusivity measurements by the laser flash method, the measured results for fixed specimen thicknesses have been compared at different temperatures from room temperature to 1700 K. The collaborative measured results of the temperature dependences of the thermal diffusivity are shown in Figs. 2, 3, and 4 for tantalum, niobium, and molybdenum, respectively. In the figures the various symbols represent the measured data and are consistent with the participating institutions as mentioned in Section 3. Symbols of ⦿ and ◎ represent data measured by the B-Lab, ▣ and ⧈ by C-Lab, ⧫ by D-Lab, ● and ○ by E-Lab, ■ and □ by G-Lab, ▲ and △ by H-Lab. respectively. The solid (or filled) symbols represent data for the material supplied by the Nilaco Co., and the open symbols represent data for the material supplied by the Good Fellow Co. The solid lines represent recommended values from the TPRC Data Series, which are still considered as standard values from the 1970s [7].

Laser flash instruments of the participating institutions were obtained from different manufacturers, and the performances of the different instruments varied. The uncertainties of the different instruments are estimated to be within 5% .

When we compare the values measured by the participating institutions, it can be seen that the measured values agree within 10%, and no large differences in thermal diffusivity are found for different specimens by different institutions, and also no significant differences are observed for materials from two suppliers. When the measured values are compared with the recommended values of the TPRC data series, thermal diffusivity data for the molybdenum specimens agree well, while the results for tantalum and niobium in the high-temperature range show significant differences with those of the TPRC data series. These differences of the niobium data are more remarkable than those for tantalum at temperatures to 1700 K. These might be caused by the high-temperature stability

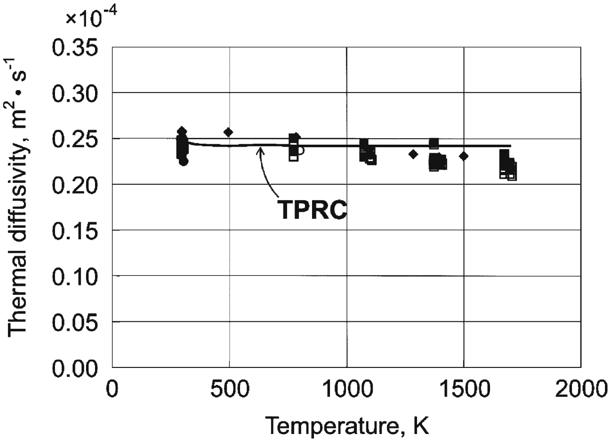

Fig. 2. Temperature dependence of the thermal diffusivity of tantalum: ⦿, ◎ B-Lab; ▣, ⧈ C-Lab; ◆ D-Lab; ●, ○ E-Lab; ■, □ G-Lab; ▲, △ H-Lab (solid/filled symb1ols—Nilaco Co; open symbols—Good Fellow).

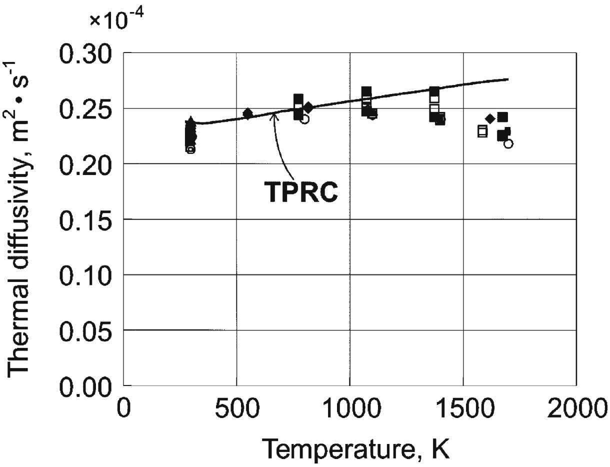

Fig. 3. Temperature dependence of the thermal diffusivity of niobium. (Symbols are the same as in Fig. 2.)

of the material. Some further measurements and study are needed for evaluating the values of tantalum and niobium at high temperatures.

The high-temperature stability of molybdenum is found to be the best. The results of the participating institutions show good agreement, and the differences between these values are much smaller than those

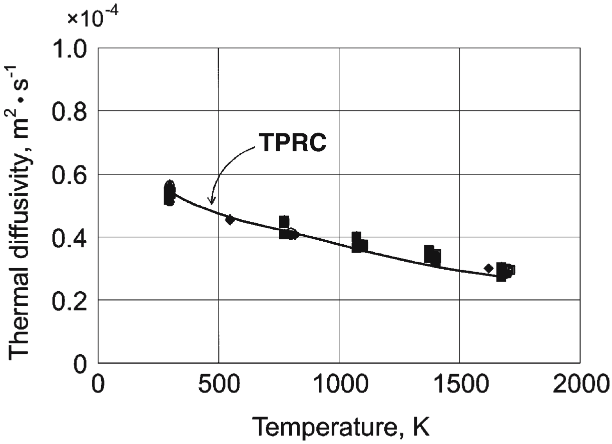

Fig. 4. Temperature dependence of the thermal diffusivity of molybdenum. (Symbols are the same as in Fig. 2.)

between these measured values and TPRC data. Therefore, molybdenum is recommended as a candidate for a thermal diffusivity reference material for practical use.

6. CONCLUSION

The high-temperature stability and thermal diffusivity of three standard metals, tantalum, niobium, and molybdenum, are examined in this work to evaluate their potential use as standard reference materials. According to the results for thermal diffusivity from the participating institutions, the measured values agreed well with one other for different specimens by different institutions, and no significant differences have been observed for materials from different suppliers. When the measured values are compared with the recommended values of the TPRC data, thermal diffusivity data for the molybdenum specimens agree well, while the results for tantalum and niobium in the high-temperature range show significant differences. This result may be caused by the high-temperature stability of the material. Some further measurements and analysis are needed for evaluating the values of tantalum and niobium at high temperatures.

The high-temperature stability of molybdenum is found to be the best. The thermal diffusivity data of the participating institutions show good agreement with one other and the TPRC data. Therefore, molybdenum is recommended as a candidate for a thermal diffusivity reference material for practical use.

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