THERMAL DIFFUSIVITY MEASUREMENTS OF REFRACTORY METALS AS CANDIDATE REFERENCE MATERIALS BY THE LASER FLASH METHOD[1]

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ABSTRACT

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 the candidate reference materials, those with high purity, high-temperature stability and easy-to-get on commercial base, have been selected, which are tantalum, niobium, and molybdenum. Thermal diffusivity values of the specimens cut out of these materials have been measured independently by some members of the working group. Comparisons of their results have performed for different high-temperature stability, repeatability and manufacturer, as well as those from different members. The comparisons show that the measured values agreed within 10% for different specimens by different institutions, and no systematic difference has been found for materials from different manufacturer. The measuring result of molybdenum specimen agrees well with the recommended values of thermophysical properties of matter the TPRC data series, and the high-temperature stability is found to be the best. The results of tantalum and niobium, however, show significant differences with those of the TPRC data series and some further measurements are needed for recommending these values.

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

1. INTRODUCTION

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

The laser flash method can be used to determined the absolute value of thermal diffusivity theoretically. 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 of the laser flash method [2]. On the other hand, some industrial standards such as JIS have given the indication on the specification and performance of the practical instruments for the general users [3].

The standard instrument and the practical instrument can generally be classified as shown in Fig. 1. The standard one can provide absolute value accurately but is difficult to handle because the candidate specimen is restricted, while the practical one can accept the relative measurement value 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 an indication of the material, by which the standard instrument and the practical one can be connected. Then the practical instrument will keep its advantage and realize the measurement of absolute value and the evaluation of the uncertainty.

In this work, we have measured thermal diffusivity of the selected candidate reference materials for laser flash method, which are tantalum, niobium, and molybdenum by different members of the working group. Comparisons of the results are performed for different high-temperature stability, repeatability and manufacturer, those measured by different members, as well as the recommended values of thermophysical properties of matter, the TPRC data series, to select ones as the candidate of thermal diffusivity reference materials.

2. EXISTING STANDARD REFERENCE MATERIALS

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

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

3. CANDIDATE STANDARD REFERENCE MATERIALS OF THERMAL DIFFUSIVITY

Following the development of the measuring technique of thermal diffusivity of metals, we have been aiming at the standard reference materials of thermal diffusivity. Three kinds of high-temperature metals, tantalum, niobium, and molybdenum, are selected from the Nilaco Co. and Good Fellow Co., Ltd., respectively. The specimens are in shape of disk with diameter of 10 mm. For determining the system error, three kinds of materials are divided into 4 kinds of specimens by the thickness of 1.0 mm, 1.4 mm, 2.0 mm, and 2.8 mm, respectively, these is defined as one specimen group. 8 groups, named A, B, C, D, E, F, G, and H, have been made, then were distributed to the member institutions of the working group, respectively. There are six institutes carried out the measurements, which include (1) Ibaraki University-B group; (2) Japan Fine Ceramics Center-C group; (3) Kyoto Electronic Industry-D group; (4) Ulvac-Riko Inc.-E group; (5) Japan Ultra-high Temperature Materials Research Institute-G group; (6) Toray Research Center Inc.-H group.

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 are stable at high temperature. The working group has tested the stability of the selected standard reference metals, tantalum, niobium, and molybdenum, by comparing the specimen's masses, thicknesses, and thermal diffusivity before and after temperature rise up to 1700 K. The testing results are shown in Table I for mass, Table II for thickness, and Table III for thermal diffusivity. From the results for mass and thickness, it can be found 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 high temperature rise, which inform us 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 reason for the change are not clear yet.

From the results for thermal diffusivity, it can be found that those of tantalum and niobium decrease after high temperature rise. The change of thermal diffusivity in tantalum after heating would be caused by the change in the orientation of crystal. The differences in changes in thermal diffusivity after high temperature rise for different manufacturer are resulted from the manufacture and process method. For niobium, the reason has to be studied further with consideration of the reason of the film formation on the surface.

According to above results, for high temperature measurement, changes in mass, thickness, and thermal diffusivity may occur because of heating. Therefore, the measuring results had better be checked by comparing the values before and after the temperature rise. In addition, it is necessary to give the temperature range at which the standard reference materials can work stably.

5. COLLABORATIVE MEASUREMANTS

For catching the development in measuring instruments and techniques in thermal diffusivity measurements by laser flash method, the measuring results for fixed specimen thickness have been discussed at different temperature from room temperature to 1700 K. The collaborative measuring results of the temperature dependences of thermal diffusivity are shown in Fig. 2 for tantalum, Fig. 3 for niobium, and Fig. 4 for molybdenum. In the figures, the solid lines are recommended values in the TPRC Data Series in 1970s, which are still considered as standard values now [7].

It can be seen that, for all of these results, the measured values agree with each other within 10%, and no big differences in thermal diffusivity are found for different specimens by different institutions. No significant difference has been found for materials from Nilaco Co. and Good Fellow Co., Ltd..

The measuring result of molybdenum specimen agrees well with the recommended values of thermophysical properties of matter the TPRC data series, while the results of tantalum and niobium show significant differences with those of the TPRC data series. The high-temperature stability of molybdenum is found to be the best. Therefore, molybdenum is qualified as a candidate of thermal diffusivity reference material. The results of the collaborative institutions are close, and the differences between these values are much smaller than those between these value and TPRC data. Especially for tantalum and niobium at high temperature, some further measurements and discussions are needed for recommending these values.

6. CONCLUSION

The high-temperature stability and thermal diffusivity of three kinds of selected standard reference metals, tantalum, niobium, and molybdenum, are examed in this work. The high-temperature stability of molybdenum is found to be the best. According to the results from the collaborative institutions, the measured values agreed within 10% for different specimens by different institutions, and no significant difference has been found for materials from different manufacturer. The results of the collaborative institutions are close, and the differences between these values are much smaller than those between these value and TPRC data. Especially for tantalum and niobium at high temperature, some further measurements and discussions are needed for recommending these values.

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FIGURE CAPTIONS

Fig. 1 The relationship of the standard and the practical instruments.

Fig. 2 Temperature dependence of thermal diffusivity (tantalum).

Fig. 3 Temperature dependence of thermal diffusivity (niobium).

Fig. 4 Temperature dependence of thermal diffusivity (molybdenum).

Table I Measuring results of masses before and after temperature rise

Provider	Material	Mass (g)		Difference	
		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 Measuring results of sizes before and after temperature rise

Provider	Material	Thickness (mm)		Difference	
		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

Tab. III Measuring results of thermal diffusivity before and after temperature rise

Provider	Material	Thermal diffusivity ($\times 10^{-5} m^2 s^{-1}$)		Difference	
		Before temperature rise	After temperature rise	($\times 10^{-5} m^2 s^{-1}$)	(%)
Nilaco	Ta	2.41	2.37	-0.04	-1.66
	Nb	2.28	2.15	-0.13	-5.70
	Mo	5.36	5.43	0.07	1.31
GF	Ta	2.47	2.37	-0.1	-4.05
	Mo	5.43	5.38	-0.05	-0.92

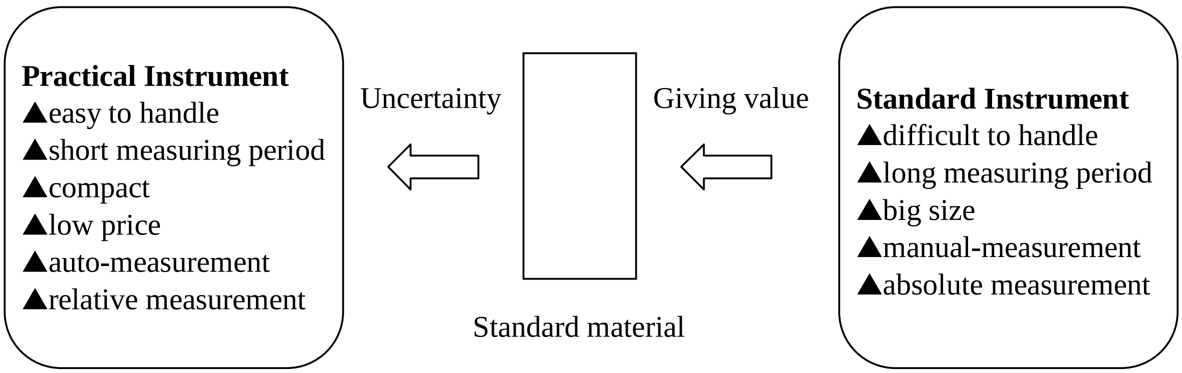

Practical Instrument
▲easy to handle
▲short measuring period
▲compact
▲low price
▲auto-measurement
▲relative measurement
Uncertainty
Giving value
Standard Instrument
▲difficult to handle
▲long measuring period
▲big size
▲manual-measurement
▲absolute measurement
Standard material

Fig. 1

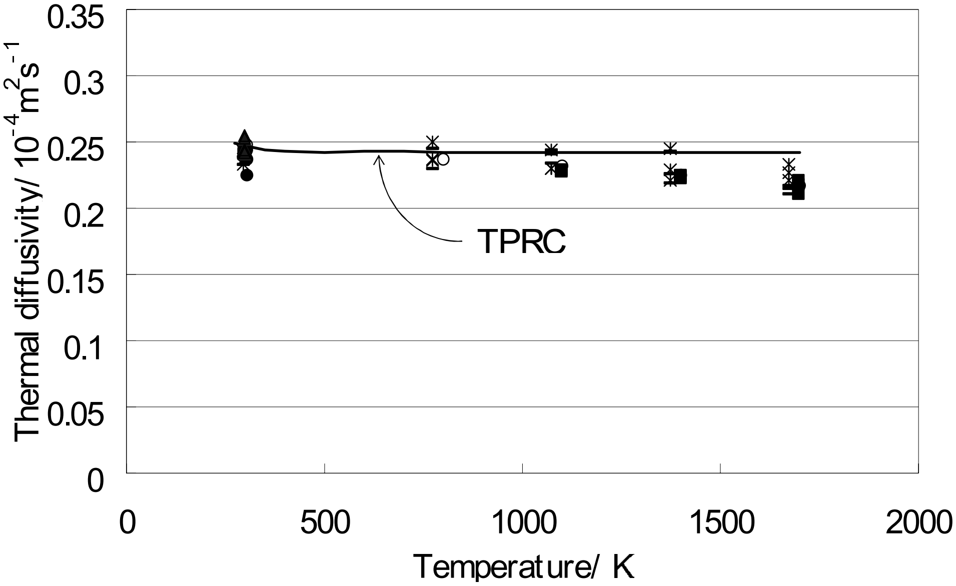

0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Thermal diffusivity/ 10-4 m2 s-1
TPRC
0
500
1000
1500
2000
Temperature/ K

Fig. 2

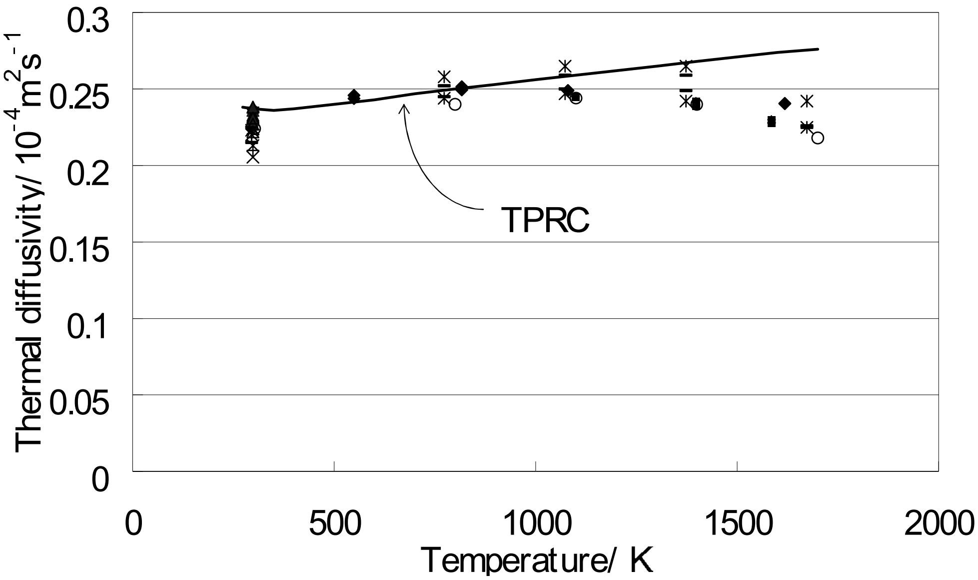
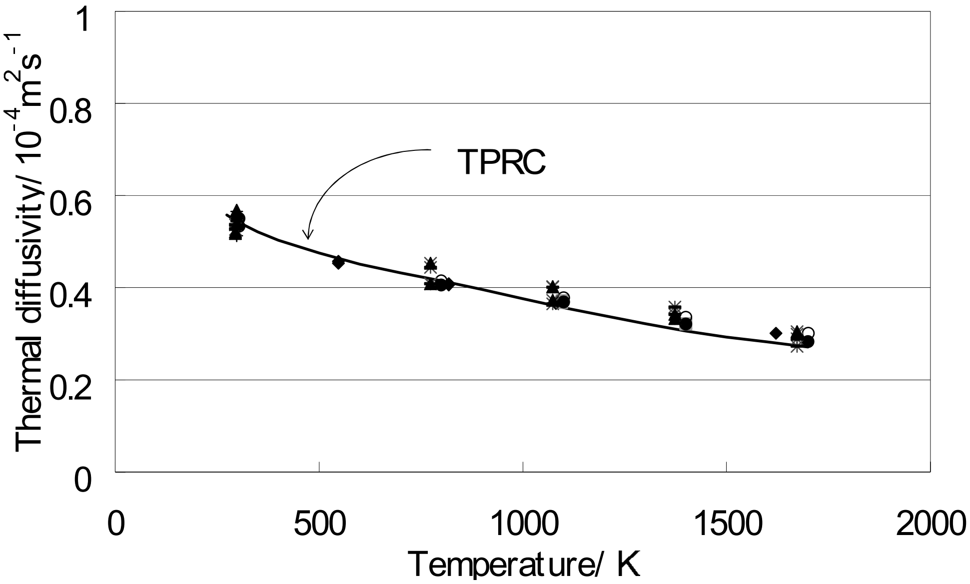

0.3
0.25
0.2
0.15
0.1
0.05
0
0
500
1000
1500
2000
Thermal diffusivity/ 10-4 m2s-1
Temperature/ K
TPRC

Fig. 3



Thermal diffusivity/ $10^{-4}m^2s^{-1}$
1
0.8
0.6
0.4
0.2
0
TPRC
0
500
1000
1500
2000
Temperature/ K

Fig. 4