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Thermal Conductivity of Reference Solid Materials[1]

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The thermal conductivity of three thermal-conductivity reference materials, Pyrex 7740, Pyroceram 9606, and stainless steel AISI 304L, has been studied. The technique employed is the transient hot-wire technique, and measurements cover a temperature range from room temperature up to 570 K. The technique is applied here in a novel way that eliminates all remaining contact resistances. This allows the apparatus to operate in an absolute way. The method makes use of a soft silicone paste material between the hot wires of the technique and the solid of interest. Measurements of the transient temperature rise of the wires in response to an electrical heating step in the wires over a period of 20 μs up to 20 s allow an absolute determination of the thermal conductivity of the solid, as well as of the silicone paste. The method is based on a full theoretical model with equations solved by a two-dimensional finite-element method applied to the exact geometry. At the 95% confidence level, the standard deviation of the thermal conductivity measurements is 0.1% for Pyrex 7740, 0.4% for Pyroceram 9606, and 0.2% for stainless steel AISI 304L, while the standard uncertainty of the technique is less than 1.5%.

KEY WORDS: AISI 304L; Pyrex 7740; Pyroceram 9606; thermal conductivity; transient hot wire.

1. INTRODUCTION

In a series of recent papers [1–3], a novel application of the transient hot-wire technique for thermal conductivity measurements on solids was described. The methodology makes use of a soft-solid material between the hot wires of the technique and the solid of interest. It is based on a full theoretical model with equations solved by a finite-element method applied

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to the exact geometry, and thus it allows the accurate, absolute determination of the thermal conductivity of the solid. With this method, the thermal conductivity of Pyroceram 9606 was measured up to 590 K [1, 2], as well as the thermal conductivity of AISI 304L [3] up to 550 K. These measurements are reported here again for comparison purposes, together with our new measurements of Pyrex 7740 up to 530 K. These three solid materials are of particular interest, as they cover a thermal conductivity range from about 1 to 14 $W \cdot m^{-1} \cdot K^{-1}$ at 298 K.

Pyrex 7740 is a borosilicate glass, which conforms to ASTM E-438, and is a certified reference material for thermal conductivity, CRM 039, by the European Union Institute of Reference Materials and Measurements. Pyroceram 9606 is a glassy ceramic, originally developed by NASA, and since it is particularly well defined and thermally stable, it is a Standard Reference Material for thermal conductivity, SRM 1415, by the National Institute of Standards and Technology (NIST), U.S.A. It is also currently considered as a candidate reference material by the National Physical Laboratory, U.K. Finally, stainless steel AISI 304L is currently considered as a Standard Reference Material traceable to NIST via SRM 1460, for thermal conductivity.

At the 95% confidence level, the standard deviations of the thermal conductivity measurements of Pyrex 7740, Pyroceram 9606, and AISI 304L are 0.13, 0.42, and 0.2%, respectively, and of the product (density × specific heat), ρC_p, are 0.1, 0.8, and 0.16%, respectively. The standard uncertainty [4] of the technique is better than 1.5% for the measurement of the thermal conductivity and better than 5% for the measurement of the product (ρC_p).

2. EXPERIMENTAL

The actual instrument employed for the measurement of the thermal conductivity of solids at elevated temperatures is described elsewhere [1]. In the case of the Pyrex 7740 and the Pyroceram 9606, the same two-wire sensor [2] was employed. Since however, AISI 304L is an electrically conducting material, a slightly different sensor [3] was employed.

The two wires of the technique, made out of 25-μm-diameter tantalum wire of 2 and 5 cm lengths, placed one after the other, are spot-welded to flattened 0.5 mm diameter tantalum wires. These, in turn are spot-welded to thick metal-sheathed Chromel wires, as shown in Fig. 1. The wires are subsequently placed in a flattened silicone paste layer (high-temperature red silicone paste, BORO 650, VersaChem, U.S.A.). The whole assembly is then placed between the two pieces of the solid of dimensions $10 \times 5 \times 2\ cm^3$,

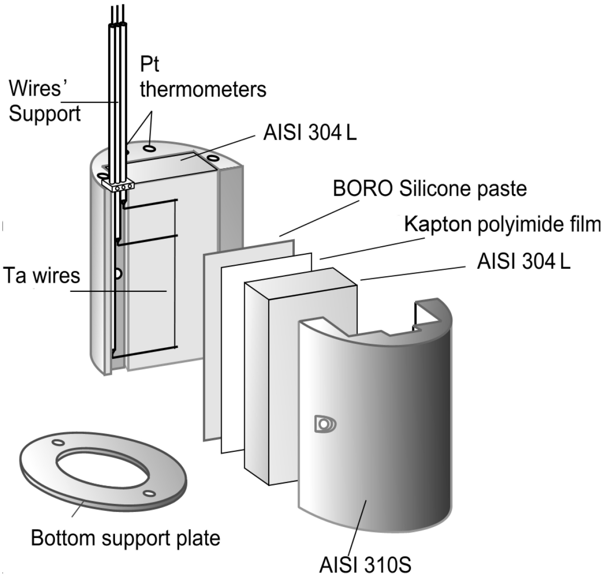

Fig. 1. Wire Sensor arrangement.

each. The advantages of employing a soft silicone layer were discussed in a previous publication [1, 2].

In the case of AISI 304L, the two wires embedded in the silicone paste are sandwiched between two 25-μm-thick polyimide films (Kapton HN polyimide film, Du Pont de Nemours). In this case, the polyimide film added, insured that no electrical contact existed between the wires and the steel. Furthermore, its great adhesive power to the metal produced a sensor that had no air gaps in its interface with the steel, while at the same time one that can easily be removed and reused. The introduction of the 25-μm-thick polyimide film results in one more heat transfer equation to be solved, together with the previously described ones [1, 2]. Hence, the full set of equations refers to the heat transfer (a) in the wire, (b) in the silicone paste, (c) in the polyimide film, and (d) in the solid, with equivalent initial and boundary conditions. This set, as described before [3], was solved by a finite-element method for the exact geometry of the sensor.

The wire-sensor arrangement with the two solid blocks is held together in two semi-cylinder parts made of AISI 304S steel (see Fig. 1). The whole arrangement is, consequently, placed in the center of an accurate, vertical three-zone tubular furnace (Model TVS 12, Carbolite), and two class-1 calibrated platinum-resistance thermometers embedded on the top and bottom of the one half cylinder, are used to record the temperature.

The wires are heated over a period of 20 μs to 20 s, by electrical current, and the thermal conductivity is determined in an absolute way from the transient temperature rise of the wire. In order to heat the wires and measure their resistance at the same time, a computer-controlled Wheatstone bridge is employed [1]. The characteristics of the silicone-paste intermediate layer (and the polyimide film in the case of AISI 304L) are evaluated from measurements at short times (typically: $t < 0.8$ s for the silicone paste alone, or $t < 0.4$ s for the silicone paste and $0.4 < t < 0.8$ s for the polyimide), whereas those of the solid are consequently derived essentially independently, from measurements at longer times (typically: $t > 0.8$ s). Hence, the thermal conductivity, λ, and the product (ρC_p), of the solid and the intermediate layers, as well as the thickness of the silicone layer are uniquely determined from a thousand measurements of the temperature rise accumulated during one run. Temperature rises employed are between 3 and 4 K over a maximum period ranging from 2 s (AISI 304 L) to 20 s (Pyroceram 9606).

3. MEASUREMENTS

3.1. Validation of Technique

The standard uncertainty of the measurement of the resistance of the wires, is a function of the uncertainties of the time intervals and the associated voltage applied [1]. Time intervals are measured with a precision of ±1 μs, while voltages are registered with a precision of 1 μV. The final result is also influenced by the standard uncertainty of the platinum resistance thermometers. These have been calibrated with a standard uncertainty of ±20 mK. Accounting for a number of other small errors, such as the measurements of the wire lengths and the temperature coefficient of resistance of tantalum, as well as errors associated with the finite-element analysis employed, it is estimated that the technique has a standard uncertainty of better than 1.5% in the measurement of the thermal conductivity, and better than 5% in the measurement of the product (ρC_p).

An important advantage of the proposed configuration is that it can also be employed to measure the thermal conductivity of fluids. So, the wires in their support, before being placed in the silicone layer, were placed in toluene at 295.15 K and the thermal conductivity, λ, and the product (ρC_p) obtained, were in excellent agreement with literature values. Liquid toluene has been proposed by the Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry as a standard with an uncertainty of 0.5% [5].

Table I. Chemical Composition (mass%) of Various Steels

Element	AISI 304L typical composition	AISI 304L measured in this work
C	0.03 max	0.02
Si	1.0	0.40
Mn	2.0	1.73
P	0.045	0.027
S	0.03	0.029
Ni	8–12	9.03
Cr	18–20	18.22
Mo		0.14
Cu		0.47
N		0.04

3.2. Results and Discussion

The blocks of Pyrex 7740, Pyroceram 9606, and AISI 304 L were all supplied by Anter Corporation, Pittsburgh, Pennsylvania, U.S.A. Table I lists the chemical composition of AISI 304 L, as provided by Anter Corporation.

Our results for the thermal conductivity (λ) and the product (ρC_{p}) for the three solids are shown in Table II. In the case of the Pyroceram 9606, two series of measurements were performed employing a different silicone paste (heat transfer compound, HTCO2S, Electrolube, U.K.), showing thus the independence of the thermal conductivity measurement from the properties of the silicone paste employed.

The thermal conductivity, λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$), values shown in Table II, were fitted as a function of the absolute temperature T (K) to an equation,

$$\lambda = \lambda(298.15\ \mathrm{K}) \sum_i a_i \left(\frac{T}{298.15}\right)^i, \tag{1}$$

where the coefficients a_i and the values of λ (298.15 K) are shown in Table III. The maximum deviations of the experimental points, presented in Table II, from the above equation, are 0.4, 1.56, and 0.64%, for Pyrex 7740, Pyroceram 9606, and AISI 304L, respectively. At the 95% confidence level, the standard deviations of the thermal conductivity measurements of Pyrex 7740, Pyroceram 9606, and AISI 304L are 0.13, 0.42, and 0.2%, respectively, which are well within the standard uncertainties of the technique.

Table II. Measured Properties of Solids as a Function of Temperature

T (K)	λ ($W \cdot m^{-1} \cdot K^{-1}$)	$\Delta\lambda^{a}$ (%)	ρC_p ($kJ \cdot m^{-3} \cdot K^{-1}$)
Pyrex 7740 (+ BORO paste and KAPTON film)			
303.674	1.16	−0.05	1772
316.283	1.17	0.12	1781
354.954	1.21	−0.01	1803
393.874	1.24	−0.12	1818
433.185	1.28	−0.14	1830
472.453	1.33	0.40	1845
489.915	1.34	−0.12	1852
522.145	1.37	−0.08	1861
Pyroceram 9606 (+ BORO paste)			
298.652	3.88	1.02	1909
318.181	3.70	−1.56	2028
351.926	3.63	−0.29	2246
391.065	3.55	0.42	2395
439.397	3.44	0.13	2584
484.475	3.36	0.08	2621
524.350	3.29	0.11	2647
569.238	3.21	0.63	2674
(+ HTCO2S paste)			
296.546	3.90	1.29	1827
322.930	3.71	−0.80	2007
361.400	3.63	0.49	2240
405.263	3.55	1.34	2518
449.227	3.43	0.35	2604
484.063	3.33	−0.84	2708
513.825	3.32	0.43	2781
AISI 304 L (+ BORO paste and KAPTON film)			
306.834	14.34	−0.55	3672
325.896	14.94	0.64	3712
364.493	15.66	−0.03	3767
374.189	15.84	−0.13	3799
398.415	16.40	0.38	(3822)
422.824	16.74	−0.32	(3861)
452.205	17.32	0.03	3909
481.939	17.78	−0.16	4001
509.320	18.23	−0.01	(4055)
536.730	18.60	−0.15	4140
545.573	18.79	0.21	4174

[a] $\Delta\lambda = 100(\lambda_{exp} - \lambda_{fit})/\lambda_{fit}$.

Table III. Coefficients and Standard Deviation of Eqs. (1) and (2)

	Pyrex 7740	Pyroceram 9606	AISI 304 L
	Eq. (1)		
λ (298.15 K) ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	1.15	3.84	14.22
a_0 (-)	0.7688	1.9219	0.3989
a_1 (-)	0.2158	−1.6939	0.7200
a_2 (-)	0.0157	0.9762	−0.1188
a_3 (-)	0	−0.2034	0
	Eq. (2)		
(ρC_p) (298.15 K) ($\mathrm{kJ \cdot m^{-3} \cdot K^{-1}}$)	1770	1868	3676
b_0 (-)	0.8716	−0.9616	1.0022
b_1 (-)	0.1634	2.7411	−0.0911
b_2 (-)	−0.035	−0.7797	0.0888

The product (ρC_p) values shown in Table II, were also fitted as a function of the absolute temperature T (K) to an equation,

$$(\rho C_p) = (\rho C_p)(298.15\ \mathrm{K}) \sum_i b_i \left(\frac{T}{298.15}\right)^i, \tag{2}$$

where the coefficients b_i and the values of (ρC_p) (298.15 K) are shown in Table III.

The maximum deviations of the experimental points, presented in Table II, from the above equation are 0.2, 2.90, and 0.56%, for Pyrex 7740, Pyroceram 9606, and AISI 304L, respectively, while at the 95% confidence level, the standard deviations of the product (ρC_p) are 0.1, 0.8, and 0.16%, respectively.

Pyrex 7740 is a well-known borosilicate glass that has been in use for many years as a reference material. In September 1990, the European Community Bureau of Reference (BCR) finally issued a certificate for Pyrex glass material [6]. This certified material is now available as CRM 039 from the European Union Institute of Reference Materials and Measurements (IRRM), in Geel, Belgium. However, it should be noted that this certificate refers only to a Pyrex glass and not specifically the 7740 grade. These certified values, characterized by a ±1.7% standard deviation at the 95% confidence level, are presented in Fig. 2.

In Fig. 2, also, the recommended values of Hulstrom et al. [7], from round-robin tests, characterized by a 10.3% standard deviation at the 95% confidence level, are shown, together with the previously reported values of Powell et al. [8], of 5% maximum uncertainty. The agreement with all

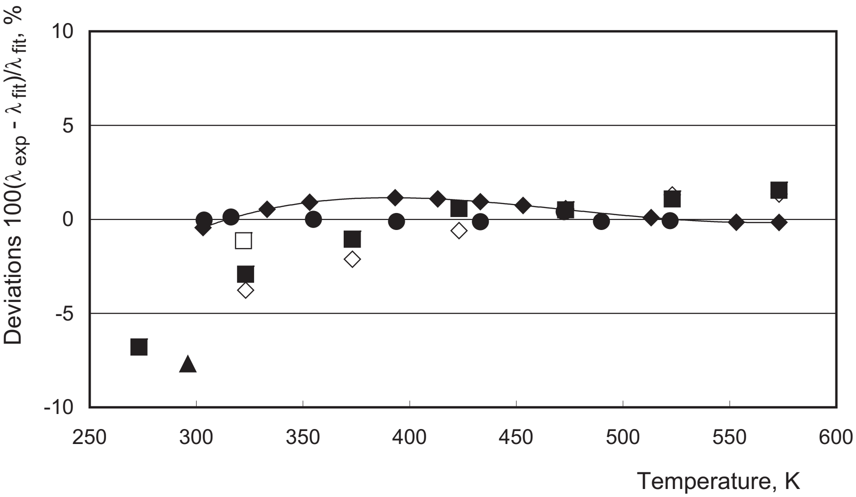

Fig. 2. Percentage deviations of the thermal conductivity measurements of Pyrex 7740 as a function of temperature, from the values calculated by Eq. (1). (●) Present work; (◆) CRM 039 [6]; (■) Powell et al. [8]; (◇) Hulstrom et al. [7]; (□) Log [9]; (▲) Miller and Kotlar [10].

these sets is excellent. More recent values are also included in the same figure:

(a) the thermal conductivity measurement of Log in 1991 [9], at 322.15 K, performed with the transient hot-strip method, and with a claimed uncertainty of 3% (no confidence level was specified), and

(b) the thermal conductivity measurement of Miller et al. in 1993 [10], at 296 K, performed in a thermal diffusivity/conductivity instrument, and with a claimed uncertainty of 5% (no confidence level was specified).

As already mentioned, Pyroceram 9606 has already been proposed by NIST as a thermal conductivity reference material, SRM 1415. The National Physical Laboratory, United Kingdom also currently considers it as a reference material. In 1988, the results for round-robin tests for the same material were published by Hulstrom et al. [7]. Their recommended values and equation, characterized by a 5.7% standard deviation at the 95% confidence level, are shown in Fig. 3, together with the previously reported values of Powell et al. [8], of 5% maximum uncertainty. The agreement with both these sets is excellent. In the same figure three other, more recent sets of measurements are also included:

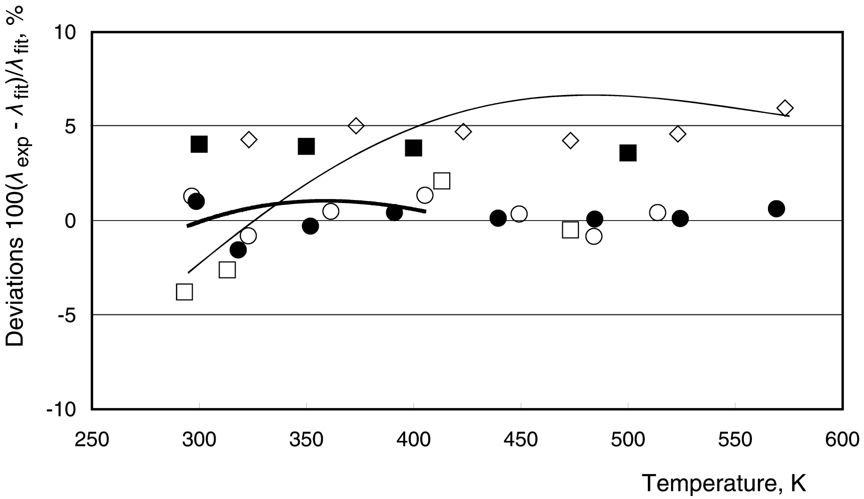

Fig. 3. Percentage deviations of the thermal conductivity measurements of Pyroceram 9606 as a function of temperature, from the values calculated by Eq. (1). (●) Present work, Series 1; (○) Present work, Series 2; (■) Powell et al. [8]; (◇) Hulstrom et al. [7]; (□) Gustafsson [11]; (——) Matsumoto and Ono [12]; (—) Suliyanti et al. [13].

(a) the thermal conductivity measurements of Gustafsson in 1991 [11], performed with a spiral wire in a hot disc arrangement, and with a claimed uncertainty of 3% (no confidence level was specified),

(b) the measurements of Matsumoto and Ono in 1992 [12], performed in a radiative heat exchange instrument, and with a claimed uncertainty of 2.5% (no confidence level was specified), and

(c) the derived values from thermal diffusivity measurements of Suliyanti et al. [13], performed with the laser flash method, and with a claimed uncertainty of 3% (no confidence level was specified).

In all cases, the deviations are within the mutual uncertainties of the instruments. It should be noted, however, that our measurements enjoy a lower degree of uncertainty.

In Fig. 4, the deviations of the data shown in Table II [3] for AISI 304 L, as well as those of other investigators, from the values calculated by Eq. (1) are shown.

(a) The AISI 304L thermal conductivity recommended values by Bogaard [14], based on an average over all the experimental

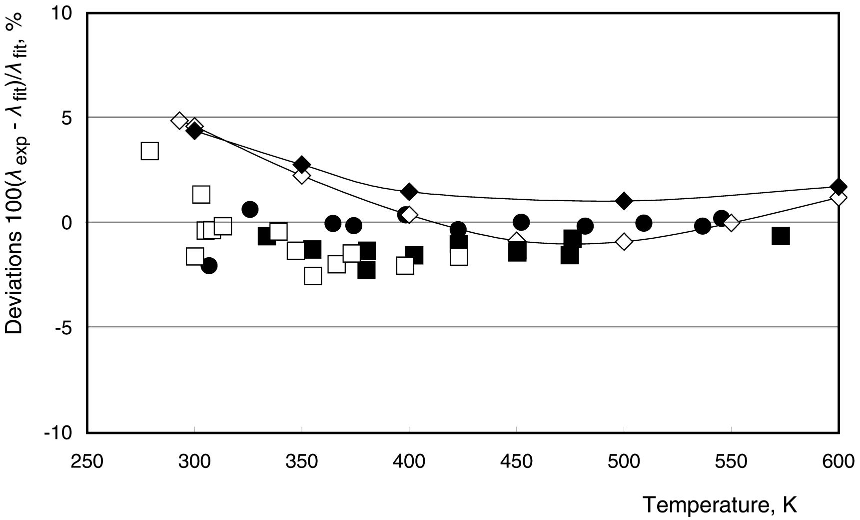

Fig. 4. Percentage deviations of the thermal conductivity measurements of AISI 304L as a function of temperature, from the values calculated by Eq. (1). (●) Present work; (◇) Bogaard [14]; (◆) Chu and Ho [15]; Graves et al. [16]: (□) Springfields Laboratory values; (■) Oak Ridge National Laboratory values.

data from 15 references, and a quoted uncertainty of 4% (no confidence level is specified), show good agreement with the present set. There is, however, a distinct difference of slopes between the two data sets.

(b) The values reported by Chu and Ho [15] with an average uncertainty of 5% (no confidence level is specified) are also shown in the same figure. Chu and Ho [15] had access to the same sets of data as Bogaard [14], but they rejected the low data values obtained by three laboratories in the temperature range 300 to 600 K and produced a smooth curve for the thermal conductivity of AISI 304L. The present set of measurements is in excellent agreement with these values.

(c) As mentioned elsewhere [3], Graves et al. [16], in order to investigate the anomalous slope behavior proposed by Bogaard [14], performed two sets of measurements on a sample of AISI 304L of very similar composition with that of Assael et al. [3]:

- In the Oak Ridge National Laboratory a high-temperature-longitudinal apparatus was employed to measure the thermal conductivity between 300 and 1000 K.

- In the Springfields Laboratory, a laser flash apparatus was used to measure the thermal diffusivity, between 300 and 420 K.

The thermal conductivity and diffusivity measurements, reported by Graves et al. [16] with quoted uncertainties of 1.5 and 2%, respectively (no confidence level is specified), are also in excellent agreement with the present set of measurements. Furthermore, the anomalous behaviour reported by Bogaard [14] was not observed.

From the above presentation it is apparent that the present set of thermal-conductivity values agree well with the three previous sets of measurements.

4. CONCLUSIONS

A novel application of the transient hot-wire technique for measurements of thermal-conductivity reference materials, Pyrex 7740, Pyroceram 9606, and stainless steel AISI 304L up to 590 K, has been described. The method is based on a full theoretical model with equations solved by finite elements for the exact geometry. At the 95% confidence level, the standard deviations of the thermal conductivity measurements of Pyrex 7740, Pyroceram 9606, and AISI 304L are 0.13, 0.42, and 0.2%, respectively, and of the product (density × specific heat), ρC_p, are 0.1, 0.8, and 0.16%, respectively. As already discussed, the technique has a standard uncertainty of better than 1.5% in the measurement of the thermal conductivity and better than 5% in the measurement of the product (ρC_p).

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