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Pulse calorimetry at high temperatures

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Abstract

Pulse-heating techniques have been developed in the last 30 years to overcome difficulties of steady-state experiments in the high temperature range. In these methods the specimen is pulse-heated to high temperatures in short times (typically less than 1 s) using Joule heating and the various experimental quantities are measured with millesecond to microsecond time resolution. Many thermophysical properties are measurable with these methods, including heat capacity, melting point and enthalpy of fusion. In the high temperature range (above 1000 K) these absolute techniques provide accurate calorimetric data and have been used to characterize different materials taking advantage of the possibility to determine several properties in a single experiment of subsecond duration. The state-of-the-art of pulse calorimetry is reviewed making reference to the apparatus developed at the Istituto di Metrologia "G. Colonnetti" (IMGC, Torino, Italy), with a particular emphasis on the characterization of some reference materials (molybdenum, tungsten and platinum) in the temperature range 1000–3600 K.

Keywords: Heat capacity; High temperature; Pulse methods; Reference materials; Thermophysical properties

1. Introduction

Pulse-heating techniques are new measuring methods that have gained wide acceptance because they overcome several limitations of steady-state experiments. Measurements of thermal properties at high temperatures have always been difficult with the experimental problems increasing exponentially with temperature. Classical steady-state measurements above 1000 K (generally performed in furnaces) must overcome problems associated with long times to reach equilibrium, extended operation in vacuum or controlled atmosphere, chemical interaction of the specimen with the environment, contact temperature measurements, etc. Many of these problems are drastically reduced by performing the experiment in a subsecond time scale, starting with the specimen at room temperature and pulse-heating it up to its melting point in less than 1 s. The experimental quantities (power imparted to the specimen, temperature, etc...) are measured with submillisecond time resolution using high-speed data acquisition systems. These methods have greatly benefited from continuous progresses in electronics and optoelectronics that have made available powerful computers, sophisticated data acquisition systems and integrated semiconductor detectors that satisfy most needs regarding the experimental control and the fast data acquisition.

Readers interested in developments of pulse-heating methods are referred to previous reviews by

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Table 1
Active laboratories in pulse calorimetry with millisecond time resolution

Laboratory	Country	T range/K	Reference
National Institute of Standards and Technology (NIST)	USA	1500–3700	[3]
Istituto di Metrologia "G. Colonnetti" (IMGC)	Italy	1000–3700	[4]
Boris Kidric Institute of Nuclear Sciences (VINÇA)	Yugoslavia	300–1900	[5]
Institute for High Temperatures of the Russian Academy of Sciences (IVTAN)	Russia	1000–3700	[6]
Physikalisch-Technische Bundesanstalt (PTB)	Germany	400–1500	[7]
National Research Laboratory of Metrology (NRLM)	Japan	1000–3000	[8]

Cezairliyan that cover the measurement principles [1] and the practical realization of a measurement apparatus [2]. This paper reviews specifically the state-of-the-art in pulse calorimetry with millisecond time resolution, making reference to the apparatus developed at the Istituto di Metrologia "G. Colonnetti" (IMGC, Torino, Italy) and the related experimental measurements. Particular emphasis is given to the characterization of reference materials in the temperature range above 1000 K.

The main laboratories active in pulse calorimetry with millisecond time resolution are listed in Table 1. A literature reference is provided for each laboratory, indicating a significant publication describing the apparatus. Some laboratories measure temperature using spot-welded thermocouples on the specimen and consequently they start at temperatures of 300–400 K, but are limited to 1500–1900 K. Laboratories using high-speed pyrometry can measure from approximately 1000 K, but have no high temperature limitation (a value of 3700 K, close to the melting point of tungsten, is used in Table 1 as the high temperature limit).

Most of the laboratories in Table 1 are the national measurement institute in each country: pulse-heating techniques are promising measurement methods that still require considerable research work in the measurement technique itself, and therefore, their main development has been done in standards laboratories around the world. Pioneering work in the development of the first modern apparatus in this research area was done by Cezairliyan and co-workers [3] at the National Bureau of Standards (NBS, USA, presently the National Institute of Standards and Technology, NIST). The major difference among the laboratories involved in pulse calorimetry is the implementation of high-speed pyrometry for the temperature range above 1000 K. This remains a delicate research problem that requires specially built instruments with appropriate characteristics and specific calibrations. A recent review [9] describes the state-of-the-art in high-speed pyrometry applied to pulse-heating methods.

Pulse-heating techniques are multiproperty measurements that permit the simultaneous determination of several thermophysical properties in one experiment. Heat capacity, electrical resistivity and hemispherical total emissivity are measured in the basic experiment. Developments through the years have improved the basic experiment, adding the measurement of normal spectral emissivity [10,11], of thermal expansion [12,13], and of thermal conductivity [14,15]. In the context of this review, attention will be focused on the basic experiment for the measurement of heat capacity, including a complementary technique for the determination of the enthalpy of fusion.

2. Measurement technique

A pulse calorimetry experiment consists of the rapid heating of a specimen by the passage of a current pulse of subsecond duration (Fig. 1). During this short time the central portion of the specimen is self-heated to high temperatures with minimal loss of energy by thermal conduction toward the clamps; in this way a specimen at uniform high temperature (central zone, see Fig. 2) is obtained without the need of furnaces and other cumbersome auxiliary equipment. A block diagram of the experimental apparatus is shown in Fig. 3. The experiment is completely under computer control: on the closing of the switch large currents (several thousand amperes) pass through the specimen that self-heats to high temperatures. The maximum tem-

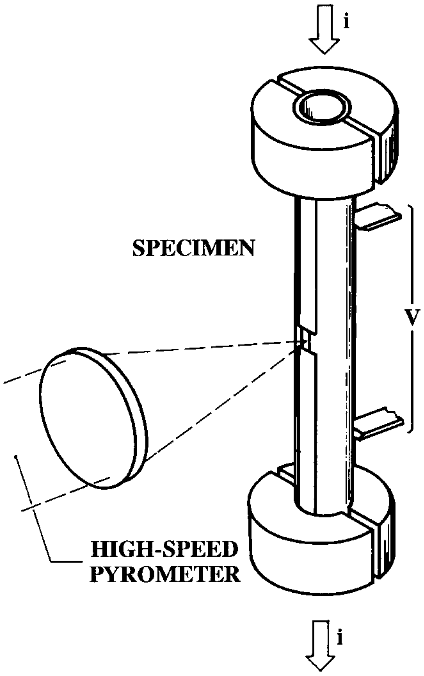

Fig. 1. Schematic representation of a pulse calorimetry experiment.

perature is defined by the current pulse length (generally less than 1 s); alternatively the pyrometer may interrupt the experiment when a preset temperature is reached. The experimental quantities (current, voltage drop in the central portion of the specimen, temperature) are measured with submillisecond time resolution.

The most accurate experiments are performed on tubular specimens (Fig. 1) with the following typical dimensions: length, 70–100 mm; diameter, 6–10 mm; and wall thickness 0.5–1 mm. A rectangular hole in the middle of the specimen defines a blackbody cavity with an emissivity greater than 0.98. The cross-sectional area is equalized by grinding away a strip of material to compensate for the material removed in providing a blackbody cavity. The upper clamp if fixed; the lower clamp is movable to permit the thermal expansion of the specimen. The experiment is performed in an experimental chamber; measurements are possible either in vacuum or in a controlled atmosphere.

Temperature is measured by a high-speed pyrometer specifically designed and built at the IMGC for

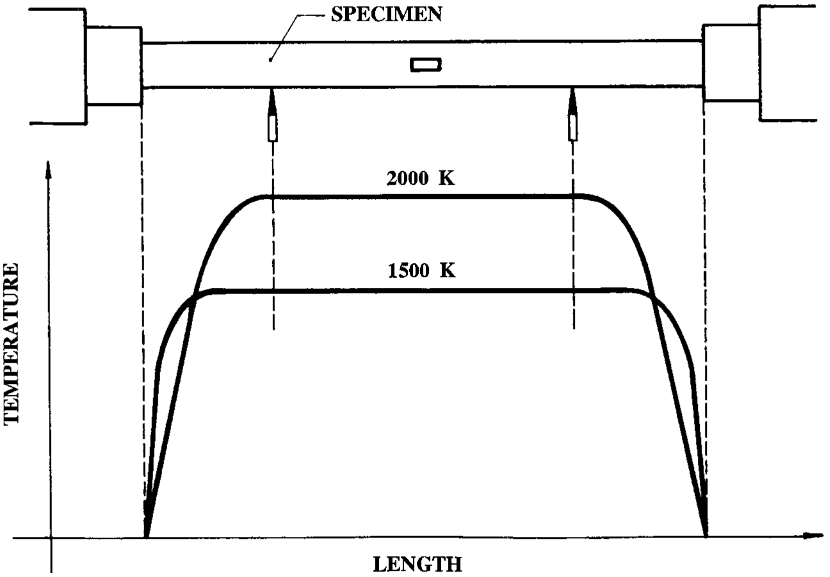

Fig. 2. Typical temperature profiles during a pulse calorimetry experiment. Thermophysical properties are measured in the central zone at uniform high temperature (between the probes).

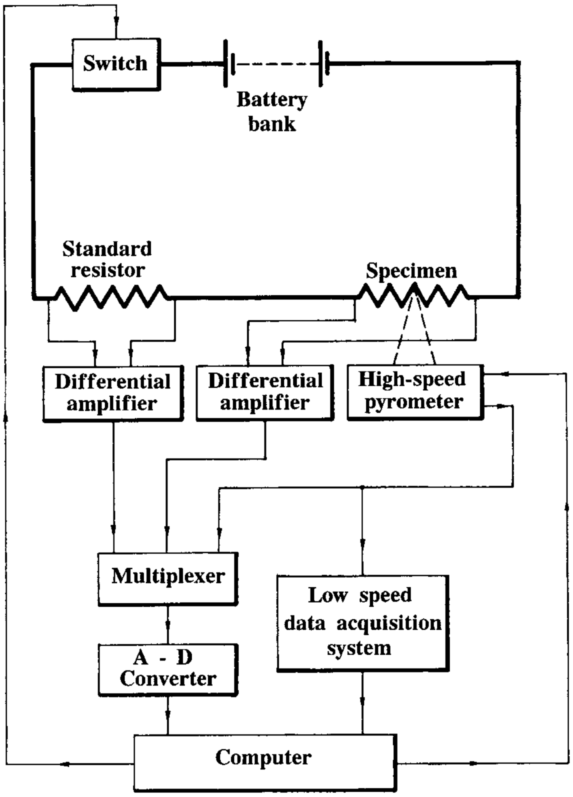

Fig. 3. Block diagram of the experimental apparatus developed for measurements by the pulse technique.

these experiments. Various instruments are available with different target areas (circles from 0.2 to 1 mm in diameter) and time resolutions. All the pyrometers are monochromatic instruments based on silicon detectors working in the visible or in the near infrared according to the interference filter mounted at calibration time. Specific autorange techniques for high-speed pyrometry have been developed, so that very wide temperature ranges (examples: 1000–3000 K or 1800–3700 K) are covered in one experiment. Complete technical details on the high-speed pyrometers and on their calibration methods are presented in an earlier publication [16].

Pulse calorimetry may also be performed on strip specimens with the simultaneous determination of the normal spectral emissivity of the strip during the pulse experiment using a reflectometric technique (Fig. 4). The strips have the following typical dimensions: length, 80–100 mm; width, 8–10 mm; and thickness 0.5–1 mm. Strip specimens are simpler to machine, but the measurement of their normal spectral emissivity requires a more complex experimental apparatus. This consists of a small integrating sphere inserted in the experimental chamber. The radiance temperature on one side of the strip is measured by a high-speed pyrometer with submillisecond time resolution. The other side of the strip is placed outside a port-hole

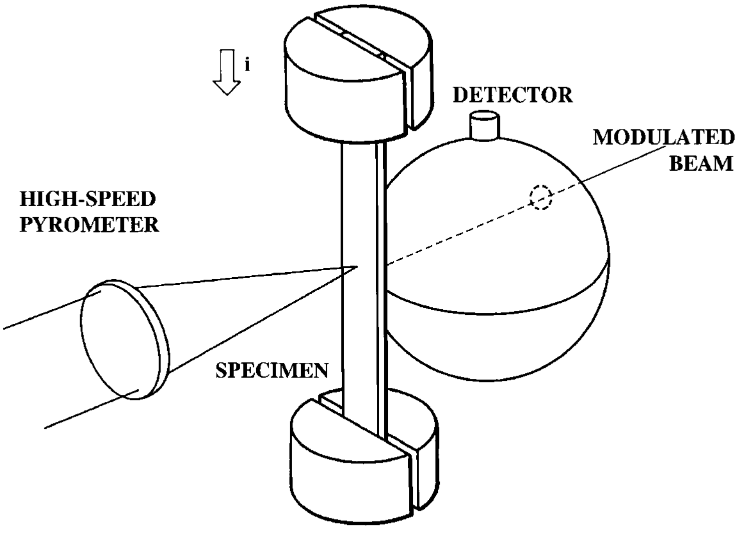

Fig. 4. Schematic diagram of the pulse-heating reflectometric technique.

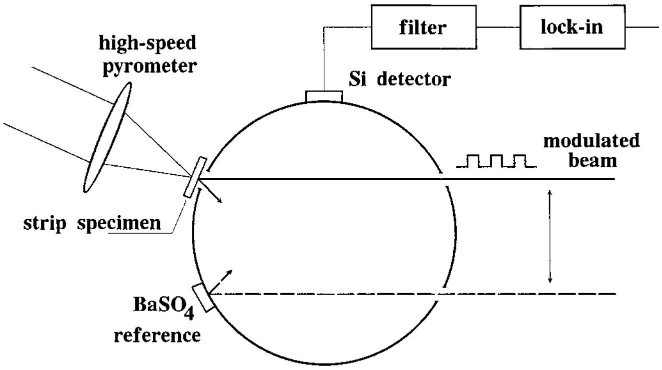

Fig. 5. Cut-off view of the integrating sphere reflectometer, indicating the relative position of the different components.

of the small integrating sphere. A modulated beam generated by a laserdiode strikes the side of the strip facing the sphere. The reflected beam is collected hemispherically by the integrating sphere (schematic diagram in Fig. 5) and measured by a silicon detector placed in the sphere ceiling and operated at the same wavelength of the high-speed pyrometer and of the laserdiode (at present near 900 nm). A fast lock-in technique is used to discriminate between the reflected beam (that is modulated) and the continuous component generated by the specimen itself when it reaches high temperatures. The instrument is a high-speed version of an integrating sphere reflectometer of the comparison type, in which the reflectance of the specimen is measured in comparison to that of a known $BaSO_4$ reference standard. The strip specimen is pulse-heated using as power supply a set of lead acid batteries and can be brought to high temperatures (up to its melting point) in times ranging from 0.5 s to several seconds, depending on the signal to noise ratio acceptable in the lock-in measurements. The quantity that is measured by the integrating sphere is the hemispherical spectral reflectivity: normal spectral emissivity is then obtained in accordance with Kirchhoff's law for opaque materials. Recent measurements performed at the IMGC on niobium with the simultaneous determination of the normal spectral emissivity [17] and of the thermophysical properties [18] of the niobium strip in the temperature range 1100–2700 K indicated that the results of measurements on strips are compatible with similar measurements performed on tubular specimens with a blackbody hole, with a small loss of accuracy due to the indirect method of temperature measurement (via radiance temperature and normal spectral emissivity).

An alternative method for the determination of the normal spectral emissivity of a cylindrical specimen using laser polarimetry during pulse heating has been developed at the NIST [19]. The technique is based on determining the reflectivity of the specimen from the measurements of the polarization states of a laser radiation reflected from the surface of the specimen. Two optical rails support the incident polarization optics and the analyzer optics. The input beam to the polarization optics consists of a He–Ne laser at 633 nm. This beam enters an acousto-optic modulator, which provides amplitude modulation of the transmitted radiation with a frequency of about 25 kHz. The modulated laser radiation then passes through two Glan Thomson linear polarizers: the first polarizer serves as an attenuator, while the second polarizer is fixed at 45° with respect to the plane of incidence. The reflected radiation from the specimen is collected by suitable imaging optics and is focused onto a field stop. Radiation transmitted through the field stop is then recollimated and analyzed by the four-detector polarimeter. The outputs of the polarimeter and the pyrometer are digitized, recording the four polarimeter and one or more pyrometer signals at the rate of 2 kHz. Details of the laser polarimeter, its integration into the pulse-heating facility at the NIST, and the results of the experiments on molybdenum and tungsten are given in a recent publication [19].

Pulse calorimetry requires complex experiments, but is very simple from a mathematical point of view. The quantities measured during the experiment are the current through the specimen, the voltage drop across the central portion of the specimen (between the voltage probes) and the temperature. The electrical resistance (hence the resistivity) is obtained directly from the experimental quantities measured during heating. With the experimental conditions shown in Fig. 2, power balance equations referring to the central portion of the specimen can immediately be written for the heating period and for the initial part of the cooling period, considering that the input power is partly absorbed by the specimen and partly lost by thermal radiation. In this way a set of two simple equations in two unknowns (heat capacity and total hemispherical emissivity) is obtained and can be easily solved. All the other quantities in these equations are either experimental data (input power, temperature, heating and cooling rates) or specimen data (geometrical factors, mass). In the classical method of computation of properties, least-squares fittings of the experimental quantities versus time smooth out the data and heating and cooling rates are computed analytically from the smoothed temperature versus time polynomials. Two alternative mathematical methods that do not require the direct computation of the heating and cooling rates have also been presented [20] and proved to provide results of comparable accuracy. Complete details regarding the mathematical formulation for the computation of properties using the classical computing method are available in an earlier review [2].

Pulse calorimetry is not limited to the solid phase, but may be extended to the solid–liquid transition. The time of the melting plateau and of the hydrodynamic collapse of the column of liquid metal is long (approximately 100 ms) in the time scale of these experiments. Measurements are possible during the initial phase of the melting plateau and a series of joint experiments between the IMGC and the NIST has demonstrated that the radiance temperature of metals at their melting point is a reproducible quantity irrespective of the initial surface conditions. The radiance temperature of a melting strip can, therefore, be used as a secondary temperature standard for the calibration of complex experimental apparatus and of high-speed pyrometers. Complete details about these measurements are available in a review publication [21].

Pulse calorimetry may also be extended to measurements of the enthalpy of fusion by making use of composite specimens (see Fig. 6) made up of three strips. The outer material must have a higher melting point than the inner material and the outside strips act as a container during the melting process. When the composite specimen is pulse heated through the melting point of the inner material, the entire melting plateau is observed (Fig. 7). The enthalpy of fusion is computed by integrating the input power and by subtracting the energy lost via thermal radiation during the time of the melting plateau.

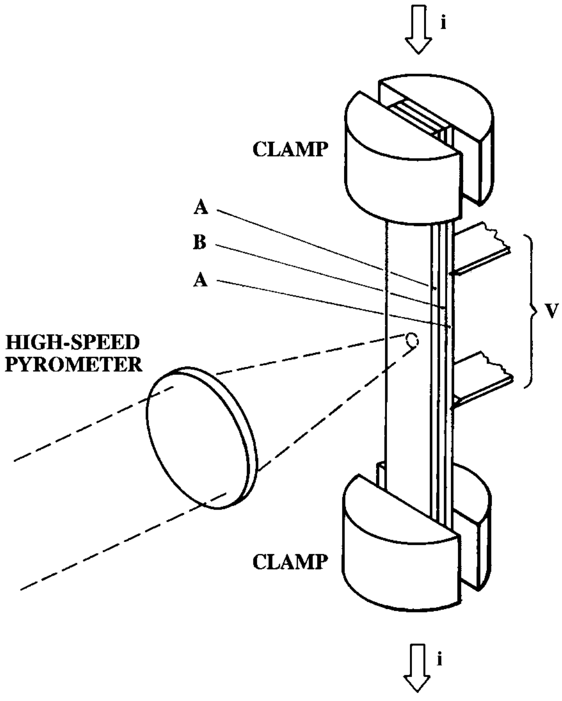

Fig. 6. Schematic representation of a pulse experiment for the measurement of the enthalpy of fusion.

Pulse calorimetry is a measurement technique that provides absolute values. The final uncertainty on heat capacity determinations depends on the realization of the physical model during the experiment and on accurate measurements of current, voltage drop, and temperature. Other quantities that may affect the final result are geometrical and mass measurements of the specimen performed before the experiments. In this paper uncertainties are presented according to the ‘Guide to the Expression of Uncertainty in Measurement’ [22], distinguishing between purely statistical considerations (Type A uncertainty) and adding to the

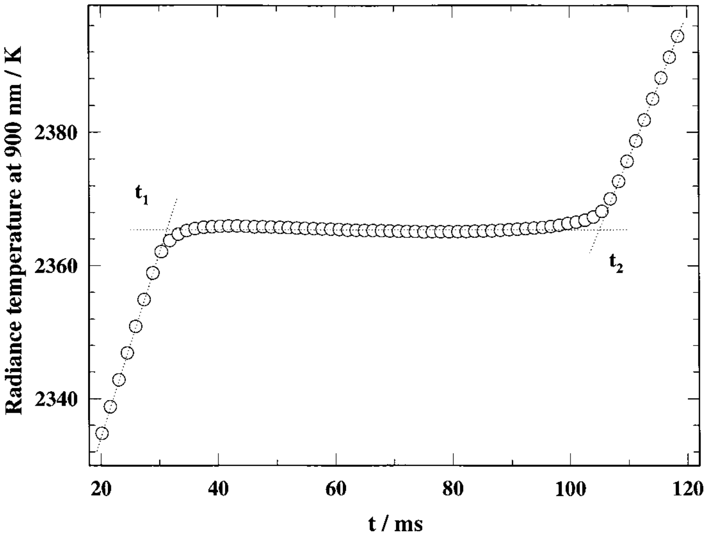

Fig. 7. Typical melting plateau in a pulse experiment to determine the enthalpy of fusion of niobium, using tantalum strips as containers.

statistical considerations realistic estimates of other effects (uncertainties remaining after the various calibrations, deviation of the experiment from the physical model, etc...) to obtain the Type B uncertainty. All uncertainties are expressed at the two standard deviation level. Typical figures for pulse calorimetry experiments are presented in Table 2. The biggest contribution is generally due to the realization of the temperature scale, both regarding the accuracy of the scale realization in different laboratories, but also in relation to other factors like the use of specimens with blackbodies, the blackbody realization and evaluation, etc...

Table 2
Typical uncertainty values of measured and computed quantities in pulse calorimetry experiments

Quantity	Type A uncertainty	Type B uncertainty
Temperature (1000 K)	0.2 K	2 K
(2000 K)	0.1 K	3 K
(3000 K)	0.3 K	6 K
Voltage	0.02%	0.1%
Current	0.02%	0.1%
Length	0.02%	0.1%
Mass	0.02%	0.1%
Time	0.002%	0.01%
Hemispherical total emissivity	0.5–1%	5–7%
Electrical resistivity	0.1–0.2%	1–1.5%
Heat capacity	0.3–0.6%	2–4%
Enthalpy of fusion	2%	10%

3. Characterization of reference materials

Many different materials have been measured using pulse calorimetry techniques in the high temperature region. A detailed list of the measurements performed up to 1980 is available in the literature [1]. The attention is focused here on measurements of potential reference materials for the high temperature range (above 1000 K), presenting specific results obtained mainly at the IMGC and the NIST with some intercomparison of results. The experimental results obtained at the IMGC for the heat capacity of molybdenum, tungsten and platinum are presented in Fig. 8. All temperatures reported in this paper are based on the International Temperature Scale of 1990 (ITS-90) [23].

3.1. Molybdenum

In the early 1980s the NIST research group prepared some tubular specimens with a blackbody hole from molybdenum SRM 781, a reference standard material available from the NIST SRM office. These specimens were used to measure at the NIST the certified values

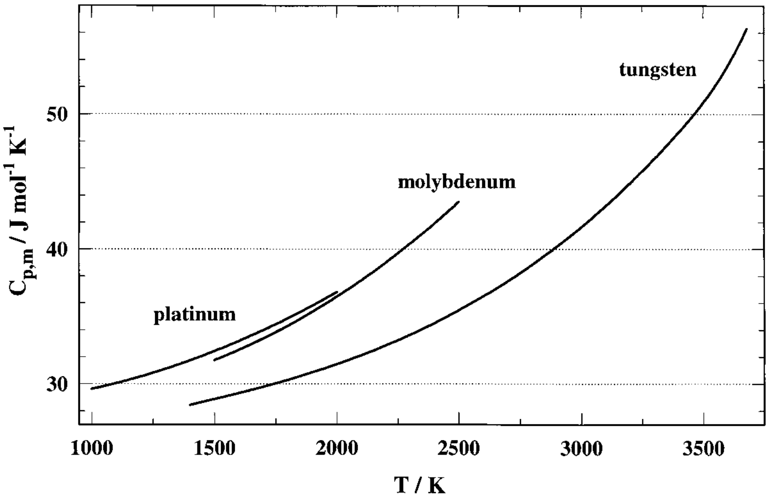

Fig. 8. Experimental results obtained at the IMGC for measurements of the heat capacity of platinum, molybdenum and tungsten at high temperatures.

[24] of heat capacity of this material in the high temperature range [25]. One of the specimens was loaned to the IMGC for a blind intercomparison that has been reported in the literature [26]. The results are shown in Fig. 9. The maximum difference in the overlapping temperature range is ±0.6%, to be compared with an estimated uncertainty of ±3% declared by both laboratories. It should be noted that the results refer to data obtained on the same specimen, and therefore, are indicative mainly of differences in measured experimental quantities and in the temperature scale realizations, with smaller contributions attributable to mass and geometrical measurements. Complete technical details about this intercomparison are presented in the earlier publication [26].

3.2. Tungsten

This material was measured at the NIST in the early 1970s [27] and at the IMGC in the early 1990s [28].

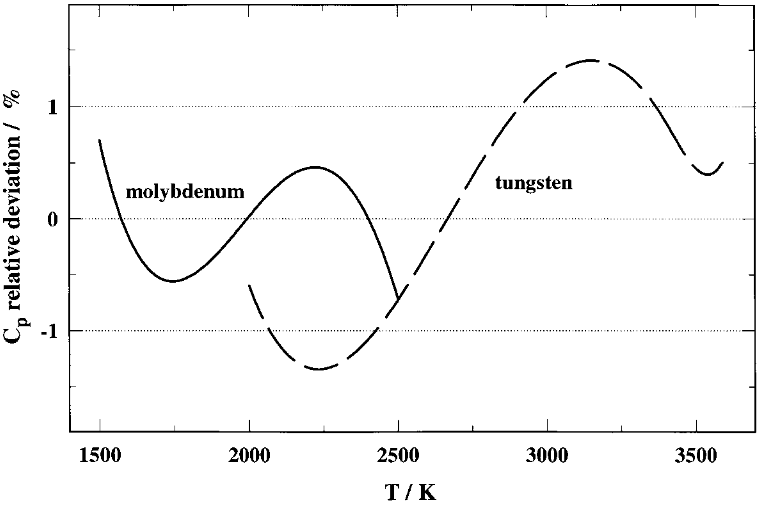

Fig. 9. Results of intercomparisons of measurements performed at the IMGC and at the NIST on the heat capacity of molybdenum and of tungsten in the temperature range 1500–3600 K.

The tungsten had comparable purity but came from completely different sources. The results are reported in Fig. 9. The maximum difference is of the order of ±1.5%, with respect to an estimated uncertainty of ±3% for the NIST data and ±4% for the IMGC data. The larger uncertainty of the IMGC results is due to the fact that experiments were performed on rods, using the normal spectral emissivity at the melting point of tungsten as a reference value [29] and literature data for the temperature dependence of the normal spectral emissivity of tungsten from 1200 K to the melting point. The IMGC results exhibit approximately the same differences (of the order of ±1.5%) with two recent reviews [30,31] that critically analyze the limited number of data sets available for the heat capacity of tungsten at very high temperatures. This indirect intercomparison extends the temperature range up to 3600 K and indicates a close agreement of measurements performed independently at two national standards laboratories using the same measurement technique, but performing measurements on unrelated specimens and using different versions of the experimental apparatus. This is particularly remarkable because the high-speed pyrometers used in each laboratory derive from independent designs and use different calibration methods. Complete technical details about the measurements performed at the IMGC on tungsten are available in the literature [28,32].

3.3. Platinum

The heat capacity of platinum in the temperature range 1000–2000 K was measured at the IMGC in the late 70s [33]. Unfortunately no recent significant intercomparison is available, but the results deviate from -2% to -0.5% from adiabatic calorimetry data [34] in the temperature range 1000–1900 K. Platinum is an important candidate reference material on account of its wide possible usage in all environments.

4. Conclusions

In the last decades pulse calorimetry has made enormous progresses and can now be considered an established technique. Measurements performed using pulse-heating methods in some national standards laboratories have led to the thermal characterization of several materials in the high temperature range, with the determination of heat capacity, electrical resistivity, thermal radiation properties (total hemispherical emissivity and normal spectral emissivity), and thermal expansion. Results obtained on molybdenum, tungsten and platinum indicate them as suitable heat capacity reference materials in the high temperature range. In view of these experimental results, pulse calorimetry may be considered the most accurate measuring technique for the determination of heat capacity of electrical conductors at high temperatures.

Recent efforts to simplify the measurement technique using specimens in the form of strips (at the IMGC) or cylinders (at the NIST) have indicated the way for application work, but high-speed pyrometry remains a prerequisite for accurate measurements.

Further research activities in this area will likely be centered on additional efforts to simplify the measurement method and to extend the measurements to lower temperatures. The major present limitation of pulse-heating techniques is their applicability only to materials that are good electrical conductors. It is likely that some of the future research efforts will be devoted to the development of new measuring techniques attempting to extend pulse-heating methods to materials that are poor electrical conductors.

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