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New Apparatus for Thermal Diffusivity and Specific Heat Measurements at Very High Temperature[1]

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The thermal characterization of a material under its conditions of use (temperature, pressure, etc.) is an essential step to check its adequacy with regard to a specific application and to predict its behavior. For needs of material characterization, *Commissariat à l'Energie Atomique (CEA)* has developed with *Laboratoire National de Métrologie et d'Essais (LNE)* a new apparatus to study thermophysical properties of solid materials in the range from 300 to 3300 K. This setup allows measurements of either the thermal diffusivity by the laser flash method or the specific heat by drop calorimetry. First, thermal diffusivity measurements have been performed on Armco iron and POCO AXM-5Q1 graphite. The measured values are in agreement with results obtained by other laboratories with a relative deviation of less than 6%.

KEY WORDS: drop calorimetry; high temperature; laser flash method; specific heat; thermal diffusivity.

1. INTRODUCTION

Within the framework of its missions, the *Commissariat à l'Energie Atomique* (*CEA*) needs to thermally characterize materials in a broad range of temperature and from microscopic to macroscopic scale. Until now, efforts have been made for the measurement of thermal diffusivity at microscopic scale at temperatures up to 1300 K [1]. But, at macroscopic scale,

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thermal diffusivity and specific heat measurements were only performed at temperatures up to 800 and 1000 K, respectively. Consequently, the *CEA le Ripault* center decided to develop a new setup for the determination of the thermal diffusivity by the laser flash method for the temperature range of 300 to 3300 K, and the specific heat by the ballistic method between 600 and 3300 K. This apparatus satisfies two essential points:

- To allow the measurement of these thermal properties with high sensitivity for a wide range of materials, from superinsulating materials to high thermal-conductivity materials,
- To be completely automated in order to facilitate its use to improve the repeatability of the measurements, to insure the traceability of the experimental conditions, and to protect the users by the control of safety barriers.

CEA, which has already developed a drop calorimeter [2], subcontracted the construction of this new setup to the *Laboratoire National de Métrologie et d'Essais (LNE)*. *LNE* has carried out for many years this kind of measurement, with equipment that it developed itself, for its own metrological needs [3–5]. The present paper describes the design of this apparatus and presents the first test results.

2. PRINCIPLE OF MEASUREMENT

Considering the high level of temperatures (up to 3300 K) for which the measurements are performed, the most accurate and reliable measurement methods of thermal diffusivity and specific heat are, respectively, the laser flash method and drop calorimetry (or ballistic calorimetry).

2.1. Thermal Diffusivity Measurement

The thermal diffusivity is measured by the laser flash method which is based upon the measurement of the temperature rise on the back face of a thin-disk specimen resulting from a short energy pulse on the front surface [6]. The specimen is placed in a furnace and isothermally heated at a uniform temperature. A short laser pulse irradiates one side of the sample. The transient temperature rise on the opposite face is measured by an IR detector and is recorded as a function of time. The thermal diffusivity is determined by an estimation procedure based on minimizing the difference between the experimental temperature-time curve (thermogram) and corresponding theoretical values obtained by solving the heat

conduction equation for the case of an opaque, homogeneous, and isotropic specimen.

The heat conduction equation is analytically solved in Laplace space and then an algorithm for the numerical inversion of Laplace transforms is applied to the results in order to obtain the transient temperature of the rear specimen side. The analytical solution depends on three parameters, the time t (in s), the characteristic time τ (in s), and the Biot number (dimensionless); these last two parameters are described by the following expressions:

$$\tau = \frac{e^2}{a} \tag{1}$$

$$Bi = \frac{h\,e}{\lambda} \tag{2}$$

where e is the specimen thickness (m), a is the thermal diffusivity ($m^2 \cdot s^{-1}$), h is the convection/radiation exchange coefficient ($W \cdot m^{-2} \cdot K^{-1}$), and λ is the thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$).

The estimation of the two parameters τ and Bi is performed simultaneously using a least-squares method. A knowledge of τ allows us to determine a with Eq. (1).

2.2. Specific Heat Measurement

Enthalpy measurements by drop calorimetry consist of heating a specimen having a mass M at a constant temperature T in a furnace and dropping it into a heat-flow calorimeter (maintained at temperature $T_0 < T$) placed below. The energy released by the specimen during its cooling inside the calorimeter is measured by a thermopile which provides a signal proportional to the temperature difference between the specimen and the calorimeter. The enthalpy variation $\Delta H_{T_0}^{T} = H(T) - H(T_0)$ is obtained by integration of the signal delivered by the calorimeter over the whole duration of cooling.

Measurements of the enthalpy variation $\Delta H_{T_0}^{T}$ are performed for various temperatures T in order to obtain the enthalpy variation as a function of temperature $\Delta H_{T_0}^{T}(T)$. The specific heat $c_p(T)$ is then calculated by deriving the obtained function compared to temperature;

$$c_p(T) = \frac{1}{M} \left(\frac{\partial \Delta H_{T_0}^{T}(T)}{\partial T} \right)_p \tag{3}$$

3. DESCRIPTION OF THE APPARATUS

This setup allows measurements of the thermophysical properties of materials up to 3300 K in gaseous (helium, nitrogen, argon) or vacuum environments. It consists essentially of an inductive furnace, a resistive furnace, and two setups allowing measurements either of the thermal diffusivity by the laser flash method or the specific heat by drop calorimetry (see Fig. 1). Thermal diffusivity measurements can be performed in the two furnaces, by using the same laser. Specific heat measurements are carried out only in the inductive furnace. The adapted setup (drop calorimeter or laser flash diffusivimeter) is connected to the inductive furnace depending on the studied thermal property.

3.1. Furnaces

The resistive furnace is a horizontal cylinder closed at both ends by two ZnSe windows, which are transparent to the laser wavelength and to the working wavelength range of the IR detector. The specimen, placed vertically in a sample holder situated in the center of the furnace, can be heated from room temperature to 1300 K. Its steady-state temperature is measured by a Type S thermocouple, situated close to it, and connected to a 34970A Agilent multimeter.

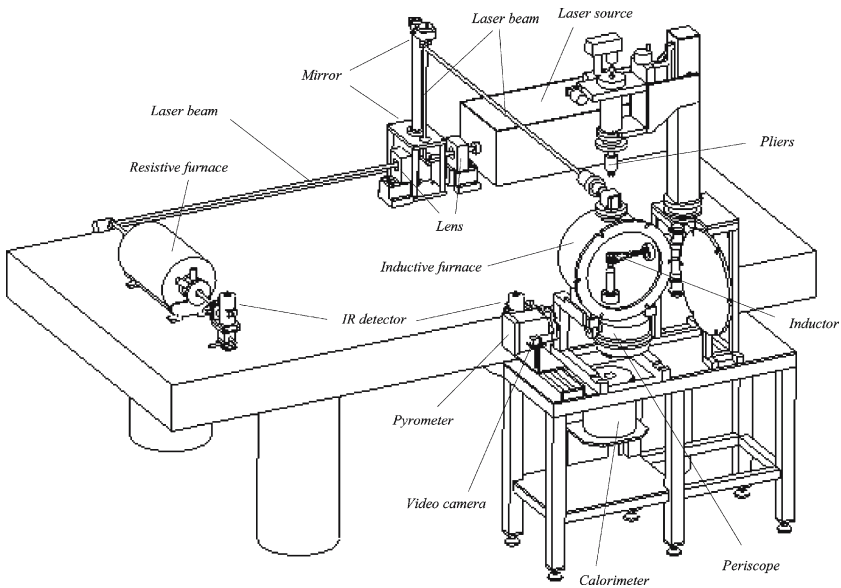

Fig. 1. Schematic diagram of CEA thermal properties apparatus.

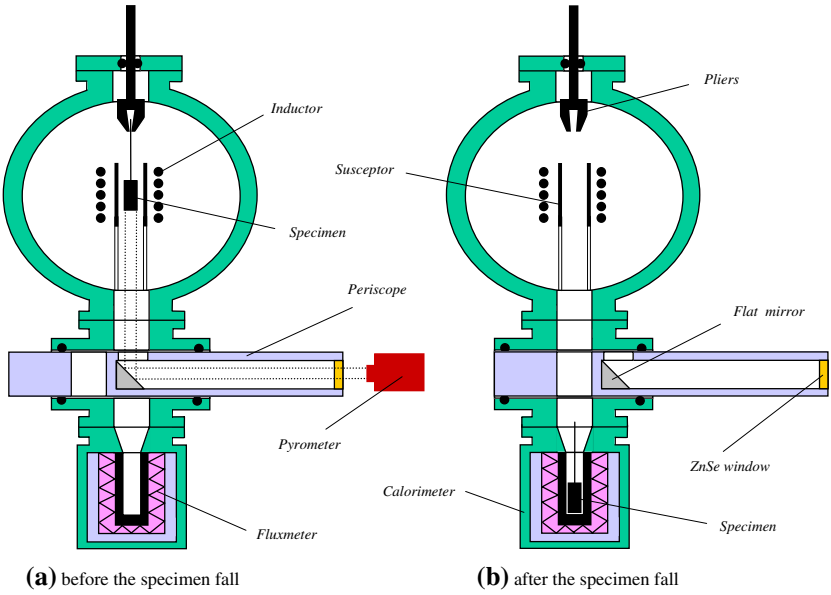

Fig. 2. Inductive furnace – "drop calorimetry" configuration.

The inductive furnace is a water-cooled enclosure in the center of which a heating inductor (or inductive coil) and a susceptor are placed along a vertical axis (see Fig. 2). The inductor is connected to a high-frequency power source and water-cooled. The susceptor is a graphite cylinder heated by induction, the specimen situated inside the susceptor being heated by radiative transfer. This inductive furnace can be used to heat a specimen extremely rapidly (absence of thermal inertia), at a very high temperature (from 600 to 3300 K) and avoid any pollution from the heating source. The specimen temperature is measured by four calibrated bichromatic infrared pyrometers having temperature operating ranges which cover that of the furnace. The distance between the specimen and the pyrometers is around 500 mm. A study of the pyrometers' optical resolution has shown that the measurement zone on the specimen has a 7–8 mm diameter.

3.2. Drop Calorimeter

For the heat capacity measurements by drop calorimetry, the specimen is attached to a tungsten wire connected to motorized pliers (see Fig. 2). The pliers, fixed at the top of the inductive furnace by an airtight

connection, are associated on a multi-axis positioning system used to place the specimen (8 mm in diameter and 10 mm thick) in the center of the graphite susceptor with a resolution of ± 0.1 mm. When the temperature of the specimen is stable, the pliers release the wire and the sample falls in the calorimeter.

The calorimeter is a Calvet-type heat-flow calorimeter consisting of a fluxmeter situated between a measuring cell and an isothermal enclosure. The heat flow exchanged between the measuring cell and the isothermal enclosure is detected by the fluxmeter comprising approximately 500 chromel/alumel thermocouples connected in series. The signal delivered by the fluxmeter is measured by the 34970A multimeter. The temperature of the isothermal enclosure is kept constant to less than 0.1 K (between room temperature and 50°C) by a thermostated bath. A molybdenum cylinder is placed in the cell in order to homogenize the field of temperature and to increase the heat capacity of the calorimeter.

The calorimeter and the inductive furnace are connected together via a mobile "periscope" which has the three following functions depending on its position (see Fig. 2):

- To thermally isolate the furnace from the calorimeter during the heating of the specimen, by positioning a radiation shield between them,
- To allow the transfer of the sample when it falls from the furnace down the calorimeter. A hole is aligned with the furnace and the calorimeter, when the pliers open. The radiation shield is repositioned immediately after the fall of the specimen.
- To optically transmit the image of the specimen via a 90° flat mirror and a ZnSe window to a video camera associated with a lighting device of the specimen, in order to visualize the specimen during its positioning in the susceptor, or to measure the specimen temperature, before its fall, with an IR pyrometer. The pyrometer and camera are installed on a linear stage used to put one or the other opposite to the mirror.

The calorimeter can be easily disconnected from the periscope and moved along a vertical axis in order to extract the specimen from the calorimeter after the test. The inductive furnace, the "periscope," and the calorimeter operate under vacuum (10^{-4} mbar) or an inert atmosphere in order to avoid any degradation or oxidation of the specimen at high temperature. The temperature of the isothermal enclosure is measured by a calibrated 100 Ω platinum resistance thermometer (PRT) connected to the 34970A multimeter.

3.3. Laser Flash Diffusivimeter

Depending on the test temperature, one furnace or the other is used to heat the specimen. For thermal diffusivity measurements performed between 300 and 1300 K, the specimen (10 mm in diameter and about 1–3 mm thick) is positioned vertically in the resistive furnace. For very high temperature measurements (600–3000 K), it is positioned horizontally on the top of the graphite susceptor, inside the inductive furnace. In this case, the calorimeter and the pliers are removed, and, respectively, replaced by a lid and by an optical device consisting of a 90° flat mirror and a ZnSe window (see Fig. 3).

The source used to irradiate the front face of the specimen is a Nd:phosphate glass laser, having a wavelength of 1054 nm and a pulse duration of around 450 μs. A flat mobile mirror, situated at the beginning of the laser path, can be used to direct the beam to one or the other furnace (see Fig. 1). It is then transmitted to either the inductive or resistive furnace by a set of lenses and mirrors in order that its diameter is approximately 10 mm on the specimen. A safety hood surrounds the laser beam over all its optical path, to avoid accidental injuries to the user.

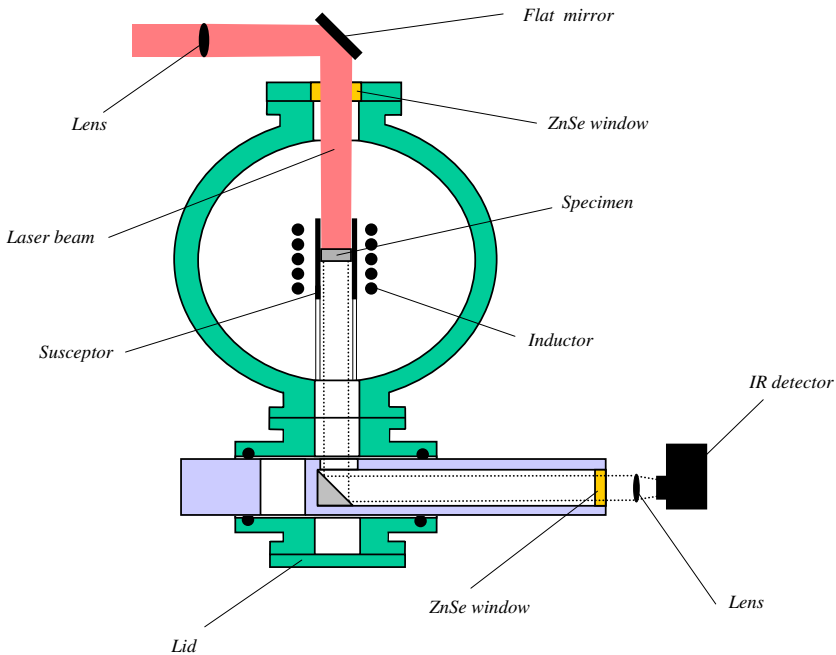

Fig. 3. Inductive furnace – "flash diffusivimeter" configuration.

The alignments of the optical elements (lenses, mirrors, diaphragm, etc.) are performed with a HeNe laser concentric with the Nd:phosphate glass laser. The beam is introduced horizontally in the resistive furnace, and vertically in the inductive furnace, by the ZnSe windows situated on its top. A photodiode is used to determine the duration, the form of the pulse, and the time origin which corresponds to the time when the laser beam irradiates the specimen.

The induced temperature rise on the rear face of the specimen is measured by optical means with two infrared detectors, an HgCdTe detector for the temperature range of 300–1300 K and an InGaAs detector for the temperature range of 1100–3300 K. An optical lens is associated with each IR detector in order that its target diameter is the same as the diameter of the specimen. In the inductive furnace, the image of the specimen is optically transmitted by the "periscope" to the IR detector situated near the pyrometer described previously.

A specific amplification system is associated with each detector in order to optimize the signal-to-noise ratio. The analog signal delivered by the detector is first amplified, with a resistance bridge device or a current/voltage converter, depending on the type of detector (photoconductor or photovoltaic). The baseline (constant signal before the flash) is then subtracted using a differential amplifier. The signal is finally filtered by a low-pass filter having a cut-off frequency of 25 kHz, before being converted by the A/D converter of a NI PCI-6052 data acquisition device.

3.4. Setup Control and Data Acquisition System

All the instruments (pliers, vacuum pump, laser, periscope, etc.) and the safety elements (shutter, safety hoods, etc.) are controlled by a Telemecanic TSX Premium PLC programmable logical controller (PLC) connected to a computer. If one of the safety requirements is not followed, then the PLC prohibits the continuation of the test until this requirement is satisfied. The computer runs a Labview program that controls both the data acquisition and the whole setup via the PLC.

The acquisition of the thermograms is performed with either the 34970A multimeter for specific heat measurements, or the NI PCI-6052 data acquisition device for thermal diffusivity measurements. All the parameters of the data acquisition (amplification gains, frequency, number of acquisition points, amount of pre-trigger, etc.) are chosen by the user from a Labview human–machine interface. The beginning of the data acquisition is synchronized, either with the laser flash using a trigger signal generated by the NI PCI-6052 data acquisition device, or with the

opening of the pliers started by the PLC. The signals coming from the IR detector or from the calorimeter prior to the trigger (corresponding to the baseline of the thermogram) are stored continuously in a circular pre-trigger memory. When the trigger is detected, the new data are stored in a post-trigger memory.

4. THERMAL DIFFUSIVITY AND HEAT CAPACITY MEASUREMENTS

The performance of this new setup has been tested by measuring the thermal diffusivity of different materials and by performing drop calorimetry tests. As there are currently no certified reference materials (CRM) for thermal diffusivity at high temperature, we selected Armco iron and POCO AXM-5Q1 graphite as test materials because they have well-known and reproducible thermal properties.

The thermal diffusivities of Armco iron and POCO AXM-5Q1 graphite are determined under an inert gas environment (argon or helium) on 2 or 3 mm thick specimens, respectively, in the temperature range of 300–1300 K and 300–3000 K. The different furnaces and IR detectors are used according to the temperature range of the test. Before carrying out the measurements, the elements (mirrors, lenses, diaphragms, IR detectors, etc.) located on the optical path upstream and downstream of the specimen are adjusted so that the laser beam is centered on the specimens, and the diameters of the IR detector target and of the specimens are the same.

Tables I and II show a comparison between our first results and values from polynomial expressions, determined by LNE [7] from results reported by several authors [8–12]. These results are the average of three successive measurements performed under the same experimental conditions. The repeatability of these three measurements is better than 1% below 1300 K and better than 3% for temperatures between 1300 and 2500 K. The relative variations between our measurements and the values resulting from the polynomial expressions are less than 1.5% for Armco iron and less than 5.5% for POCO AXM-5Q1 graphite. Above 2500 K, thin layers appear on the surface of the specimens during the test. This chipping, certainly due to the presence of residual oxygen in the inductive furnace, leads inevitably to a strong decrease of the measured thermal diffusivity.

The setup was also examined in the drop calorimetry configuration by carrying out tests under an inert gas environment on tungsten specimens of approximately 7 g in the temperature range of 800–2800 K. All the operations were correctly synchronized: opening of the pliers, displacement of the mobile periscope, fall of the specimen in the calorimeter, and

Table I. Thermal Diffusivity Measurements of Armco Iron in the Resistive Furnace

Temperature (K)	IR Detectors	Thermal Diffusivity (10^{-6} $m^2 \cdot s^{-1}$)		
		LNE/CEA results	Results from Refs. 8–12	Rel. deviation (%)
293	HgCdTe	20.30	20.36	−0.3
774	HgCdTe	8.315	8.198	1.4
1273	HgCdTe	6.311	6.240	1.1

Table II. Thermal Diffusivity Measurements of POCO Graphite in the Inductive Furnace

Temperature (K)	IR Detectors	Thermal Diffusivity (10^{-6} $m^2 \cdot s^{-1}$)		
		LNE/CEA results	Results from Refs. 8–12	Rel. deviation (%)
293	HgCdTe	63.42	65.90	−3.8
1023	HgCdTe	19.19	19.54	−1.8
1025	InGaAs	18.46	19.50	−5.4
1272	HgCdTe	15.83	15.48	2.2
1273	InGaAs	15.33	15.46	−0.8
2123	InGaAs	10.67	10.26	4.0
2273	InGaAs	9.92	9.97	−0.5
2773	InGaAs	8.91	–	–
2873	InGaAs	5.19	–	–
2973	InGaAs	4.35	–	–

acquisition of the thermogram. Since the calorimeter has not been calibrated, the enthalpy variations could not be calculated from the obtained thermograms. The next step will be to calibrate the calorimeter, either by using certified reference materials, such as molybdenum (SRM781) or synthetic sapphire (SRM720) certified by NIST (National Institute of Standards and Technology), or by electrical substitution (Joule effect calibration).

Figures 4 and 5 present, respectively, a thermogram of thermal diffusivity measurements on POCO AXM-5Q1 graphite at 2273 K, and a thermogram of the enthalpy variation measurement obtained on tungsten at 2773 K. All acquired thermograms up to 2800 K have a good signal-to-noise ratio, and those related to the thermal diffusivity measurements do not show a peak at the origin of time (usually induced by the laser flash). It was observed that above 2300 K, it was better to perform tests under helium rather than under vacuum or argon, in order to limit the appearance of electrical arcs between the susceptor and the inductor.

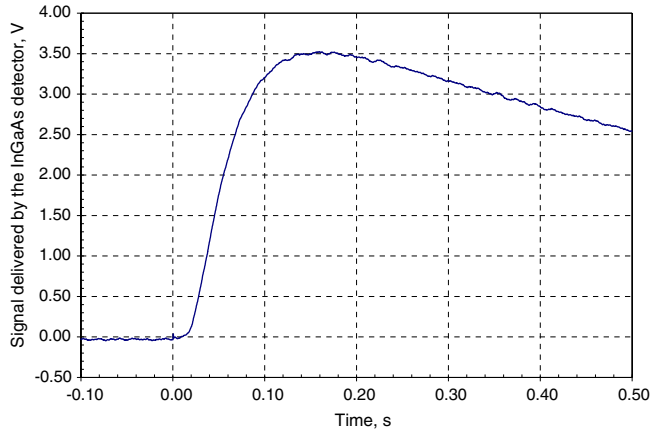

Fig. 4. Thermogram of thermal diffusivity measurements on POCO AXM-5Q1 graphite at 2273 K.

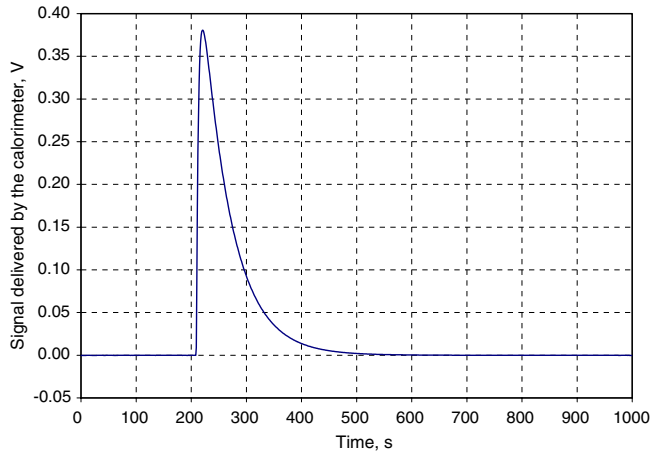

Fig. 5. Thermogram of specific heat measurements on tungsten at 2773 K.

However, beyond 2800 K, these electrical arcs cannot be avoided and they generate a strong noise in the thermograms as shown in Fig. 6 for one result obtained at 2973 K. Nevertheless, this thermogram can be fitted and the thermal diffusivity, a, is evaluated to be $4.35 \times 10^{-6}\,\mathrm{m^2{\cdot}s^{-1}}$. This thermogram can also be filtered to help the operator to appreciate the accuracy of the adjustment. Figure 7 presents the result of the filtering with the associated fit. The identified value of a is then equal to

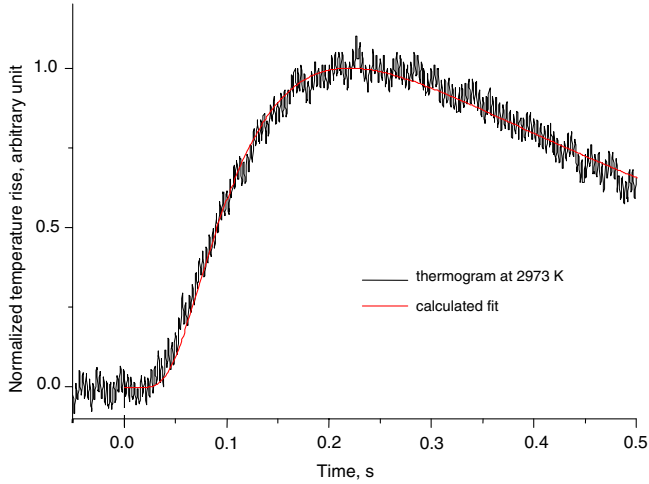

Fig. 6. Thermogram obtained for POCO AXM-5Q1 graphite at 2973 K and its theoretical fit. The calculated thermal diffusivity is $4.35 \times 10^{-6}\,m^2 \cdot s^{-1}$.

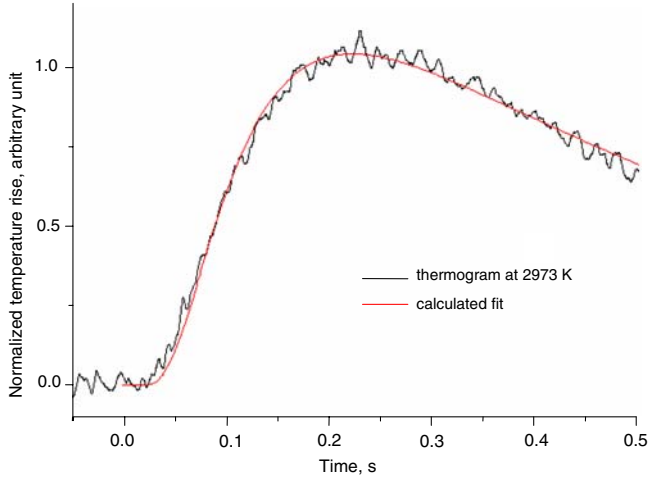

Fig. 7. Filtering result (with a fifth-order Chebyshev filter) of the thermogram obtained on POCO AXM-5Q1 graphite at 2973 K and its theoretical fit. The calculated thermal diffusivity is $4.28 \times 10^{-6}\,m^2 \cdot s^{-1}$.

$4.28 \times 10^{-6}\,m^2 \cdot s^{-1}$. The difference between calculated values of the thermal diffusivity before and after filtering is less than 1.5%, which shows the possibility to exploit noisy thermograms.

5. CONCLUSION

The *CEA* has developed a new setup for measurements of the thermal diffusivity by the laser flash method or the specific heat by drop calorimetry over the temperature range of 300–2800 K. It was tested by measuring the thermal diffusivity of Armco iron and POCO AXM-5Q1 graphite. The values obtained differed by less than 5% with data in the literature. The calorimeter will be soon calibrated to exploit the first drop calorimetry tests that were performed.

During the adjustment steps of the setup and the first tests, some problems were observed for measurements carried out above 2800 K: electromagnetic disturbances generated by the high-frequency power source appear, causing inopportune trigger of the laser and perturbing several pieces of equipment (IR detectors and pyrometers). Moreover, electrical arcs occur between the graphite susceptor and the inductor, inducing noise on the thermograms and damaging the susceptor. The design and the manufacture of the susceptor and the inductor will be improved in order to avoid these problems. Measurements could then be carried out up to 3300 K.

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