A NEW APPARATUS FOR THERMAL DIFFUSIVITY AND SPECIFIC HEAT MEASUREMENTS AT VERY HIGH TEMPERATURE[1]

B. Hay[2,4], S. Barré[3], J-R. Filtz[2], M. Jurion[3], D. Rochais[3] and P. Sollet[2]

[1] Paper presented at the Seventeenth European Conference on Thermophysical Properties, September 5-8, 2005, Bratislava, Slovak Republic

[2] Thermophysical properties laboratory, Thermal and Optical Division, Laboratoire National de Métrologie et d'Essais, 1 rue Gaston Boissier, 75015 Paris, France

[3] CEA-Le Ripault, B.P. 16 - 37260 MONTS, France

[4] To whom correspondance should be adressed. E-mail : bruno.hay@lne.fr

ABSTRACT

The thermal characterisation of a material under its conditions of use (temperature, atmosphere…) is an essential step to check its adequacy with a specific application and to anticipate its behaviour. For their own needs of material characterisation, CEA has developed with LNE a new apparatus to study thermophysical properties of solid materials in the range from 300 K to 3300 K. This set up allows to measure either thermal diffusivity by laser flash method or 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 accordance with results obtained by other laboratories with a relative deviation less than 6 %.

KEY WORDS: drop calorimetry ; flash method ; high temperature ; 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 temperature up to 1300K [1]. But, at macroscopic scale, thermal diffusivity and specific heat measurements were only performed at temperature up to 800K and 1000K respectively. Consequently, the *CEA le Ripault* centre has decided to construct a new set-up allowing the determination of thermal diffusivity by flash method (by laser excitation) on the temperature range of 300 K to 3300 K, and the specific heat by ballistic method between 600 and 3300 K. This apparatus satisfies two essential points:

- to allow the measurement of these thermal properties with a high sensitivity for a great material diversity, from super insulating 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 fences.

CEA, which already developed a drop calorimeter in the past [2], sub-contracted the construction of this new set up to the *Laboratoire National de Métrologie et d'Essais (LNE)*. The *LNE* has carried out for many years this kind of measurements, 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 characterisation 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 the drop calorimetry (or ballistic calorimetry).

2.1 Thermal diffusivity measurement

The thermal diffusivity is measured by 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 in the case of an opaque, homogeneous and isotropic specimen.

The heat conduction equation is analytically solved in the 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 being described by the following expressions:

$$\tau = \frac{e^2}{a} \quad (1) \qquad \text{and} \qquad Bi = \frac{h \cdot e}{\lambda} \quad (2)$$

with e specimen thickness (m),

a thermal diffusivity ($m^2 \cdot s^{-1}$),

h convection/radiation exchange coefficient ($W \cdot m^{-2} \cdot K^{-1}$),

λ thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$).

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

2.2 Specific heat measurement

Enthalpy measurement by drop calorimetry consists to heat a specimen having a mass *M* at a constant temperature *T* in a furnace and to drop 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 enthalpy variation $\Delta H_{T_0}^{T}$ are performed for various temperature *T* in order to obtain enthalpy variation as a function of temperature $\Delta H_{T_0}^{T}(T)$. The specific heat is then calculated by deriving the obtained function compared to temperature.

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

3 DESCRIPTION OF THE APPARATUS

This set up allows to measure thermophysical properties of material up to 3300 K in gaseous (helium, nitrogen, argon) or vacuum environments.

It consists essentially of an inductive furnace, a resistive furnace and two set-up allowing to measure either thermal diffusivity by laser flash method or 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 set up (drop calorimeter or laser flash diffusivimeter) is connected to the inductive furnace depending on the studied thermal property.

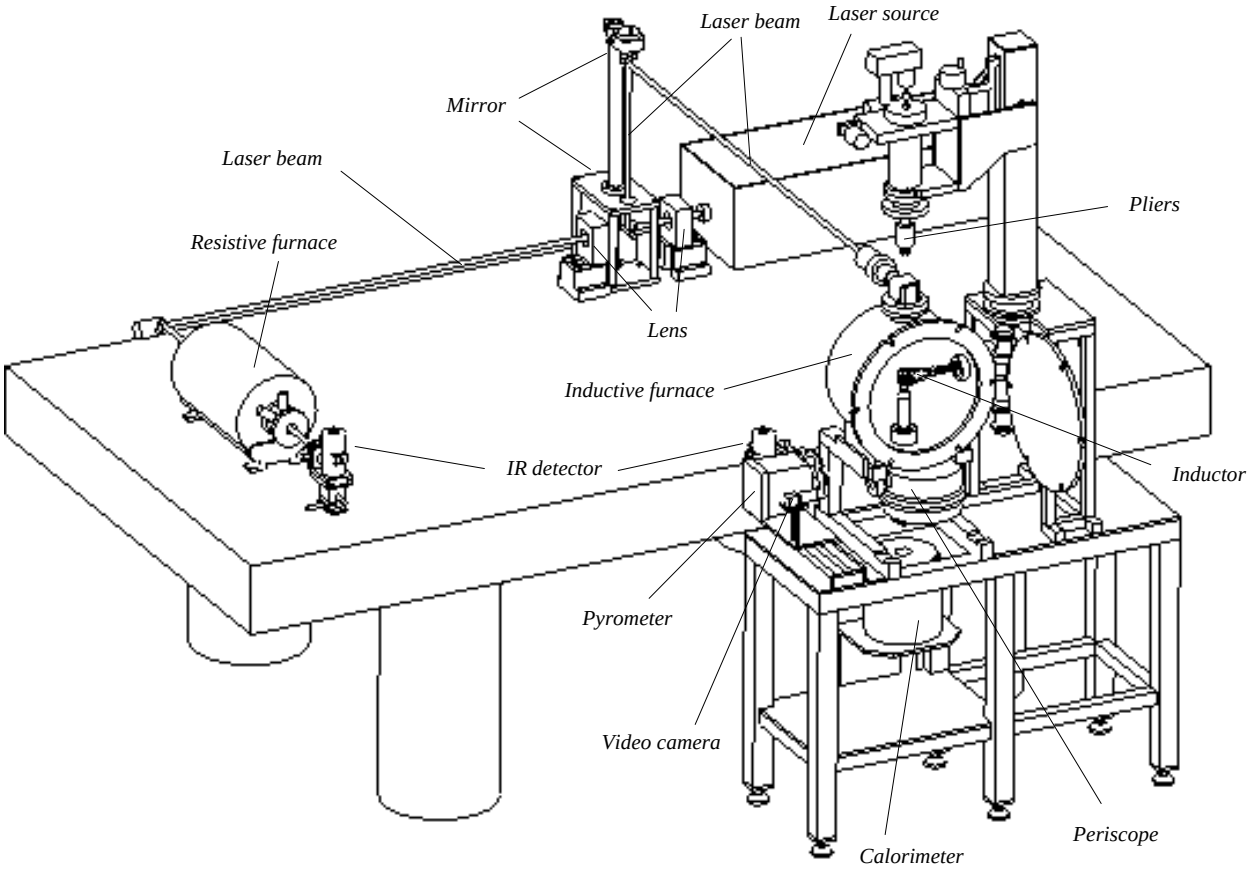


Fig. 1. Schematic diagram of CEA thermal properties apparatus

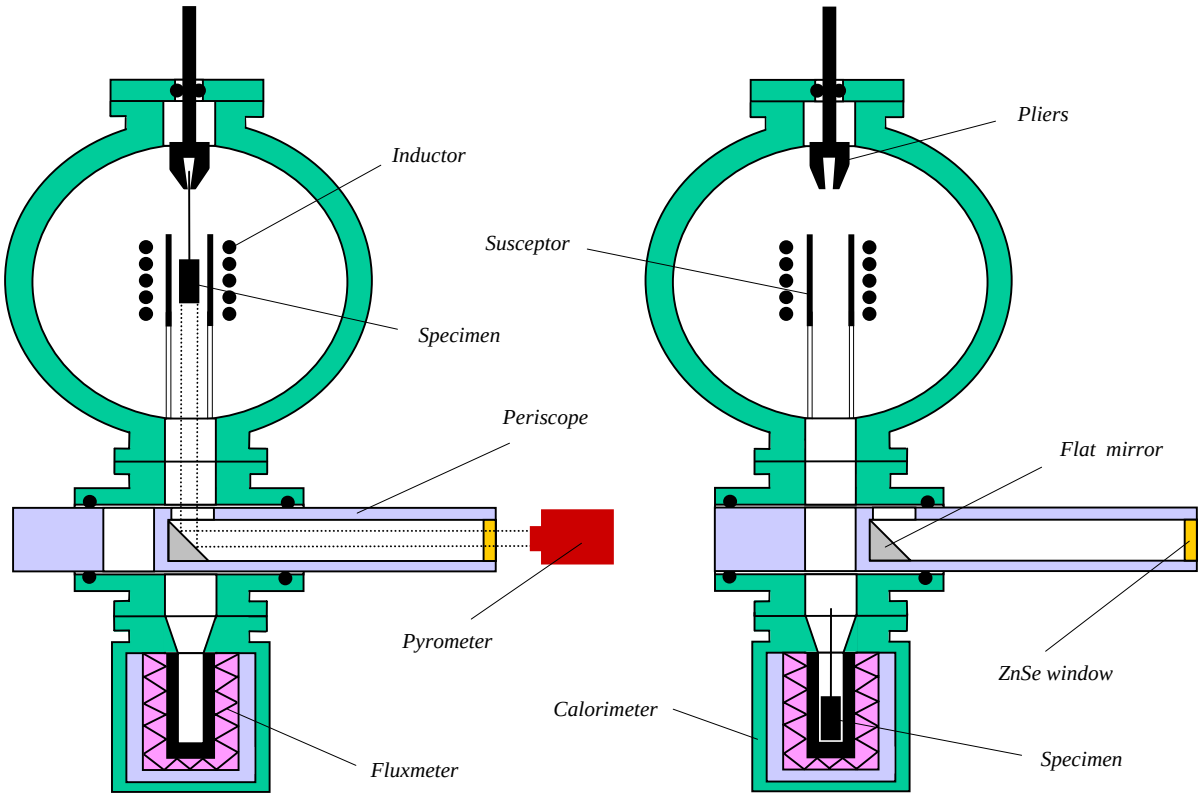
3.1 The furnaces

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 centre of the furnace, can be heated from room temperature to 1300 K. Its steady state temperature is measured by a type S thermocouple, situated in its vicinity, and connected to a 34970A Agilent multimeter.

The inductive furnace is a water cooling enclosure in the centre of which an heating inductor (or inductive coil) and a susceptor are placed in 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 allows 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 infra-red pyrometers having temperature operating ranges which cover the one 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 is a 7 to 8 mm diameter large.



a) before the specimen fall

b) after the specimen fall

Fig. 2. Inductive furnace - “Drop calorimetry” configuration

3.2 The 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 allowing to place the specimen (8 mm in diameter and 10 mm thick) in the centre 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 used is a Calvet-type heat-flow calorimeter constituted by 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 made up of 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 to 50 °C) by a thermostated bath. A molybdenum cylinder is placed in the cell in order to homogenise 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 IR pyrometer. The pyrometer and camera are installed on a linear stage allowing 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 work under vacuum (10^{-4} mbar) or 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 ohm platinum resistance thermometer (PRT) connected to the 34970A multimeter.

3.3 The 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 to 3 mm thick) is put vertically in the resistive furnace. For very high temperature measurements (600 to 3000 K), it is put 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 constituted 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, allows to direct the beam to one or the other furnace (see Fig.1). It is then transmitted to the inductive furnace or the resistive one 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 on all its optical path, to avoid that it accidentally injures the user. The alignments of the optical elements (lenses, mirrors, diaphragm…) are performed with a HeNe laser concentric with the Nd:phosphate glass laser.

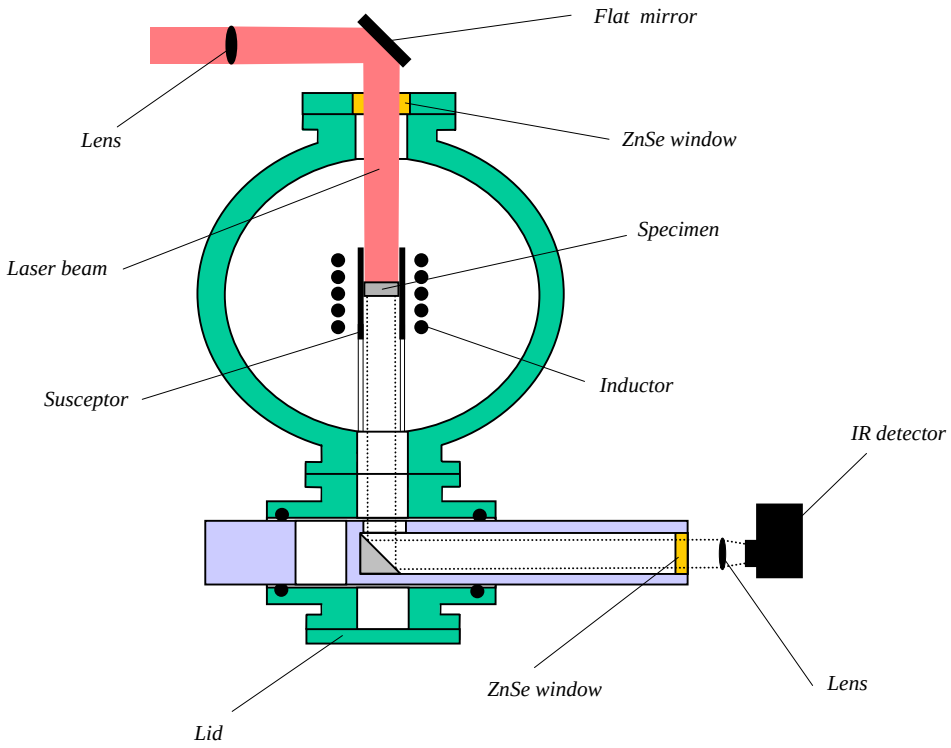


Fig. 3. Inductive furnace - “flash diffusivimeter” configuration

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 way with two Infrared detectors, HgCdTe detector for the temperature range [300 to 1300 K] and InGaAs detector for the temperature range [1100 to 3300 K]. An optical lens is associated to 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 to each detector in order to optimize the signal to noise ratio. The analogical signal delivered by the detector is first amplified, with a resistance bridge device or a current/voltage convertissor depending on the type of detector (photoconductor or photovoltaic). The baseline (constant signal before the flash) is then subtracted using a differential amplificator. The signal is finally filtered by a low-pass filter having a cut-off frequency of 25KHz, before being converted by the A/D converter of a NI PCI-6052 data acquisition device.

3.4 Set up control and data acquisition system

All the instruments (pliers, vacuum pump, laser, periscope …) and the safety elements (shutter, safety hoods …) are controlled by a Telemecanic TSX Premium PLC (programmable logical controllers) connected to a computer. If one of the safety requirements is not respected 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 set-up via the PLC.

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

4 THERMAL DIFFUSIVITY AND HEAT CAPACITY MEASUREMENTS

The performances of this new set-up have been checked by measuring thermal diffusivity on different materials and by performing drop calorimetry tests. As there are currently no Certified Reference Materials (CRM) for thermal diffusivity at high temperature, we select Armco iron and POCO AXM-5Q1 graphite as testing materials because they have well-known and reproducible thermal properties.

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

Tables I and II present a comparison between our first results and values coming from polynomial expressions, determined by the LNE [7] from results given 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 lower than 1 % below 1300 K and lower than 3 % for temperatures between 1300 and 2500 K. The relative variations between our measurements and the values resulting from the polynomial expressions are lower than 1.5 % for the Armco iron and lower than 5.5 % for the 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.

Temperature (K)	IR Detectors	Thermal Diffusivity (10^{-6} $m^2 \cdot s^{-1}$)		Rel. deviation (%)
		LNE/CEA results	Results from [8-12]	
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 I. Thermal Diffusivity measurements of Armco iron in the resistive furnace

Temperature (K)	IR Detectors	Thermal Diffusivity (10^{-6} $m^2 \cdot s^{-1}$)		Rel. deviation (%)
		LNE/CEA results	Results from [8-12]	
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*	/	/

Table II. Thermal Diffusivity measurements of POCO graphite in the inductive furnace

The set up was also examined in drop calorimetry configuration by carrying out tests under inert gas on tungsten specimens of approximately 7 g in the temperature range [800 to 2800 K]. All the actions were correctly synchronized : opening of the pliers, displacement of the mobile periscope, fall of the specimen in the calorimeter and acquisition of the thermogram.

The calorimeter not being yet calibrated, the enthalpy variations could not be calculated from the obtained thermograms. The next step will consist 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).

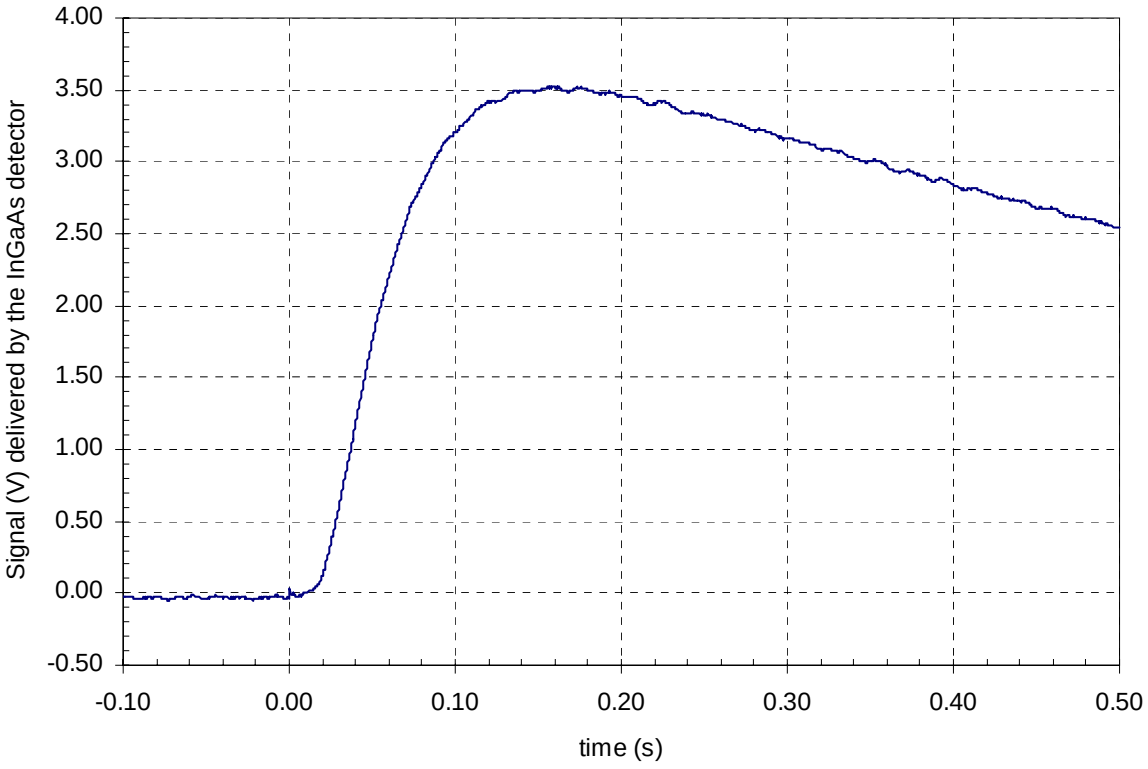


Fig. 4. Thermogram of thermal diffusivity measurement obtained on POCO AXM-5Q1 graphite at 2273 K

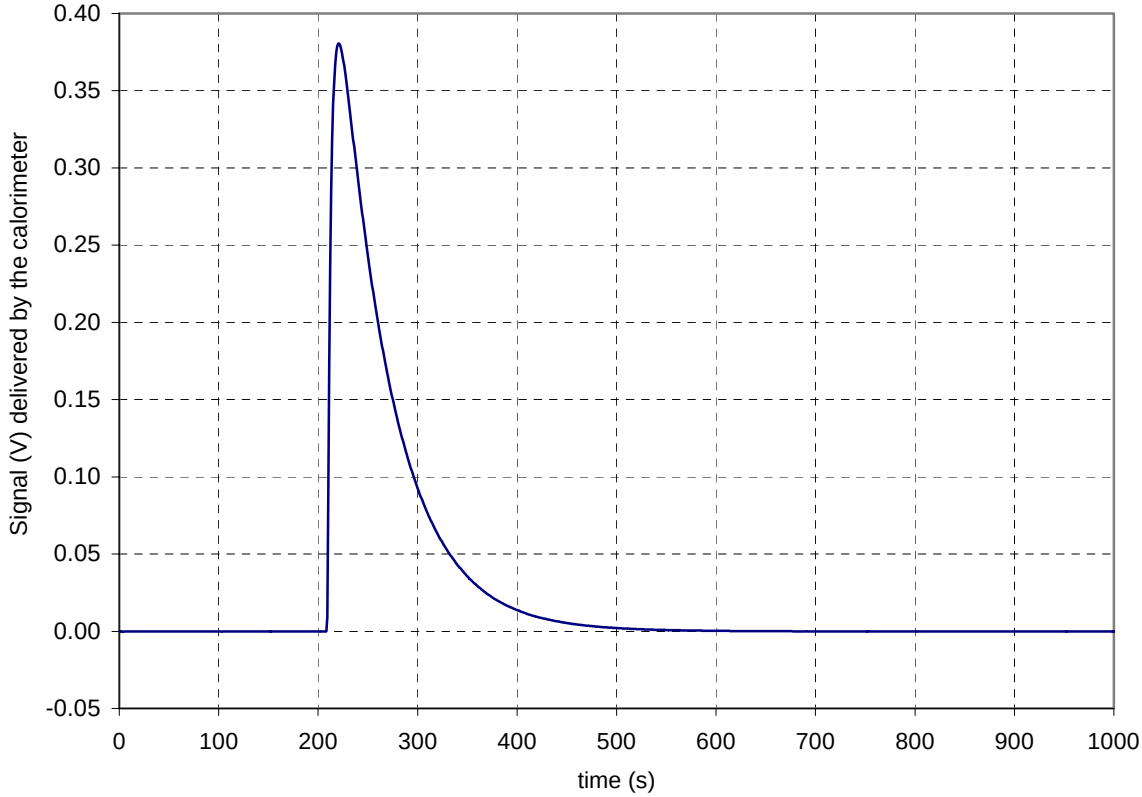


Fig. 5. Thermogram of specific heat measurement obtained on tungsten at 2773 K

Figures 4 and 5 present respectively a thermogram of thermal diffusivity measurement obtained on POCO AXM-5Q1 graphite at 2273 K, and a thermogram of enthalpy variation measurement obtained on tungsten at 2773 K. All the acquired thermograms up to 2800 K have a good signal to noise ratio and those relating to the thermal diffusivity measurements do not present any 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. However beyond 2800 K, these electrical arcs cannot be avoided and they generate a strong noise on the thermograms as shown on figure 6 for one result obtained at 2973K.

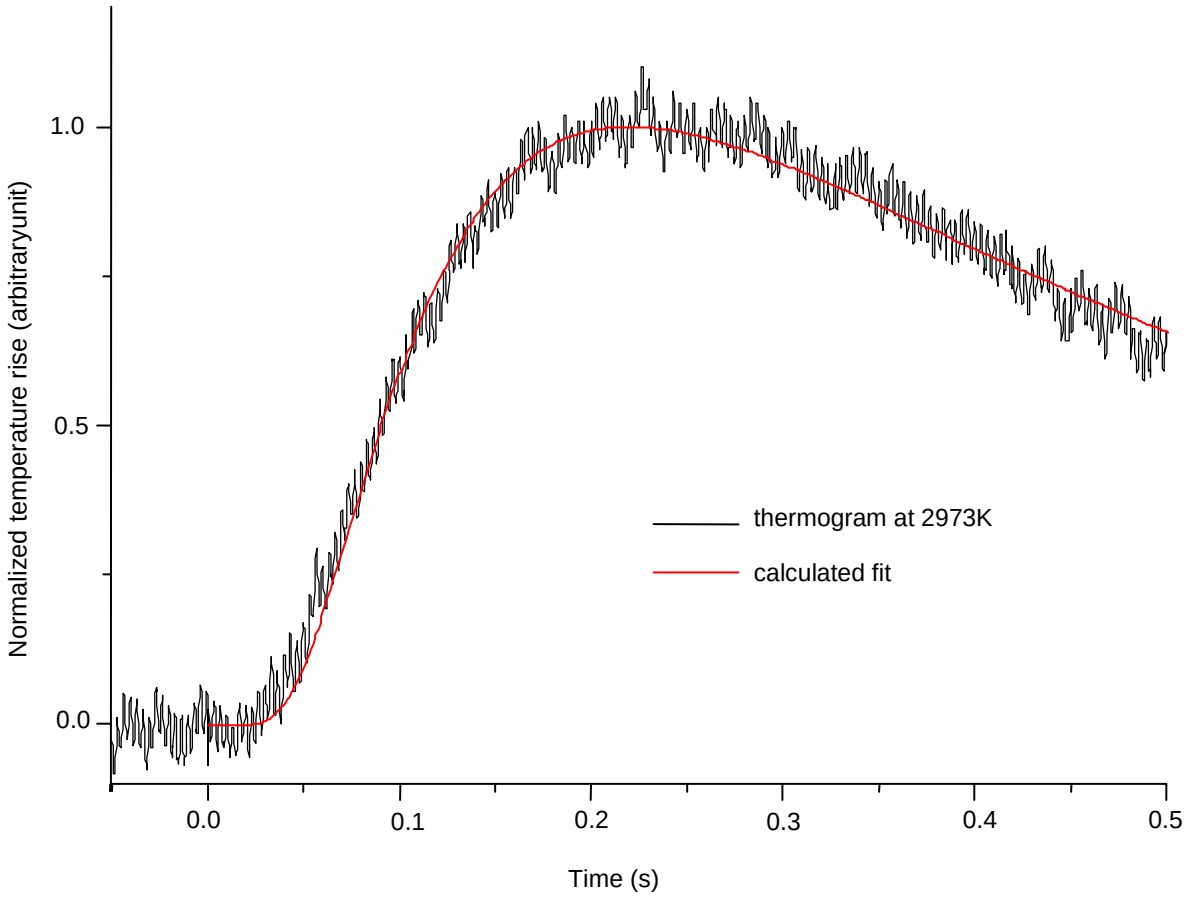


Fig. 6. Thermogram obtained on POCO AXM-5Q1 graphite at 2973 K and its theoretical fit.

Nevertheless, this thermogram can be fitted and the thermal diffusivity, *a*, is evaluated to 4.35 10^{-6} m²/s. 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 equal to 4.28 10^{-6} m²/s. 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.

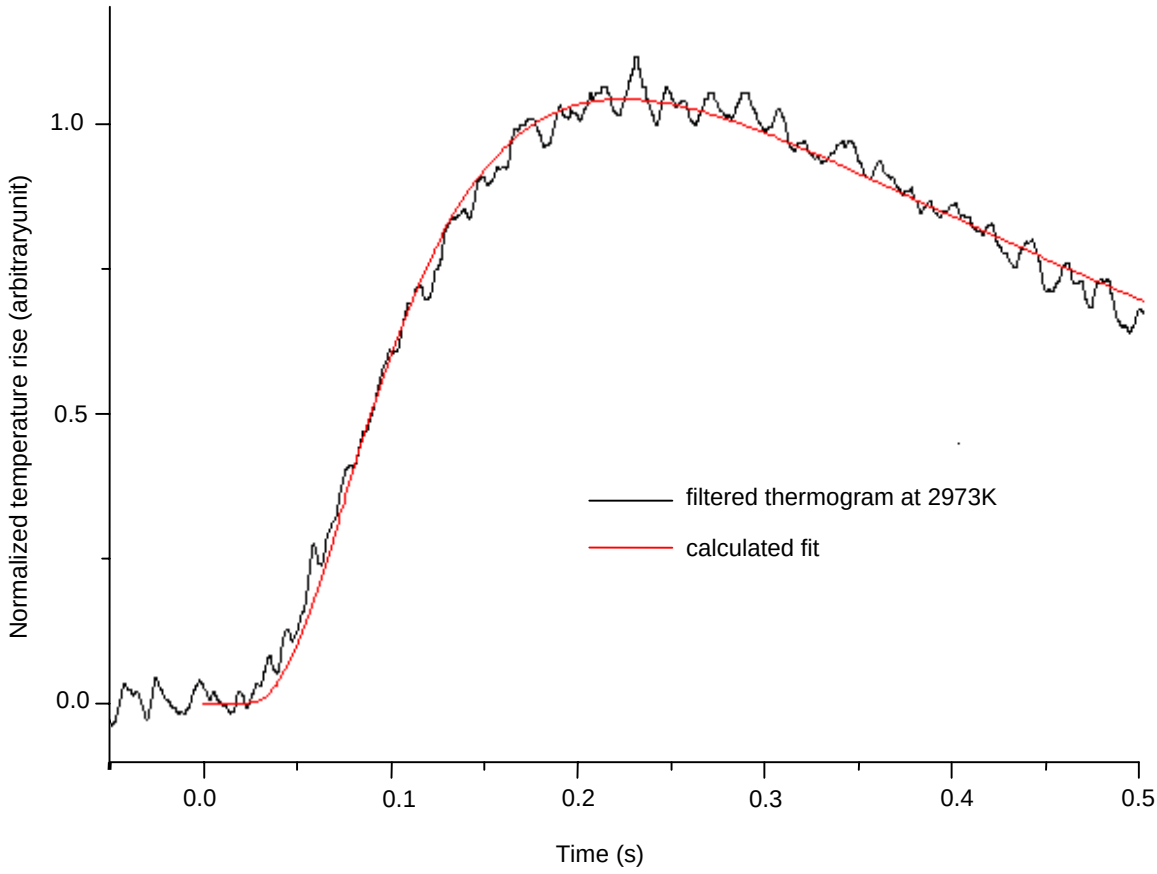


Fig. 7. Filtering result (with a fifth order Chebyshev filter) of the thermogram obtained on POCO AXM-5Q1 graphite at 2973 K and its theoretical fit.

5 CONCLUSION

The CEA has now a new set-up allowing to measure thermal diffusivity by laser flash method or specific heat by drop calorimetry on the temperature range of 300 K to 2800 K. It was tested by measuring thermal diffusivity values on Armco iron and POCO AXM-5Q1 graphite.

The values obtained differ less than 5 % with the data indicated in the literature. The calorimeter will be soon calibrated in order to exploit the first drop calorimetry tests which were performed.

During the adjustment steps of the set-up and the first tests, some problems were observed for measurements carried out higher than 2800 K : electromagnetic disturbances generated by the high-frequency power source appear, causing inopportune trigger of the laser and perturbing several equipments (IR detectors and pyrometers). Moreover, electrical arcs occur between the graphite susceptor and the inductor, inducing noises 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.

REFERENCES

1. D. Rochais, H. Le Houëdec, F. Enguehard, J. Jumel, F. Lepoutre, *Microscale thermal characterization at temperatures up to 1000°C by photoreflectance microscopy. Application to the characterization of carbon fibers*, Journal of Physic D: Applied Physics, **38**, pp 1498-1503 (2005)
2. G. Morizur, A. Radenac and J-C. Cretenet, *Calorimètre à chute 3000 K - Application à la détermination de la chaleur spécifique du tungstène*, High temperatures-High Pressures, **8**, pp 113-120 (1976)
3. B. Hay, J-R. Filtz and J. Hameury, *Propriétés Thermiques des Matériaux - la plate-forme métrologique du LNE*, 10th International Metrology Congress, Saint-Louis, France (2001)
4. B. Hay, *Construction et validation métrologique d'un calorimètre à chute*, 28^{éme} Journées de Calorimétrie et d'Analyse Thermique (JCAT), Dunkerque, France (1997)
5. B. Hay, J-R. Filtz, J. Hameury and L. Rongione, *Uncertainty of thermal diffusivity measurements by laser flash method*, 15th Symposium on Thermophysical Properties, Boulder, Colorado, U.S.A. (2003)
6. W. J. Parker, R. J. Jenkins, C. P. Bulter and G. L. Abbott, *Flash method of determining thermal diffusivity, heat capacity and thermal conductivity*, Journal of Applied Physics, **32**, pp 1679-1684 (1961)
7. B. Hay, J-R. Filtz, and J-C. Batsale, *Mesure de la diffusivité thermique par la méthode flash.* Techniques de l'Ingénieur, **R2955** (2004)
8. Y. S. Touloukian, R.W. Powell, C. Y. Ho and M.C. Nicolaou, *Thermophysical properties of matter. Thermal Diffusivity*, **10**, IFI/Plenum (1973)
9. H. R. Shanks, A. H. Klein and G.C. Danielson, *Thermal properties of Armco Iron*, Journal of Applied Physics, **38**, pp 2885-2892 (1967)

10. L. Filoni and L. Lorenzoni, *Thermal diffusivity of ceramic materials and protective coatings by laser-flash method*, High temperatures-High Pressures, **23**, pp 309-315 (1991)
11. A. Dobrosavljevic, N. Perovic and K. Maglic, *Thermophysical properties of POCO AXM-5Q1 graphite in the range 300 to 1800 K*, High temperatures-High Pressures, **19**, pp 303-310 (1987)
12. J. G. Hust, *A fine-grained isotropic graphite for use as NBS thermophysical property RM's from 5 to 2500 K*, NBS Special Publication, pp 260-289 (1984)