Deliverable D1.3

Devices for Thermo-Physical Properties Characterisation

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History of Changes

Version	Date	Author (Organization)	Change	Page
1.0	09.07.2019	Diana Vitiello (UNILIM), Ilona Kieliba (RWTH)	Creation of the first version	all
1.1	30.08.2019	Glyn Derrick (UNILIM)	English and general formatting check	all

Table 1. Related Work Packages status

Work package		Status	Description
WP 1: Improvement of measurement tools	Task 1.3: Devices for Thermo-Physical Properties Characterisation	finished	Overview about the available devices

Table of contents

1. Introduction

The ATHOR (Advanced THermomechanical multiscale mOdelling of Refractory linings) project is dedicated to the development of experimental and computational methods to characterise and model refractory materials. This requires thermo-mechanical material characterisation to determine material parameters and to verify simulation results. Furthermore, it is very important to remember that these properties evolve with the temperature, meaning the behaviour under service conditions is not the same as at room temperature.

Task 1.3 "Devices for Thermo-Physical Properties Characterisation" is entirely dedicated to the development of devices for thermo-physical properties characterisation of different refractory materials. These materials include insulating boards, fireclay bricks, microporous sheets, alumina spinel bricks and castables, magnesia carbon bricks, bauxite etc. The characterisation includes methods for the determination of thermal conductivity, thermal diffusivity, specific heat capacity, thermal expansion, thermo-gravimetric analysis etc.

In this report, a list of available devices for the characterisation of the thermo-physical behaviour and their uses in the ATHOR network is given in section 2. For some properties, such as thermal conductivity, thermal diffusivity and heat capacity, devices with different characteristics are available. The table in section 3 summarizes the most important information concerning the devices and a detailed description of each device is provided in section 4.

2. List of devices

1. Laser flash equipment for thermal diffusivity measurements at room and high temperature (IRCER-UNILIM);
2. Hot disk equipment for thermal conductivity measurements at room temperature (IRCER-UNILIM / ISISE-UC);
3. Hot disk equipment for thermal conductivity measurements at medium temperature (ISISE-UC);
4. Hot wire equipment for thermal conductivity measurements at high temperature (GHI-RWTH);
5. Dilatometry equipment for thermal expansion measurements at high temperature (IRCER-UNILIM / GHI-RWTH);
6. Thermomechanical Analysis (TMA) apparatus for thermal expansion measurements at high temperature under constraint (IRCER-UNILIM)
7. Refractoriness under Load / Creep in Compression (RUL/CIC) apparatus for thermal expansion measurements at high temperature (GHI-RWTH);
8. Differential Scanning Calorimetry (DSC) apparatus for heat capacity measurements (GHI-RWTH);
9. Differential Thermal Analysis / Thermo-gravimetric Analysis (DTA/TGA) apparatus thermal analysis (IRCER-UNILIM).

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3. Table summarizing the most important information

Nr.	Purpose	Sample geometry	Application temperature	Atmosphere	Main interest	Disadvantage
1	Thermal properties measurement.	Disk shape: diameter = 10 mm; thickness = 2 mm	25-1500°C	Air, argon	Thermal diffusivity of a wide range of materials.	It is not suitable for refractory materials with large grain sized due to the small sample sizes required. The heat capacity and density data are required for calculating the thermal conductivity.
2	Thermal properties measurements.	Two samples of any shape with dimensions depending on the dimensions of the sensor used.	Room temperature	Air	Thermal conductivity of a wide range of materials.	One drawback of TPS measurement is that both of the samples need to have one entirely planar side. This makes it difficult for some materials, especially powders or granules.
3	Thermal properties measurements.	Two samples of any shape with dimensions depending on the dimensions of the sensor used.	25-500°C	Air	Thermal conductivity of a wide range of materials.	The oxidation of the sensor does not allow use at higher temperatures. A vacuum system is needed.
4	Thermal properties measurements.	Three rectangular samples: 250x114x50 mm^3	25-1400°C	Air	Thermal conductivity of a wide range of materials.	It gives an average value of thermal conductivity, so it is not suitable for anisotropic materials.
5	Thermal properties measurements.	Rectangular shape: 5x5x25 mm^3	25-1500°C	Air, argon	Thermal expansion.	The samples need to have two flat and parallel faces to ensure contact with the push rod.
6	Thermal properties measurements.	Rectangular shape; the maximum length (included the two alumina plates) has to be of 20 mm.	25-1600°C	Air, argon	Thermal expansion.	Small sample sizes.
7	Thermal properties measurements.	Cylindrical test piece: 50 mm in diameter and height with coaxial bore of 12.5 mm.	25-1700°C	Air	Thermal expansion.	The samples need to have two flat and parallel faces
8	Thermal properties measurements.	Powder.	25-1350°C	Air, Argon	Heat capacity.	The heat capacity value is not accurate at especially at room temperature.
9	Thermal properties measurements.	Powder.	25-1600°C	Air, Argon	Heat capacity, mass loss, physical phenomena.	

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4. Some details about experimental devices

4.1. Laser flash equipment for thermal diffusivity measurements at room and high temperature

The laser flash method measures directly values of thermal diffusivity (α) of a wide range of materials [1]. The thermal conductivity (λ) is then calculated with the Equ. 1:

$$\lambda = \alpha c_p \rho \qquad \textit{Equ. 1}$$

where c_p is the heat capacity and ρ is the density.

The device operates at room and high temperatures (up to 1500°C). The vertical set-up is composed of (Figure 1):

- Laser system at the bottom connected to the measurement part by an optical fibre;
- Sample carrier alumina tube in the centre;
- IR detector on the top.

The sample is placed on a sample holder made of alumina and covered by a cap of silicon carbide. This is then mounted on a carrier system, which is located in the furnace. To control the temperature increment, a thermocouple is located on the alumina tube close to the sample. After the sample reaches a predetermined temperature, a burst of energy emanating from a pulsed laser impacts on the front face of the sample. This high intensity energy diffuses throughout the material and an IR detector records the resulting time dependent temperature on the opposite face. The device is equipped with a cooling thermostat to guarantee the long-term temperature stability. In addition, the IR detector is cooled by liquid nitrogen, which is added every 3 hours of measurement. Typically, the entire measurement is made under an inert atmosphere (argon) thanks to the presence of a vacuum system, which allows the removal of the air from the furnace.

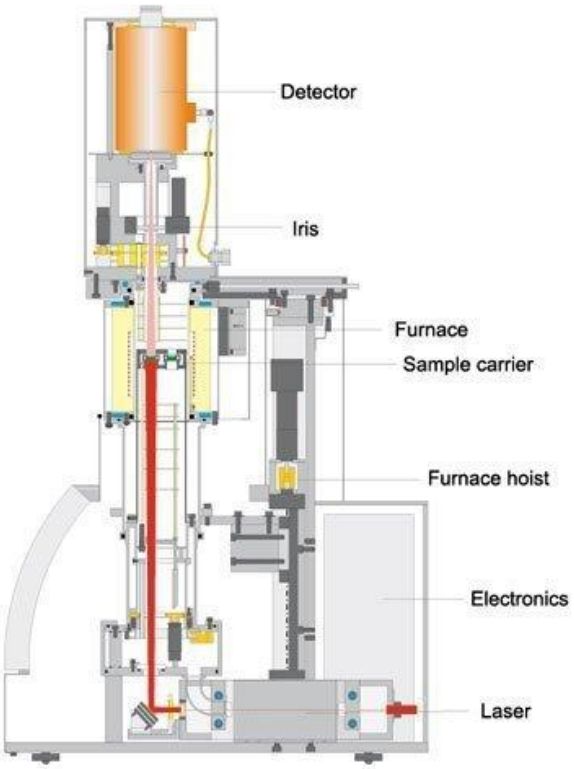

Figure 1: Scheme of the laser flash device.

A software program computes the data acquired by the IR detector in order to evaluate the thermal diffusivity. The advantages of this technique are: small samples (typical dimensions: diameter = 10 mm and thickness = 2 mm) with a simple geometry (disk shape); fast measurements (generally a few seconds at room temperature) and ease of handling.

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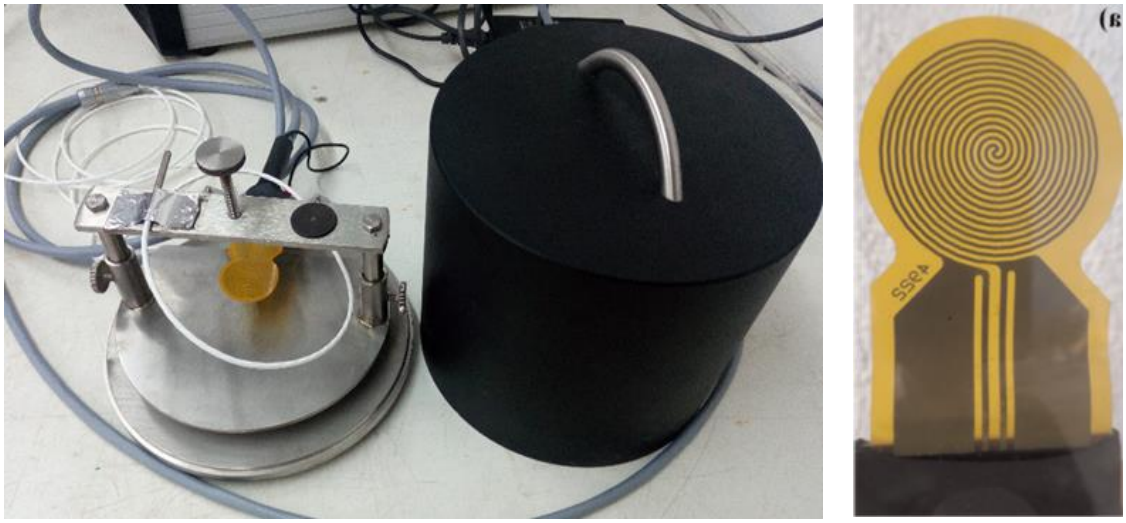
4.2. Hot disk equipment for thermal conductivity measurements at room temperature

Simultaneous measurements of thermal conductivity, thermal diffusivity and specific heat capacity [2], [3] can be achieved using the hot disk device. The device (Figure 2) is comprised of:

- Steel support for holding the sensor and the sample;
- Cap to ensure uniform temperature and humidity;
- Platinum resistance thermometer (PT100) to measure the temperature.

The TPS (transient plane source) sensor is a double nickel spiral supported by two thin sheets of an insulting material (kapton, mica or teflon), placed between two halves of the same material (Figure 2). This sensor has a double function: as a heat source for increasing the temperature of the materials and as a "resistance thermometer" for recording the resistance (temperature) increase as a function of time. Certain parameters need to be chosen: the radius of the probe (depending on the dimensions of the samples); the kind of sensor (depending on the temperature range to measure); the heating power (to have a temperature increment of 2-5 K); the measurement time (for recording n-points and having a total characteristic time of at least 0.4). All these parameters are chosen to guarantee a maximum probing depth, which is less than the minimum distance between the sensor and the borders of the sample, in radial and axial directions. This is important because the theory considers the sample as an infinite medium. In addition, a perfect contact is assumed between the sensor and the two surfaces in contact with it. In fact because this is not the real situation, the initial data points are excluded from the analysis for evaluation of the thermal properties.



a) b)

Figure 2: a) hot disk device for room temperature measurements; b) TPS sensor.

The advantages of this technique are: wide thermal conductivity range measured in a short time; application to liquids, gels and solids; easy sample preparation (only flat surfaces in contact with the probe are required); different sensor sizes to accommodate different sample types; it is non-destructive and high accuracy.

4.3. Hot disk equipment for thermal conductivity measurements at medium temperature

Measurements can be also made at medium temperatures (up to 500°C). There are only two differences compared to the previous paragraph (§ 4.2.): the steel support for holding the sensor and the sample is in a furnace (Figure 3) and the kind of sensor used. It is not possible to make measurements at higher temperatures due to the absence of a vacuum system to prevent the oxidation of the sensor.

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Figure 3: Hot disk device for medium temperature measurements.

4.4. Hot wire equipment for thermal conductivity measurements at high temperature

The hot wire and the hot disk methods work with the same principle. The difference is that in this case, the sensor is a platinum wire. Furthermore, this technique gives a thermal conductivity value, which is an average value of two heat-flow directions. For this reason, this method is not adapted for anisotropic materials [4].

For each measurement, three samples are needed (Figure 4). The wire is placed between the sample at the bottom and the sample in the centre. Then a thermocouple is placed parallel to the (heating) wire at a specific and known distance. A second thermocouple is placed between the sample in the centre and the sample of the top in an orthogonal direction compared to the previous one.

Figure 4: Hot wire device for high temperature measurements.

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4.5. Dilatometry equipment for thermal expansion measurements at high temperature

Dilatometry measurements yield precise information on dimensional changes, such as expansion or shrinkage, during a heating/cooling cycle [5]. The measurement is based on a pushrod technique, which means that dimensional changes are detected by the displacement system with a pushrod, connected to the sample undergoing microstructural changes. For an accurate determination, it is necessary to calibrate the equipment by using a reference material (generally alumina) that has a known and reproducible thermal expansion. The values obtained for the reference materials are then subtracted from the values obtained for the analysed sample. The equipment measures the change in length as a function of temperature, and the coefficient of thermal expansion (CTE) is then calculated with the Equ. 2 :

$$\mathrm{CTE} = \frac{1}{\mathrm{L_0}}\frac{\Delta \mathrm{L}}{\Delta \mathrm{T}} \qquad \textit{Equ. 2}$$

The dilatometry equipment for high temperature measurements is shown in Figure 5.

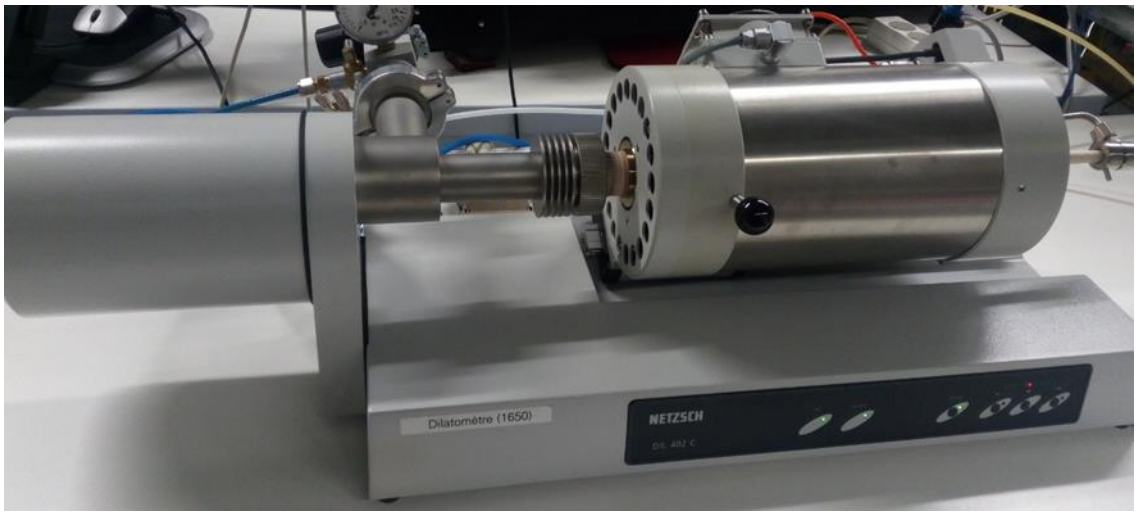

Figure 5: Dilatometry equipment for high temperature measurements.

The following information can be obtained from dilatometry measurements:

- Linear thermal expansion;
- Coefficient of thermal expansion (CTE);
- Volumetric expansion;
- Shrinkage steps;
- Softening point;
- Glass transition temperature;
- Phase transitions.

4.6. Thermomechanical analysis (TMA) apparatus for thermal expansion measurements at high temperature under constraint

The thermomechanical analysis a technique in which a deformation of the sample under non-oscillating stress is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. The stress may be compression, tension, flexure or torsion. This technique is used to simulate the service condition in a steel ladle. The lining is in a compressed state due to the operating temperature. The sample is inserted into the furnace and is touched by the probe, which is connected with the length detector. The thermocouple for temperature measurement is located near the sample. The sample deformation, such as thermal expansion and softening with changing temperature, is measured as the probe displacement by the length detector. Linear Variable Differential Transformer (LVDT) is used for length detection sensor. The principle is the same describe in the previous section (§ 4.5.).

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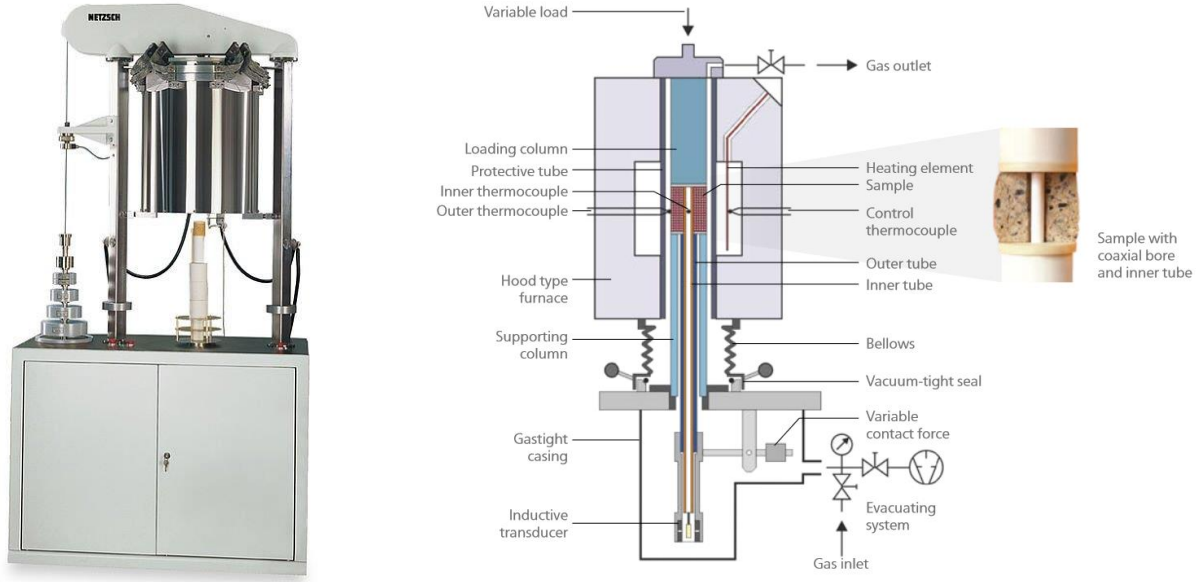
4.7. Refractoriness under Load / Creep in Compression (RUL/CIC) apparatus for high temperature measurements

Refractoriness under Load / Creep in Compression apparatus is a dedicated device to measure dimensional changes due to applied temperature and/or load. The apparatus is shown in Figure 6.

The measuring unit consists of:

- Console;
- Furnace guide frame;
- Furnace balance weight of the loading device;
- Differential measuring system.



a) b)

Figure 6: a) RUL/CIC apparatus for high temperature measurements [6]; b) detailed scheme of the apparatus.

The sample is placed on the supporting column; the furnace is lowered and the load is applied by counterbalancing the weight of the furnace. In the principle, during thermal expansion measurement, the applied load should be minimized as much possible. The length change is monitored by a measuring system consisting of an inner and outer alumina tubes, which act differentially and are connected to an inductive transducer. Calculated thermal expansion is based on the dimensional change of the inner tube, which corresponds to the change in sample dimension.

4.8. Differential Scanning Calorimetry (DSC) apparatus for heat capacity measurements

Differential Scanning Calorimetry is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and a reference is measured as a function of temperature. Both the sample and the reference are maintained at nearly the same temperature throughout the experiment. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. With this technique, it is possible to evaluate the heat capacity of the material, but also to detect any change that alters the heat flow in and out of a sample. This includes more than just glass transitions and melting; it also includes solid state transitions, such as eutectic points, melting and conversions of different crystalline phases like polymorphic forms, dissolution and precipitation from solutions, crystallization and re-crystallizations, degradation, loss of solvents, and chemical reactions.

The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic (Figure 7). For example, as a

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solid sample melts to a liquid, it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid.

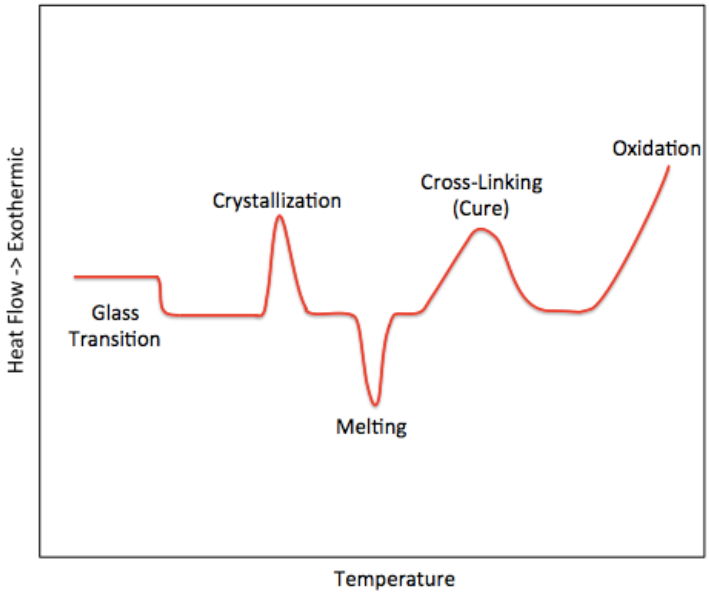

Figure 7: Some exothermic and endothermic reactions.

The apparatus (Figure 8) is composed of:

- Furnace;
- Sample carrier with two Platinum crucibles (one for the sample and one for the reference material);
- Vacuum system.

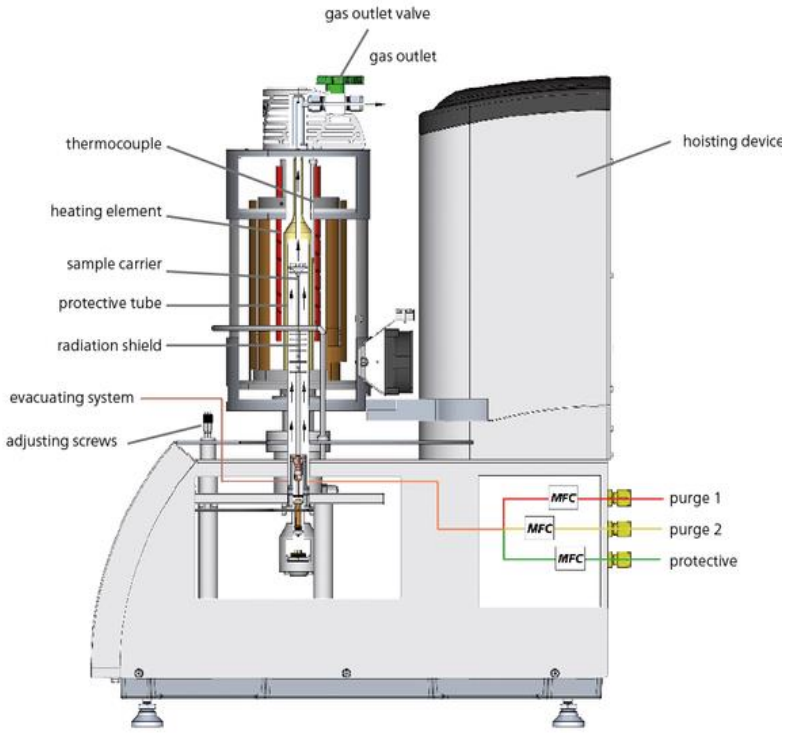

Figure 8: Scheme of DSC apparatus.

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4.9. Differential Thermal Analysis / Thermo-gravimetric Analysis (DTA/TGA) apparatus thermal analysis

Differential Thermal Analysis is a technique similar to the Differential Scanning Calorimeter (Section 4.8.). While the Thermo-Gravimetric Analysis measures the change of weight of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum as low as 30 mTorr.

The apparatus is composed of:

- Sample holder with two crucibles;
- Thermocouples;
- A furnace;
- A temperature programmer;
- A recording system.

The key feature is the existence of two thermocouples connected to a voltmeter. One thermocouple is placed in an inert material such as Al_2O_3, while the other is placed in a sample of the material under study. As the temperature is increased, there will be a brief deflection of the voltmeter if the sample is undergoing a phase transition. An example of a typical result is shown in Figure 9:

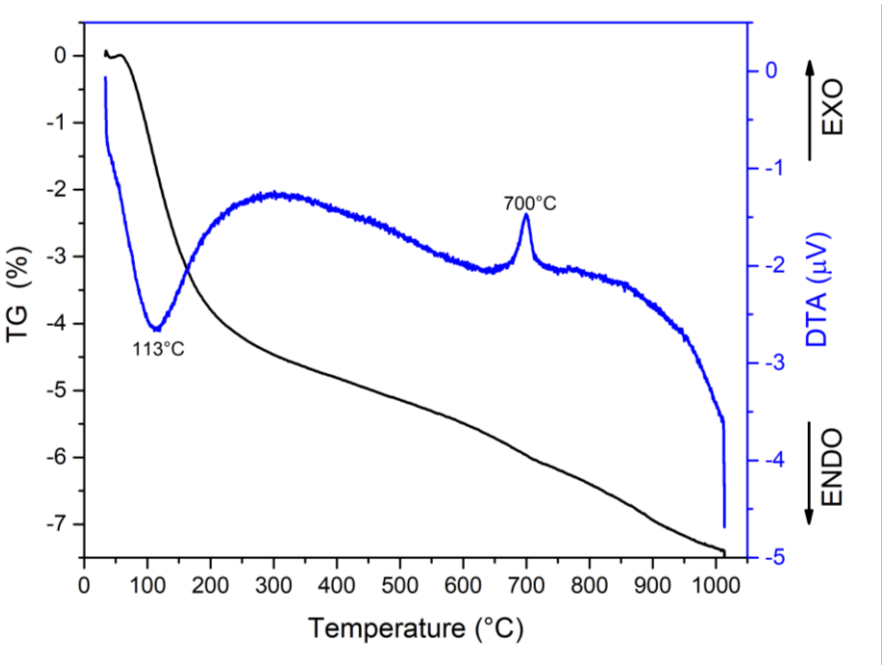

Figure 9: Example of DTA/TGA result.

5. References

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