- Comparative methods

  We encountered the same geometries than the absolute methods. Geometries are adapted to the range of thermal conductivity :

  1. divided-rod (or cut-bar) method (ISO 8301, ASTM Standard C518 - 10) [14] (see figure 3.4). With a sample between two reference materials, the divided-rod is improved in terms of accuracy and robustness. On the other hand, the divided-rod allows the determination of the contact thermal resistance at the interface (fig. 3.5). The temperature difference ΔT at the contact interface is obtained by extrapolation of temperature profiles in reference material and sample. The ratio of ΔT by heat flux gives the contact thermal resistance. This parameter depends on thermal conductivity, Young's modulus, hardness, rugosity, flatness of two materials in contact, and applied pressure and interstitiel fluid properties [15].

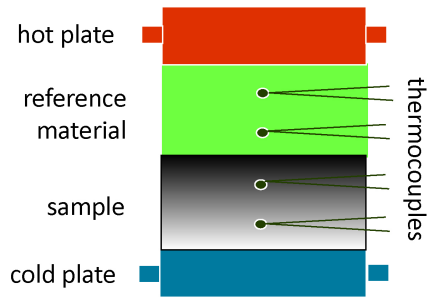

Figure 3.4: Divided rod method

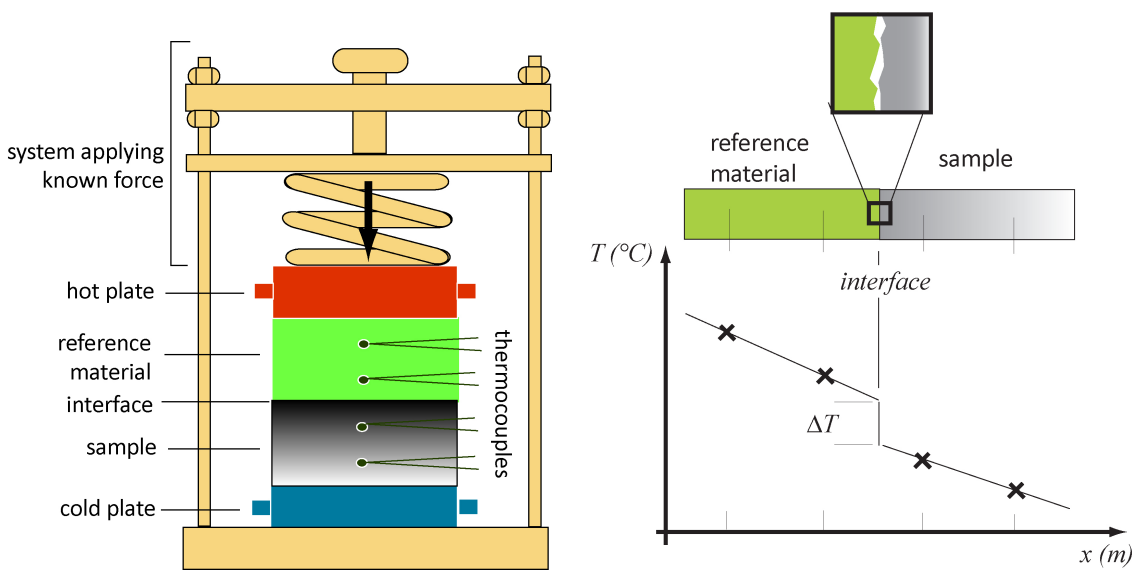

Figure 3.5: Experimental device and principle of measurement of the contact thermal resistance.

  2. Plate (or disk) method (ASTM Standard E1225-04)

3. Heat flow meter (ASTM E1530) (see figure 3.6)

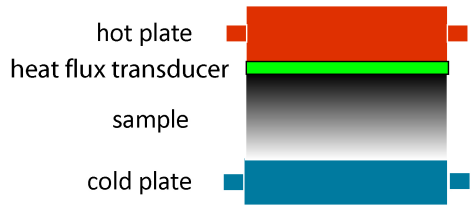

Figure 3.6: Heat flow meter method with heat flux transducer

We can noticed also the Lee's disk method suitable for low thermal conductivity sample. A disk of material is being heated by steam on one side and the other side cooled down by air.

Finally, Searle's bar method consists of a bar that is being heated by steam on one side and the other side cooled down by water while the length of the bar is thermally insulated. This method is more suitable for high thermal conductivity sample.

Transient heat flow methods

In transient methods, a sample is heated at one end by a periodic source (sinusoidal), by a step of temperature or heat flux (Heaviside) or by a short energy pulse (Dirac). The limits of these methods are linked to the properties of heat source (temperature range, radiative or conductive transfer, thermal inertia and homogeneous temperature...)

Periodic heat flow

This method is performed firstly by Angström in 1863. The edge of a bar or a plate is submitted to periodical temperature variation (see figure 3.7). The temperature measured at any point in the interior of the specimen varies periodically. When the steady state is reached, the thermal diffusivity may be evaluated from the temperature recorded at two selected fixed points.

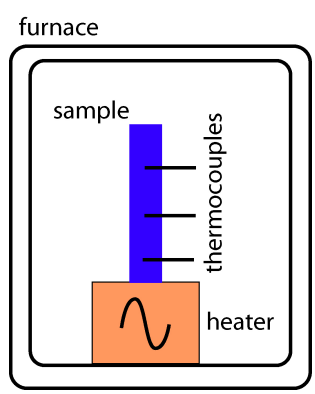

Figure 3.7: Schematic drawing of the Angström experimental apparatus

The thermal diffusivity is obtained from the following equation :

$$a = \frac{\pi L^2}{\phi \ln(A_1/A_2)} \tag{3.3}$$

where L is the distance between two thermocouples, A_1 and A_2 the amplitudes of the first and second curve, ϕ is the phase difference between the curves.

A specific apparatus is developped at PROMES lab (see figure 3.8). This apparatus consists in measuring temperatures in a bar of macor submitted to solar irradiation. An heliostat reflects the solar beam to a paraboloïd concentrator. The concentrated irradiation heats the surface of one end of the bar. The periodical variations are obtained by rotation of carbon fiber blades placed between heliostat and concentrator. A temperature controller is used to drive the opening of the blades with respect to the surface temperature signal measured by a solar-blind pyrometer located above the sample at the center of the parabolic mirror. The controller regulates the surface temperature of the sample to predetermined temperature patterns, even compensating the variations of the incoming solar energy due to changing weather conditions.

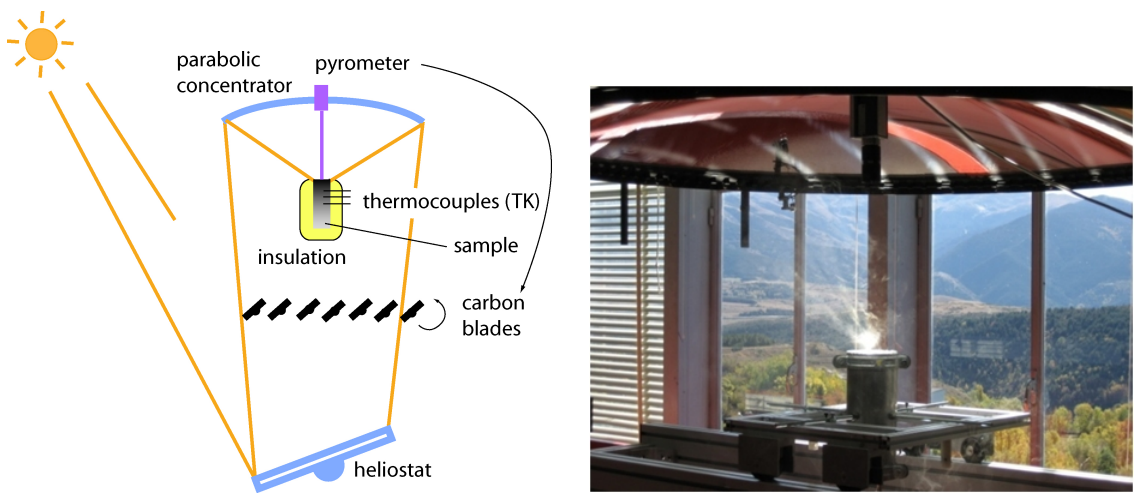

Figure 3.8: Schematic view and photograph of the solar Angström experimental device

In the case of a sample of macor under solar irradiation, we obtain periodical temperature variations as shown by figure 3.9. From these results we can estimate the thermal diffusivity of macor sample at $6.9.10^{-7}$ m^2 s^{-1}. The values identified are in good agreement with values from literature.

Flash method

This method is based upon the measurement of the temperature rise at the rear face of the specimen produced by a short energy pulse on the front face (ISO/DIS 22007-4). The short pulse can performed by, for example, a xenon lamp or a laser (Fig. 3.10 and 3.11).

The calculation is based on the analytical solution of the heat conduction problem within a infinite plate of thickness L, initially at a uniform temperature and heated on one of the two surfaces by a Dirac energy pulse.

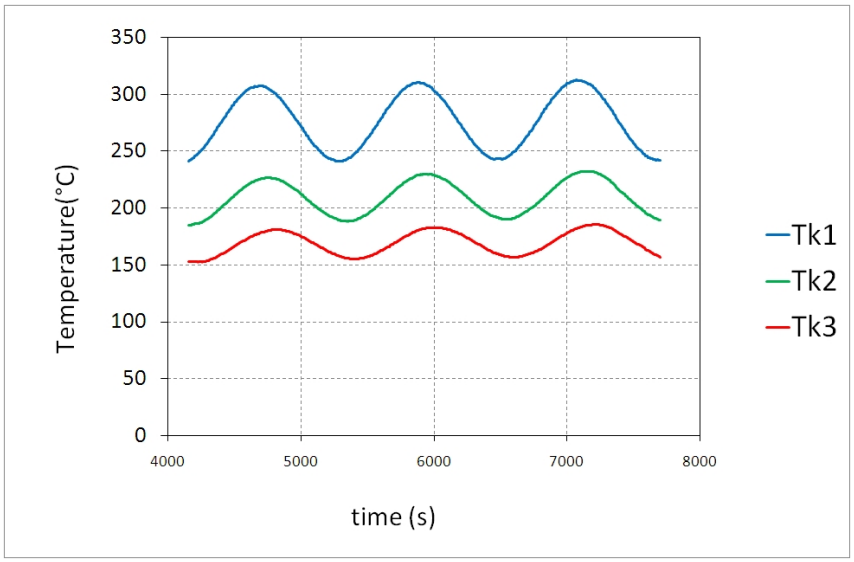

Figure 3.9: Periodical temperature variations in a bar of macor under solar irradiation.

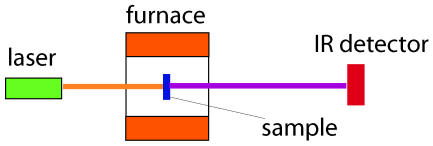

Figure 3.10: Schematic drawing of the laser flash method

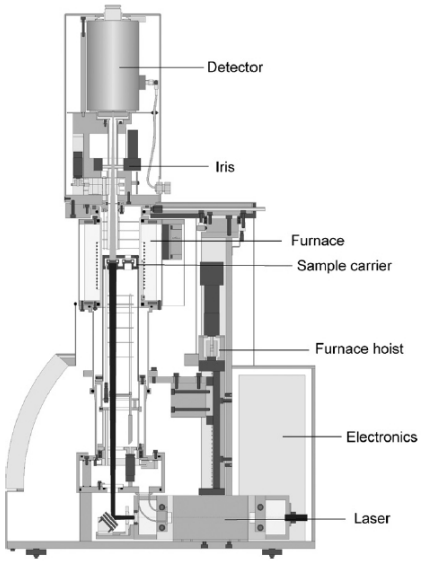

Figure 3.11: Measurement part of the NETZSCH LFA 457 MicroFlash [16]

The solution proposed originally by Parker [17] is given by :

$$a = 0.1388 \frac{L}{t_{1/2}} \tag{3.4}$$

where $t_{1/2}$ is the time corresponding to the half maximum increase of the dimensionless temperature on the rear face of the plate. Some improvements can be brought for the thermal diffusivity identification such as partial times estimation.

Main advantages are easy sample preparation, fast measurement times, high accuracy ($\approx 3\%$), non-contact, non-destructive testing technique [16]. An example of results obtained by laser flash measurements is shown in figure 3.12.

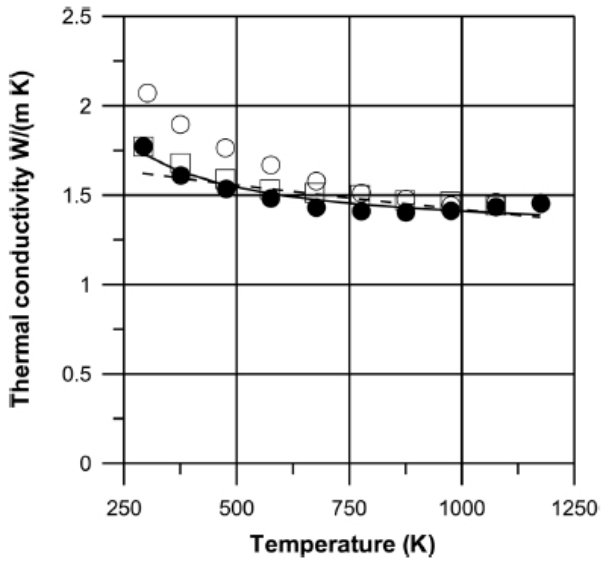

Figure 3.12: Thermal conductivity of ceramics as function of temperature. (○) First heating, (□) first cooling, (●) second heating [18]

Line heat source and others small-area contact method

- Transient plane-source method - Hot Disk - ISO/DIS 22007-2 : in this technique, a thin resistive element, in the form of a bifilar spiral, plays the role of a heat source and a temperature sensor (Fig. 3.13). The element is mounted between two planar specimens of the same material. A known amount of electrical power is supplied to the element and its change in resistance as a function of time, due to its increase in temperature, is recorded. For a disk-shaped sensor, the thermal conductivity and diffusivity can be obtained from $\Delta T(t)$ that is given by the following equation :

$$\Delta T(\theta) = \frac{\dot{Q}.D(\theta)}{\pi^{3/2}.R.k} \tag{3.5}$$

with $\dot{Q}$ the total output power, R the radius of the sensor, θ a non dimensional variable ($\theta = (a.t/R^2)^{1/2}$) and $D(\theta)$ a theoretical expression of the time dependent temperature increase [19].

Figure 3.13: Hot disk

The sensors are made from a double spiral of Nickel of about 10 μm in thickness between two electrical insulation thin films (Kapton or Mica according temperature range). Some commercially available devices have a wide temperature range of measurement (from -40 to 1000°C) thanks to the use of Mica. The accuracy of these measurements is within 3-5%.

- Temperature wave analysis - ISO/DIS 22007-3 : the principle of the technique is to measure the phase shift of an oscillating temperature wave travelling through the specimen by using a two-phase lock-in amplifier. The temperature wave is generated and sensed by electrical resistors, typically sputter coated onto opposing sides of the specimen, with one resistance element acting as the heater and the opposing element as the sensor. The thermal diffusivity is calculated from the temperature wave's phase shift across the specimen as a function of the angular frequency of the temperature wave and the specimen thickness [20].

- Transient line-source method - ASTM D5930. This method consists of heating the sample by an electrical wire (Fig. 3.14) [21]. We consider an infinite line source with constant power per unit length. Theorically, the temperature of the electrical wire follows a linear profile as $Ts(t) - Ts(0) = f[ln(t)]$. The slope is proportionnal to the thermal conductivity :

$$Ts(t) - Ts(0) = \frac{\dot{Q}}{4\pi.k} ln(\Delta t) \tag{3.6}$$

The principal source of incertainty is the heat flow rate value. The expected accuracy

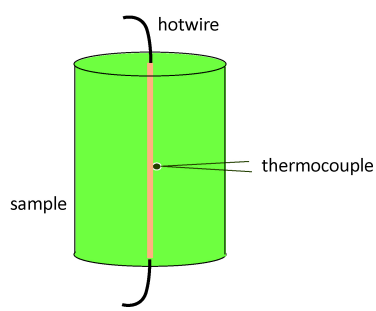

Figure 3.14: Hot-wire method

is approximatively 5% for a thermal conductivity between 0.05 and 15 W m^{-1} K^{-1}. The hot wire technique is not adapted to thermal conductivity higher than 15

W m^{-1} K^{-1} and for electrical conducting materials. The first limitation can be partially solved with compromise the reliability of the results obtained : a bigger time interval available for calculations or an increased sample size. Insulation between the hot wire and the samples may be introduced to extend the application of this technique for electrical conducting materials.

- Hot-strip : the principle of the method of the hot-strip is to insert between two identical flat samples a heating resistance. We apply a level of power (by a stabilized power supply) and we follow the evolution in time by the temperature measured by a very fine thermocouple, placed between the hot strip and the sample [22]. We can observed the temperature distribution obtained by numerical simulation on the figure 3.15. The most limitation is the temperature range supported by the hot strip (generally less than 80°C).

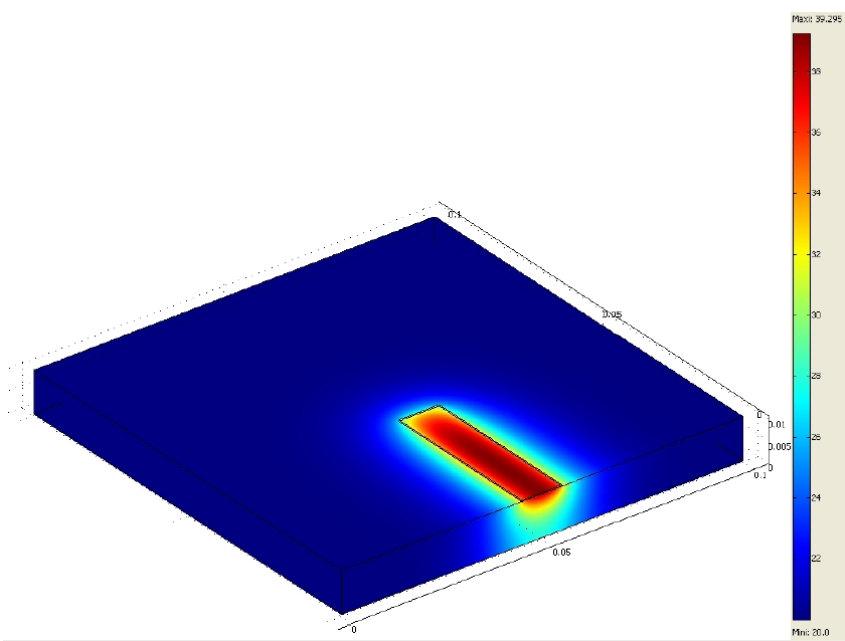

Figure 3.15: Example of simulation results about a hot-strip experiment

Finally, the choice of the more adapted method is given by the value of the thermal conductivity, the geometry and size of the sample (Fig. 3.16).

3.3 Thermomechanical properties : Thermal expansion, Young's modulus, fatigue tests

To check the thermal stability of energy storage materials under cyclic high temperatures conditions, we have to impose successive thermal cycles. Furthermore, the sensitivity of thermomechanical properties to chemical composition can be examined by comparison of the different experimental results. During this typical heat treatment, Young's modulus

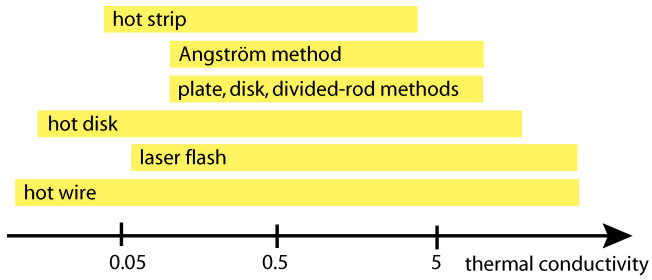

Figure 3.16: Choice of the method according to the range of thermal conductivity

(E) evolution has measured by pulse echography technique in long bar mode. As E is highly sensitive to microstructure changes, this elastic parameter gives advantageously accurate informations of thermal shock resistance and life-time expectancy under operating conditions. In situ and non destructive, this method is also very well adapted to characterize heterogeneous samples containing coarse aggregates and defects (e.g. porosity, cracks). Young's modulus measurements are also correlated to SEM observations and thermal expansion measurements. This comparison is interesting to better understand the different microstructural mechanisms occurring during heating/cooling stages in order to identify the more suitable temperature range of industrial application.

Dilatometry is a method by which the thermal expansion of a material may be measured. There are many types of dilatometers. Dilatometers may use a pushrod, capacitor, or optical system to sense expansion. Dilatometers utilize a Linear Differential Variable Transformer (LVDT) to convert a pushrod displacement to a voltage. This voltage is recorded and converted to a recordable displacement signal by software. By carefully controlling and recording, via thermocouple, the temperature of a sample at the free end of the pushrod, the thermal elongation characteristics of a sample may be determined.

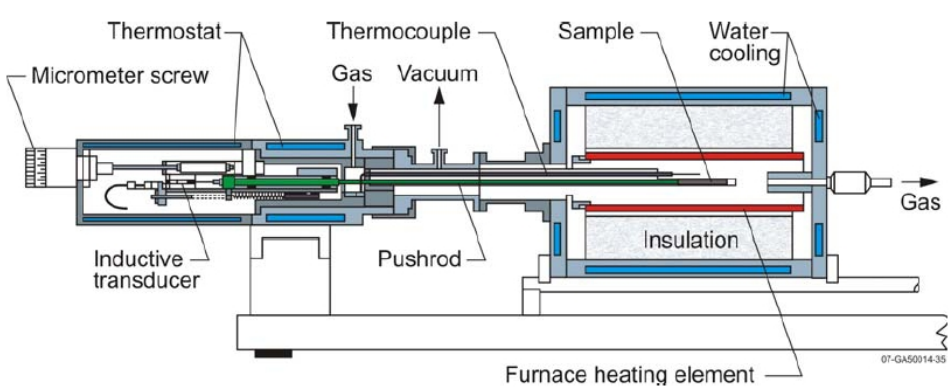

Figure 3.17: Schematic of dilatometer in horizontal configuration [23]

Typically, linear thermal expansion can be measured during two successive identical thermal cycles. Heating and cooling rates have been fixed at a value of 5°C min^{-1} with a plateau of 1 hour at the maximum temperature (1000°C). This thermal treatment has been chosen because it is suitable to reproduce the widest specific real service conditions imposed to thermal storage materials such as gas turbine air CSP towers. A commercial

dilatometer Netzsch-DIL 402 PC has been used with samples dimensions ($5 \times 5 \times 20$ mm^3). The slope of the curve $\Delta L/L_0 = f(T)$ corresponds to the coefficient of thermal expansion (CTE) determined in a considered temperature range. An example of results can be seen in figure 3.18.

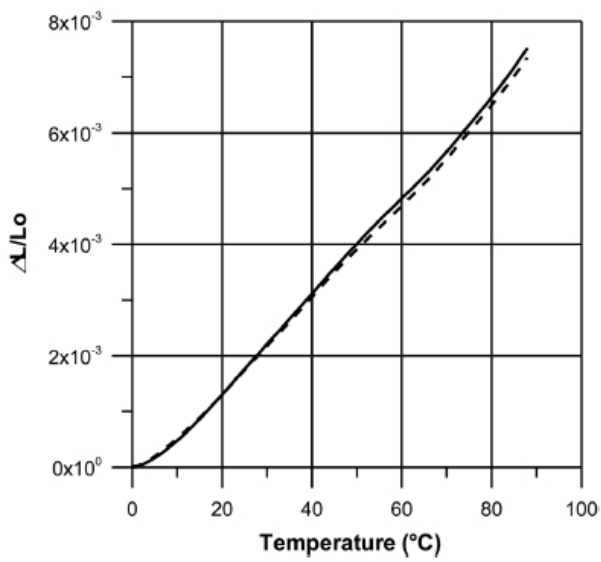

Figure 3.18: Thermal expansion of ceramic material from room temperature to 900°C[18].

The Young modulus of material can be estimated using, for example, a Nano-Indenter II (MTS System Corp., TN) with a Berkovich diamond indenter 65.3 deg in angle. Every Young modulus data is the mean value of twelve successive measurements.

We present here a non destructive method to measure Young's modulus. The measurements have been carried out using a high temperature ultrasonic technique operating in a long bar mode (lateral dimension of the propagation medium smaller than the wavelength). This method has already been successfully used to investigate the microstructural evolutions of various ceramics at high temperatures [24]. In this case, a low frequency of investigation is required and typical dimensions of tested specimens have to be optimized in regards to the size of heterogeneities (solid phases and defects). Ultrasonic compressional waves are generated by a magnetostrictive transducer. The ultrasonic pulse is sent toward a parallelepipedic sample through an alumina wave guide. The coupling between the guide and the sample is ensured by aluminous refractory cement. Electronic equipment (signal acquisition by a digital oscilloscope and a specific software package) automatically measures and records the time delay τ corresponding to one round-trip of the wave through the sample. Then, the Young's modulus E of the material can be calculated with the following equation [25] :

$$E = \rho . \frac{2L}{\tau} \tag{3.7}$$

where L and ρ are the sample length and density, respectively. The different characteristics of the ultrasonic line components have been adapted to highly heterogeneous

refractory concretes exhibiting large grains and/or a high pore volume fraction (a low frequency of 110 kHz and typical dimensions of $11\times11\times120$ mm^3 for these studied ceramic specimens). Ultrasonic and thermal expansion measurements can be performed under the same conditions : a rate of 5°C min^{-1} for heating and cooling steps and a 1 hour isothermal plateau at 1000°C.

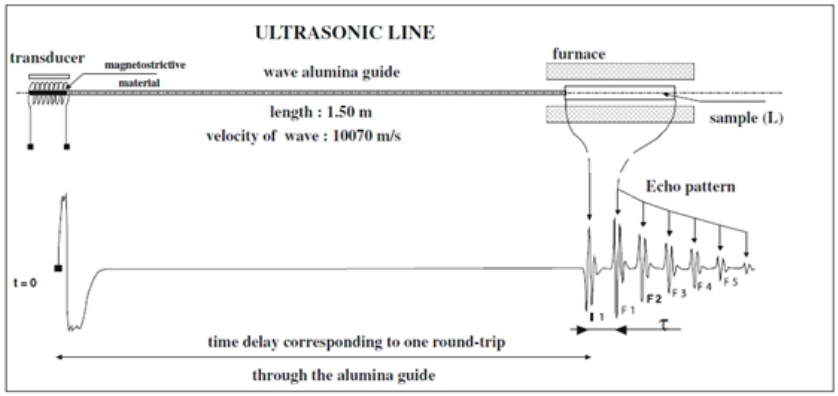

Figure 3.19: Schematic representation of the pulse echography apparatus.

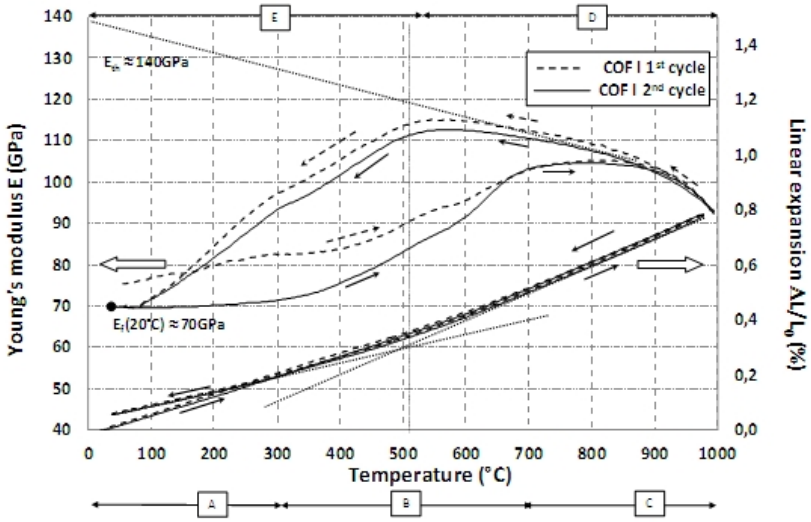

Figure 3.20: Young's modulus and linear thermal expansion vs temperature for sample of recycled materials [26].

We discuss about fatigue tests that indicate the stability of materials under cyclic conditions. Under operation, the thermal storage materials could be subjected to strong and repeated temperature gradients. Dynamic solar intermittencies (cloud effects) could induce very severe thermal shocks (in temperature and power), toward the TES system. It is therefore necessary to prove initially their refractory behavior and resistance to thermal shock. The utilization of certain materials is limited by the variation of mechanical properties with temperature. In the case of thermal shocks, stresses are generated in the

material and cause cracks. Failure can occur according to the thermal shock fracture resistance that depends on a number of material properties including the thermal expansion coefficient, thermal conductivity, thermal diffusivity, elastic modulus, fracture toughness, tensile strength, and upon the additional parameters of heat transfer coefficient, specimen size and duration of thermal shock [27].

Samples have been tested under the operating conditions of thermal energy storage by using the same device than used for measurements of thermal diffusivity (Fig. 3.8). This device consists on a temperature controlled loop device coupled to a concentrated solar test facility. Under concentrated solar flux, only one face of the sample is heated. This equipment allows monitoring a heating rate up to 2500°C min^{-1} (Fig. 3.21). Compared to previous complementary echography and thermal expansion techniques operating at a lower heating rate (5°C min^{-1}), thermal shock severity and aging were here enhanced. During these severe thermal cycles, the temperature profile inside the cylindrical sample has been measured to highlight the stability and refractoriness of the material.

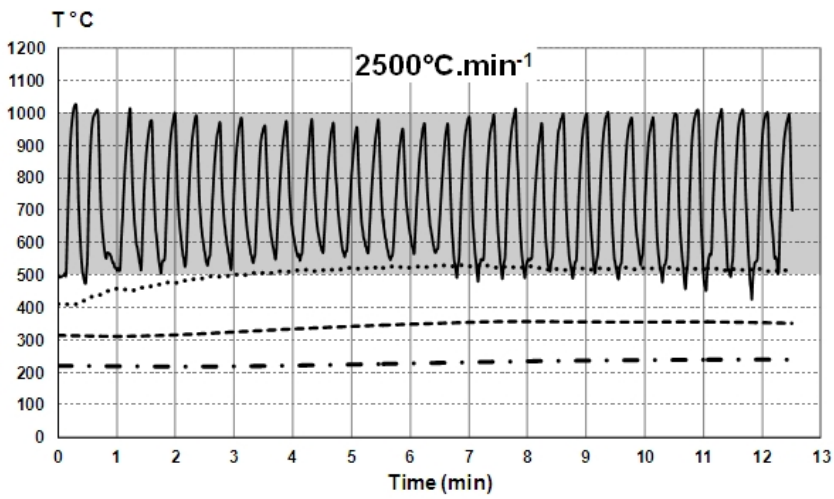

Figure 3.21: Fatigue test under dynamic repeated thermal cycling (heating rate corresponding to 2500°C.min^{-1})

Coupling pulse echography technique and concentrated solar test facility is an efficient way to characterize future materials under industrial thermal stresses. In situ and non destructive, these methods provide complementary informations about thermal fatigue resistance.

3.4 Characterization of porous materials for thermal storage

3.4.1 Introduction

For application of porous materials in thermal storage a thermal fluid (e.g. air) flows through the porous structure and exchanges heat with the porous material. The accurate