

Advanced thermal analysis techniques

Laboratory work

Student:

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Academic year:.....

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Laboratory no. 1

Sample preparation for differential scanning calorimetric analysis (DSC) and equipment calibration

The laboratory work aims to familiarize students with the preparation of samples used in differential scanning calorimetry (DSC) as well as the calibration of the equipment. In the laboratory, samples of various materials are prepared and the device used for calibration is DSC F3 Maia calorimeter.

1. Theoretical considerations

Differential scanning calorimetry (DSC) is one of the most important thermal analysis (TA) techniques with the best measurement accuracy [Chrostek, 2016]. This experimental method is used to identify thermal effects related to phase transformations that occur in materials. At the transition from one phase to another, there is a change in the way the particles are arranged, and the transition is accompanied by a change in the thermodynamic properties of the material. These thermal effects can be studied as a function of temperature or time by applying a well-defined temperature program.

DSC analysis measures the difference in heat variation between a sample and a reference, while they are subjected to a predefined temperature program (heating/maintaining/cooling). The reference is made of a material that does not undergo phase transformations in the studied temperature range (the most often used as a reference is an empty crucible), figure 1.

Lab. 1. Sample preparation for differential scanning calorimetric analysis (DSC) and equipment calibration

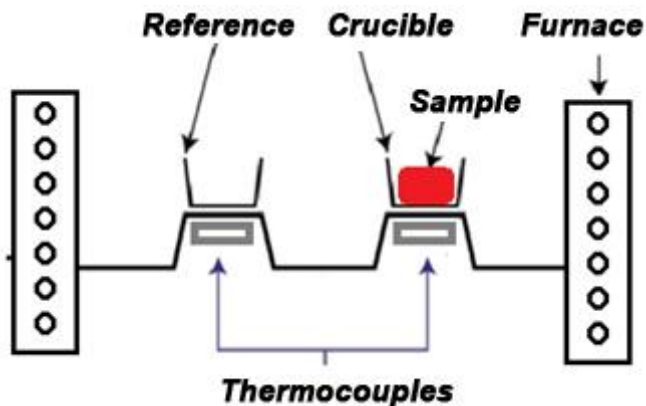


Figure 1. Diagram of the interior of a DSC calorimeter

Following the analysis, a thermogram is recorded that illustrates the heat flow variation as a function of time or temperature. Figure 2 shows a thermogram in heat flow - time coordinates for a material heated to a temperature of 200°C. During heating to about 160°C (red curve) an endothermic minimum is observed which represents the melting of the material. During cooling, at a temperature of about 155°C (blue curve) an exothermic maximum is observed which is attributed to the phenomenon of crystallization (solidification) of the analyzed material.

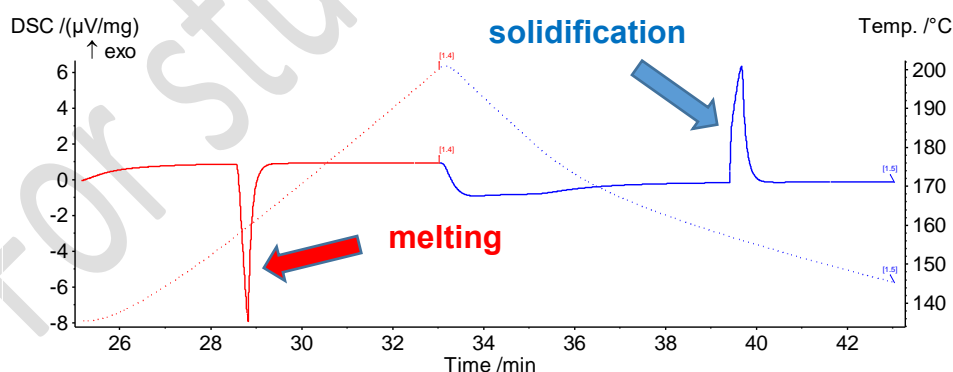


Figure 2. DSC thermogram illustrating the melting and solidification of pure indium

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Many phase transformations (transitions) in materials are accompanied by a release (exothermic reaction) or absorption (endothermic reaction) of heat. Transformations that take place at a strictly determined temperature, where some properties vary discontinuously at the moment of reaching it, are called first-order transformations. First-order transformations are those that involve latent heat, and examples of such transformations are: vaporization-condensation, melting-solidification, sublimation-desublimation, etc. During the transformation, a system either absorbs, or releases a fixed amount of energy per volume. This type of transformation is detected on a DSC curve as an exothermic maximum (heat release) or an endothermic maximum (heat absorption) [P.J. van Ekeren, 1998].

Second-order transformations are those transformations that do not occur at strictly determined temperatures, but over a temperature range and are not associated with the release or absorption of heat. These types of transformations vary in quantities related to the symmetry properties of the system, such as: compressibility, heat capacity, coefficient of expansion in volume, etc. Examples of such transformations are glass transition in amorphous polymers or the order-disorder transition in metal alloys. In this case, sudden changes in the specific heat occur and are observed on the DSC thermograms as a change in the linearity of the recorded signal [F. Paladi, 2013].

DSC analysis can be used to investigate a wide variety of materials:

- compact solids such as: plastics, rubber, resins or other metallic materials, ceramics, glass, composite materials, organic materials, etc.;
- powders, such as pharmaceuticals or minerals;
- textile fibers;
- liquids.

Among the phenomena that can be identified by the DSC analysis the following are mentioned [M. Wagner, 2009]:

1. melting;
2. crystallization;
3. solid-state transformations;
4. evaporation;
5. sublimation;
6. adsorption;
7. desorption;
8. glass transition;
9. dehydration;
10. decomposition;
11. oxidation;
12. polymerization and the temperatures characteristic of these phenomena, enthalpy and caloric capacity.

2. Working plan

2.1. Sample preparation for the DSC analysis

The correct preparation of the samples and the appropriate choice of crucibles as well as the conditions of the experiment are aimed at obtaining the best possible results for an experiment. Careful sample preparation guarantees reproducible and consistent DSC analysis results. Good thermal contact and low thermal resistance between the sensor and the crucible sample is essential. Any factor affecting contact must be taken into account when preparing the sample.

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The samples that can be studied with the DSC equipment are part of the entire range of natural materials, biological and organic materials, minerals and inorganic chemicals, plus a very large number of synthetic and composite materials. They have very different physical characteristics, from very high density such as impermeable ceramics, to organic powders, metals, to liquids with a wide range of viscosity. Many of them require a special preparation procedure, the results of the thermal analysis being influenced by this procedure [S. Vyazovkin *et al.*, 2014]. Thus, samples can be analyzed in solid state, in powder form, fibers, thin films, liquids and solutions, pastes and viscous liquids.

The following factors can influence a DSC analysis [www.netzsch.com]:

a) Crucible material

The crucible must be made of a material that provides good thermal conductivity and it is also important that it does not interact with the material to be analyzed. Depending on the maximum working temperature, there are many types of crucibles. Thus, for samples that require a temperature program up to 600°C, Al crucibles can be used, and for materials that undergo transformations at higher temperatures, ceramics, platinum, gold, silver, alumina, graphite, steel, or fiberglass are used. Table 1 and Figure 3 show different types of crucibles.

Table 1. Types of crucibles and the temperature ranges [www.tainstruments.com]

Material	Working temperature (°C)
Aluminum	-180 ...+ 600
Platinum	-180 ...+ 725
Gold	-180 ...+ 725
Graphite	-180 ...+ 725
Ceramics	-180 ...+ 1990

b) Crucible Lid

Only OIT (Oxidation induction time) measurements are carried out in open crucibles. All other types of analyses are carried out in closed crucibles with lids.

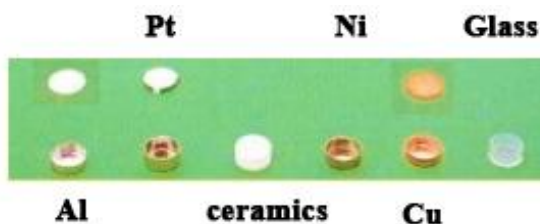


Figure 3. Types of crucibles used in DSC analysis [www.netzsch.com]

The use of a lid results in a more homogeneous distribution of heat in the crucible. Aluminum crucibles with lids are usually used in an encapsulated state. If the samples to be measured allow, the lids are perforated to prevent breakage at higher temperatures.

c) Number of samples

A single sample is sufficient for DSC analysis of compact samples. Using two or more samples may result in discontinuous peaks on the DSC thermogram.

d) Shape of sample

To achieve the best heat transfer between the sample and the bottom of the crucible, the sample should have as much flat surface as possible to allow optimal contact. Samples should not be too large to avoid deformation at the bottom of the crucible when it is closed. In the case of powders, it is advisable to compact them as much as possible.

e) Sample mass

Most standards for polymer testing – such as ISO 11357, DIN 53765, and ASTM D3895 (OIT) – recommend a mass between 5 mg and 20 mg. For the determination of the glass transition, it is recommended to use samples with a higher mass (10 mg to 20 mg) than for the investigation of melting and crystallization phenomena (5 mg to 10 mg). In the case of

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metals and metal alloys, due to their higher density, it is recommended that the mass of samples should not exceed 50 mg.

In the case of solid samples, there are several steps in the sample preparation process [www.netzsch.com]:

i. Cutting sample

The dimensions of the sample vary depending on the material. For low-density samples, the maximum width and length should not exceed the dimensions of the crucible bottom in order to provide the best contact with the crucible. For materials with a high expansion coefficient, the sample size should be smaller to prevent the crucible lid from being pressed during the test.

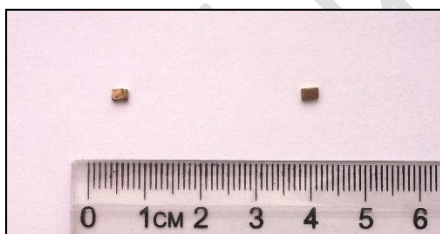


Figure 4. Samples for DSC analysis

ii. Cleaning of impurities

The presence of impurities on the samples can reduce the quality of the signal, with the possibility of obtaining erroneous results by the appearance of maxima or inflections on the DSC thermograms. These additional features on the thermograms can be misattributed to the samples and affect the interpretation of the results.

iii. Weighing samples

Weighing is performed using an analytical balance. This step is necessary because the results obtained are interpreted according to the weight of the sample. Depending on the

type of material and the phenomenon being followed, the calorimeter manufacturer will recommend the amount of material to be used (Table 2).

For the DSC F3 Maia calorimeter, the maximum mass of the sample should not exceed 50 mg.

It is recommended that tweezers and gloves be used for all specimen handling and preparation to prevent contamination of specimens with contaminants.

*Table 2. Recommended sample mass for various materials and phenomena
[www.neztsch.com, www.tainstruments.com]*

Material	Recommended mass, mg
Polymers	5-10
Metals	3-5
Liquid/Paste Sample	5-10
Analyzed phenomenon	Recommended mass, mg
Melting / crystallization	<10
Glass transition	10-15
Specific heat	5-6
Comparison of two samples	10

Samples for DSC analysis of solid materials in the form of wires and slides are prepared in the laboratory. Their outer surfaces are visually inspected for any impurities that could affect the calorimetric effect. The samples are cut to dimensions that do not exceed those of the crucibles in which they will be heated, which has an internal diameter of 5 mm.

The cut samples are then weighed using the electronic laboratory balance. The results are then centralized in Table 3.

Table 3. Mass of samples prepared for DSC analyses

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Sample	Mass, mg

2.2. Differential Scanning Calorimeter Calibration

Temperature and heat flow calibrations play a very important role in the accuracy of the data obtained by the DSC calorimeter. According to international standards, calibration should be performed regularly or after a significant change in experimental conditions (including cleaning of the measuring cell) [P. Gabbott, 2007].

The more accurate the calibration procedure, the more time is required to correctly calibrate the DSC calorimeter. Since calibration is required for each change in experimental conditions (crucible material, heating rate, purge gas, etc.), the time spent calibrating a calorimeter is often measured in tens of hours per year [A. Shimkin, 2013].

There are a number of methods for calibrating temperature and heat flow for DSC calorimeters. Most require two heating-cooling cycles for each calibration material sample, with only the second cycle used for calibration.

To calibrate the temperature part of an instrument, reference materials are required that are pure, stable to decomposition and oxidation, preferably with low volatility, and have transitions with distinct, reproducible maxima and minima that have been accurately measured previously. It is therefore essential to have standards that have been independently tested and fully investigated with thermal method standards.

Lab. 1. Sample preparation for differential scanning calorimetric analysis (DSC) and equipment calibration

Very few materials are available that have been studied with sufficient precision. There are difficulties in calibrating at very low temperatures and at very high temperatures.

For each element used in the calibration of the device, the operator must:

1. use samples with a maximum mass of 50 mg;
2. perform experiments in a gas-shielded environment;
3. select the temperature regime to be approximately 30 degrees higher/lower than the transformation temperatures;
4. use heating and cooling rates of about 10 K/min;
5. evaluate the start and end temperatures of the transformation after recording the curves;
6. record the values obtained.

In the laboratory, the DSC F3 Maia calorimeter is calibrated using five samples of pure elements with known melting and crystallization temperatures. They are placed in encapsulated crucibles purchased with the calorimeter from the manufacturer.

Calibration is performed for temperature and sensitivity.

2.2.1. Temperature calibration

The crucibles containing each of the specified elements are placed in turn in the calorimeter furnace and subjected to three heating-cooling cycles according to the program suggested in Table no. 4:

Table 4. Temperature programs for the materials used in calibration process

Material used for calibration	Melting temperature, °C	Temperature program
Mercury (Hg)	-38.5	-60 la -15°C (Heating segment)
		-15 la -60°C (Cooling Segment)
		-60 la -15°C (Heating segment)

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		-15 la -60°C (Cooling Segment)
		-60 la 25°C (Heating segment)
Indium (In)	156.6	20 la 210°C (Heating segment)
		210 la 50°C (Cooling Segment)
		50 la 210°C (Heating segment)
		210 la 50°C (Cooling Segment)
		50 la 210°C (Heating segment)
Tin	231.9	20 la 280°C (Heating segment)
		280 la 130°C (Cooling Segment)
		130 la 280°C (Heating segment)
		280 la 130°C (Cooling Segment)
		130 la 280°C (Heating segment)
Bismuth	271.4	20 la 320°C (Heating segment)
		320 la 170°C (Cooling Segment)
		170 la 320°C (Heating segment)
		320 la 170°C (Cooling Segment)
		170 la 320°C (Heating segment)
Zinc	419.6	20 la 470°C (Heating segment)
		470 la 320°C (Cooling Segment)
		320 la 470°C (Heating segment)
		470 la 320°C (Cooling Segment)
		320 la 470°C (Heating segment)

After recording the thermograms for each sample, the PROTEUS program evaluates the melting and crystallization temperatures for the last two melts and crystallizations, respectively.

The temperature is determined after marking each curve and by selecting the Peak option from the Evaluation menu.

The data obtained is centralized in Table 5.

Table 5. Values recorded from the evaluation of DSC thermograms

Sample	Sample mass,	Melting tem	Crys talli zati	Temperature range	Heating rate	Aria
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Lab. 1. Sample preparation for differential scanning calorimetric analysis (DSC) and equipment calibration

	mg			Heating, °C	Cooling, °C		
Bismuth							
Indium							
Tin							
Zinc							
Mercury							

The data obtained is then entered into the calorimeter program and the temperature calibration is performed according to the steps indicated in the calorimeter manual.

2.2.2. Sensitivity calibration

For quantitative evaluation of the maximum ranges recorded on the DSC thermogram (determination of enthalpy) or Delta cp values, the sensitivity of the measuring sensor as a function of temperature must be recorded.

An instrument must be calibrated with known melting enthalpy calibration standards at different temperatures under identical test conditions (crucible, atmosphere, heating rates, sample mass).

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To determine the heat flow in a sample from the measured signal, it is necessary to know the temperature sensitivity calibration factor. This is the determination of a temperature dependent proportional factor between peak area and enthalpy (enthalpy = heat). Only when sensitivity calibration is included in a measurement will the peak area result be expressed in J/g.

To calibrate the sensitivity of the instrument, follow the same procedure as for temperature calibration. Use the same five samples of pure elements with known melting and solidification temperatures. The temperature program to which the samples are subjected is the same. After registering the DSC thermograms using the PROTEUS program, the areas of the exothermic maxima corresponding to the solidification of the samples used and the endothermic minima corresponding to their melting are determined.

The data obtained are then entered into the calorimeter program and the sensitivity calibration is performed according to the steps indicated in the calorimeter manual.

It should be noted that the Area parameter required for sensitivity calibration depends on the heating rate, the atmosphere used, and the crucible material. Therefore, sensitivity calibration should be performed for the conditions that will be used for subsequent measurements. For quantitative and accurate results, any change in these three experimental conditions requires an additional calibration curve.

It is important that calibration be performed periodically or whenever there are external factors that may affect the results obtained.

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Laboratory no. 2

Specific sample preparation for mechano-dynamic analysis and equipment calibration

The goal of the lab is to familiarize students with specific sample preparation for Dynamic Mechanical Analysis (DMA) and instrument calibration. In the lab, students will prepare samples of various materials and calibrate the Artemis DMA analyzer.

1. Theoretical considerations

Dynamic Mechanical Analysis (DMA) is a technique used to characterize the properties of materials as a function of temperature, time, frequency, stress, atmosphere, or a combination of these parameters.

This type of analysis, in which the sample is subjected to a periodic (sinusoidal) mechanical stress, provides information about the mechanical properties of viscoelastic materials as a function of time, temperature, and frequency. DMA analysis is used to measure vibration damping capacity, Young's modulus, and transformation temperatures [Lofthouse, 1978].

DMA analysis has been widely used in the characterization of polymers [Haponiuk, 2009] and is currently being used as an alternative technique to study the viscoelastic and damping properties of metallic materials [Martinez-Flores, 2009]. Other applications include the analysis of novel composite materials, the pharmaceutical field or applications for the identification of glass transitions in powders, hot extruded materials, pellets and enteric polymer films [Soutari, 2012].

Lab. 2. Specific sample preparation for mechano-dynamic analysis and
equipment calibration

The instrument used to perform such measurements is called a mechano-dynamic analyzer, and it can record the following signals

- Force amplitude;
- Displacement amplitude;
- The phase difference between the force signal and the displacement signal.

One of the results of a DMA analysis is the complex modulus of elasticity (E^*) of the specimen. E^* is the ratio of force amplitude to strain amplitude and represents the stiffness of the material.

For a viscoelastic material, the modulus is a complex quantity, E^* [E. E. Martinez-Flores et. al, 2009] with the following form:

$$E^*(\omega) = E'(\omega) + iE''(\omega)$$

were:

E' is storage modulus,

E'' is loss modulus.

E' affects the elastic response of the material, while E'' describes the strain energy that is completely dissipated or lost due to internal friction.

The force applied to a specimen during the measurement must be within the linear range defined by Hooke's law.

The sample temperature or the frequency of the applied force is often varied, resulting in variations in E^* ; this approach can be used to localize the glass transition temperature of the material, as well as to identify other solid state transformations.

2. Sample preparation for DMA analysis

Proper sample preparation for DMA analysis ensures that accurate results are obtained. There are standards that require specific steps in sample preparation and it is recommended that the user follow these. DMA analysis can be performed on solid, powder or gel samples. DMA samples should be cleaned of oxides and degreased to prevent errors. Powder samples require more extensive preparation. For these types of materials, a special equipment is available to ensure that the material is compacted and formed into slides that can then be analyzed.

In the laboratory, students will prepare samples for DMA analysis using the Artemis DMA 272 E analyzer. The samples used will be: Fe-based metal alloys, ABS (acrylonitrile butadiene styrene butadiene styrene) polymer, and liquid wood slides.

The sample preparation steps for DMA analysis are as follows:

1. **Sample cutting.** The DMA Analyzer is equipped with a specimen holder for 3-point flexure testing. For this type of holder, the specimen dimensions must be within the values shown in Table 1.
2. **Cleaning oxide samples** by grinding them on metallographic paper;
3. **Degreasing of samples.**

Table 1. Maximum values for sample dimensions

Sample holder type	Length, mm	Width, mm	Height, mm
3-point bending	10	1...4	0,5...1
	20	4...12	1...2

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	20	4...12	2...3
	40	4...12	2...3
	40	4...12	3...4
	50	4...12	4...5

After preparation, the samples will be measured with a caliper and their dimensions will be listed in table 2.

Table 2. Sample sizes

Sample	Length, mm	Width, mm	Height, mm

2.1. Calibration of the DMA 242 E Artemis Analyzer

Obtaining correct results in DMA analysis depends on a number of factors, such as: proper calibration of the instrument used, proper preparation of the specimen using a specific geometry and application of a heating and/or cooling rate, and appropriate strain stress.

To know the behavior of the instrument in terms of force, deformation, temperature, etc., a complete calibration of the instrument is required. It is recommended that the DMA Analyzer be re-calibrated after it has been transported or moved to a new location.

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There are no standards that require DMA analyzers to be calibrated. In general, calibration is performed according to the manufacturer's recommendations.

In the laboratory, calibration of the DMA 242 E Artemis analyzer is performed according to the manufacturer's instructions in the instrument manual. Four calibrations are recommended (Figure 1):

- Dynamic mass calibration;
- Empty System Calibration;
- System stiffness calibration;
- Rotation tuning calibration.

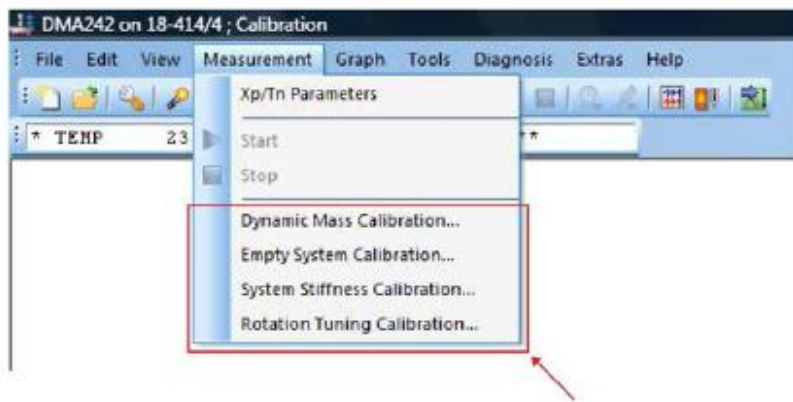


Figure 1. DMA Analyzer Calibration

The order of calibrations is specified by the manufacturer and is shown in Figure 2:

Lab. 2. Specific sample preparation for mechano-dynamic analysis and equipment calibration

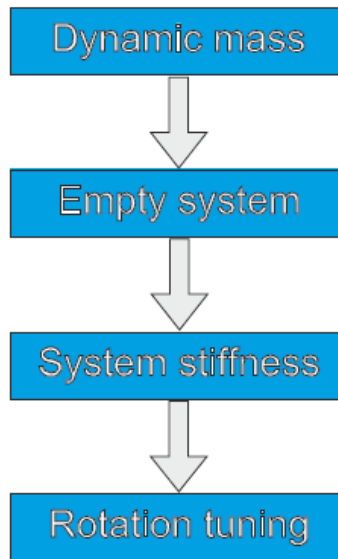


Figure 2. The correct order of calibration for DMA 242 Artemis



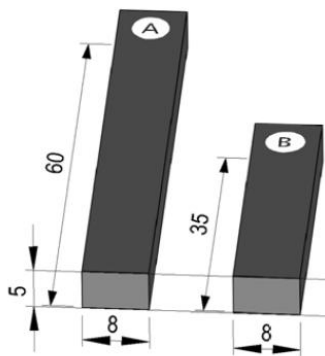
Figure 3. The cylinder used in the first calibration step

Dynamic mass calibration (Figure 3) is performed at a frequency of up to 100 Hz, once with and once without a known weight coupled to the system. The dynamic constant of the system is determined by comparing the two measurements. The sensitivity of the transducer and oscillator is affected by this constant.

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Empty system calibration determines the elastic constant of the instrument at room temperature. This calibration method requires that the initial calibration be performed. It is performed without a sample but with the sample holder mounted, at room temperature, and with a well-defined frequency program.

System stiffness calibration is performed to determine the system compliance (a measure of the degree of elasticity of a mechanical system) as a function of the type of sample holder, temperature program, frequency, and force used.



*Figure 4. Rigid specimens used for calibration of the 242 E Artemis analyzer:
A - Test used for three-point flexure and double flexure; B - Sample used for
double flexure*

Rotation tuning calibration - This type of calibration is used to obtain a high accuracy of the internal friction, especially for very stiff specimens (metallic, composite). Assuming that the internal friction has small values for steels and constants for frequencies between 1 and 100 Hz, the deviations

Lab. 2. Specific sample preparation for mechano-dynamic analysis and
equipment calibration

introduced by the electronic part can be more easily highlighted. This type of calibration is performed on a lamellar specimen.

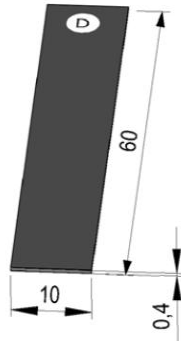


Figure 5. Sample used to calibrate errors introduced by the electronic part

The accuracy of temperature measurements can be affected by changes in the instrument. One of the reasons for these variations is the aging process of thermocouples. The dynamics of these changes depend primarily on the number of measurements and the measurement conditions. Therefore, temperature calibration is also necessary.

Temperature calibration eliminates deviations that are assumed to be constant during a measurement. To do this, calibration materials whose transformation temperatures are known with sufficient accuracy must be measured in an experimental test independent of the actual measurement and then stored.

In the laboratory, the DMA 242 E Artemis analyzer is calibrated by following and completing all the steps described in the instrument manual.

Laboratory no. 3

Determination of the critical transformation temperatures on a DSC thermogram using the tangent and the integral method. Determination of area using a rectilinear and a sigmoidal baseline

The objective of the lab is to familiarize students with the methods used to determine the critical transformation points recorded on DSC thermograms. In the lab, DSC analyses will be performed on a material that undergoes solid state transformations during heating. The determination of the transformation temperatures on the DSC thermograms will be performed using the tangent and integral methods, and the determination of the area will be performed using a rectilinear and a sigmoidal baseline.

1. Theoretical considerations

The results of calorimetric measurements are typically presented as a thermogram or a DSC curve. The measurement curve is the continuous graphical representation of measured values as a function of time or temperature.

The shape and size of a typical DSC curve is determined by the working atmosphere and material properties. Figure 1 (a) shows a theoretical and a real melting curve. During melting, the reaction should stop when all of the material has changed from a solid to a liquid state and the reaction responsible for heat absorption has stopped; therefore, the curve should abruptly return to the baseline, as in the case of curve (b). Most of the time,

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the curve will return to the baseline more slowly, as shown in case (a). Therefore, we can speak of a theoretical and a real value of the critical temperatures specific to the transformations.

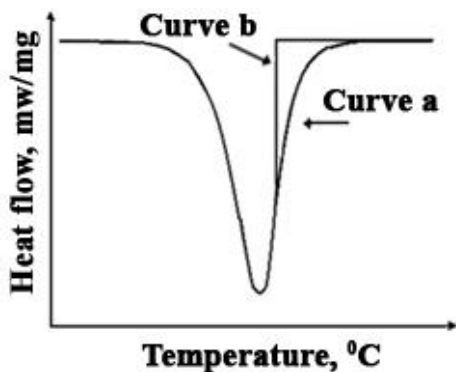


Figure 1. DSC thermogram, (a) – real curve; (b) – theoretical curve

There are situations where the curve does not return to the original baseline, but to another arbitrary line above or below the original baseline, as shown in Figure 2. The situation can be even more complex when the final baseline not only has a different level but also a different slope.

DSC thermograms are evaluated using commercial software.

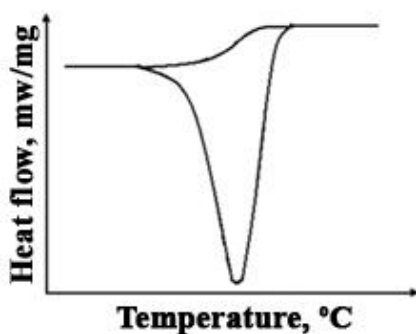


Figure 2. DSC thermogram illustrating the signals return to an arbitrary line above the original baseline

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The determination of the critical transformation temperatures can be achieved by several methods. Among them, we mention:

1. tangent method;
2. integral method.

1.1. Determination of critical transformation temperatures using the tangent method

The critical transformation temperatures are considered to be the following: the start transformation temperature (T_{start} or T_s), peak temperature (T_{50}), and the end transformation (T_{final} or T_f).

When the tangent method is used, T_s and T_f are determined, but these values correspond to the theoretical transformation temperatures. Real transformation temperatures (T_s^{real} și T_f^{real}) correspond to the geometric beginning and end of the heat flux variations, as can be seen from the schematic illustration in Figure 3. T_{50} marks the point where half of the transformation occurred (50%).

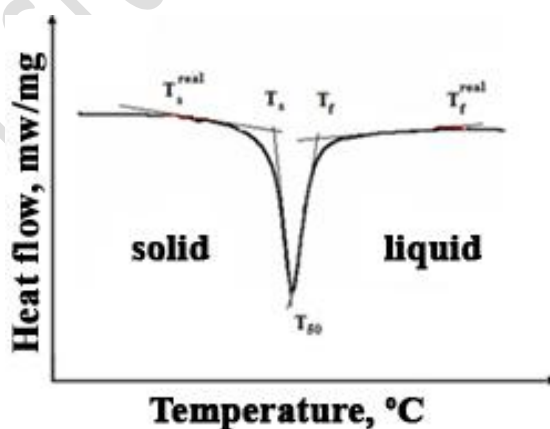


Figure 3. Schematic illustration of heat flux variation and critical temperatures determined by the tangent method for melting process

The analysis software automatically determines only the theoretical transformation temperatures, but it is also possible to manually determine the values of the real transformation temperatures. This method is very common in the evaluation of phenomena identified on DSC thermograms [Kelly L. Troni, 2016, J. P. Dumas, 2013].

1.1. Determination of critical transformation temperatures using the integral method

The integral method is a more sophisticated method for determining critical transformation temperatures. In this method, the temperature T_s corresponds to a conventionally defined fraction (which can be 5 or 10%) of the transformed phase, and the temperature T_f corresponds to 90% or 95% of the transformed phase, respectively (Figure 4).

For example, the conventional critical temperatures T_s^{10} and T_f^{90} correspond to the temperatures at which 10% and 90% of the transformation took place, respectively, and are evaluated by the respective percentage of the area bounded by the respective endothermic minimum and the baseline, as seen in the upper part of Figure 4 [N.M.Lohan et al., 2011].

The results of DSC curve analysis depend on the choice of measurement technique and the baseline used. Therefore, due to the complexity of heat flux variation at high scan speeds, the use of a straight-line baseline may be inappropriate, in which case a polynomial function is suggested.

It is usually necessary to correct the measured baseline values for DSC thermograms. Analysis programs offer the ability to use different baselines: linear, tangential, or sigmoid. Baseline correction significantly affects the

inverse reaction kinetics parameters. It is also advisable to consider physicochemical phenomena when selecting the baseline [P. J. Haines, 1998].

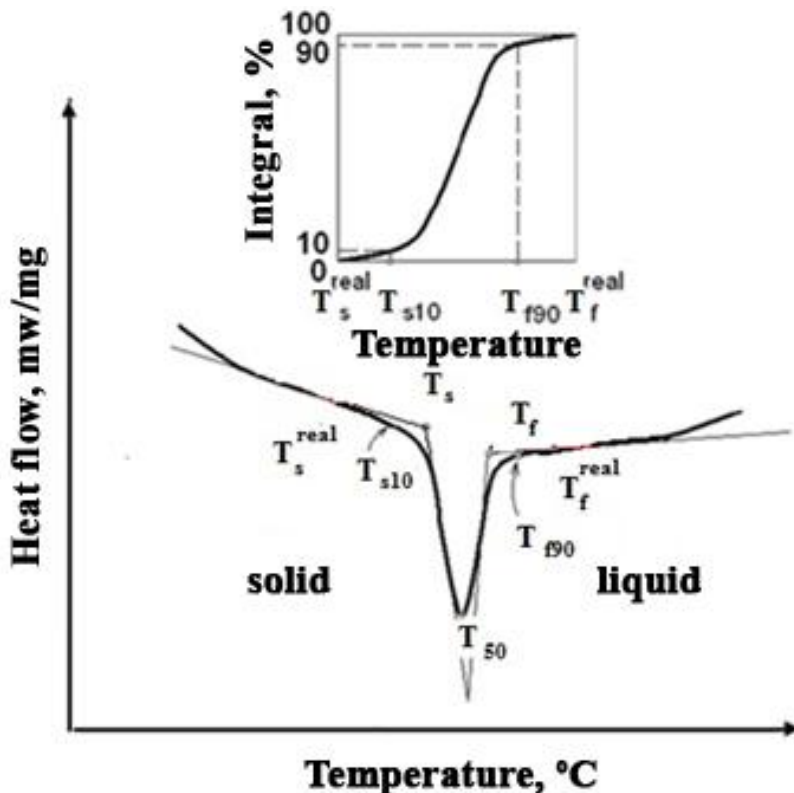


Figure 4. Schematic heat flow variation and critical temperatures determined by the integral method for the melting process

The types of baselines used to evaluate the area of the endothermic minimum or the exothermic minimum can be different. The most commonly used types of baselines are [Lohan N.M., 2012]:

1. linear;
2. sigmoidal.

Lab. 3. Determination of the critical transformation temperatures on a DSC thermogram using the tangent and the integral method. Determination of...

The area between the heat flux variation and the selected baseline is proportional to the change in enthalpy, which is the heat consumed (endothermic) or released (exothermic) by the sample.

1.2. Determination of area using a linear baseline

The linear baseline connects the start and end values of the measurement range with a continuous line. If the points corresponding to the baselines before and after the heat flux change (points A and B in Figure 5) are collinear, a linear baseline can be used.

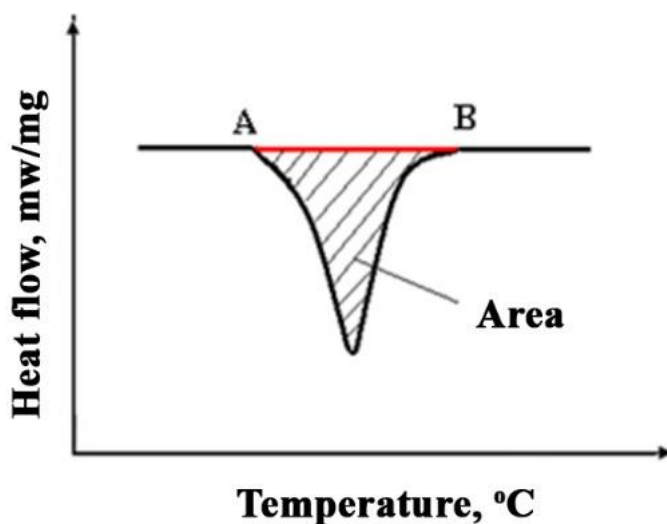


Figure 5. Measuring area using a linear baseline

1.3. Area determination using a sigmoidal baseline

If the corresponding baseline points present before and after the variation from the baseline are at different levels, a sigmoidal baseline can be used to determine the area, as seen in Figure 6.

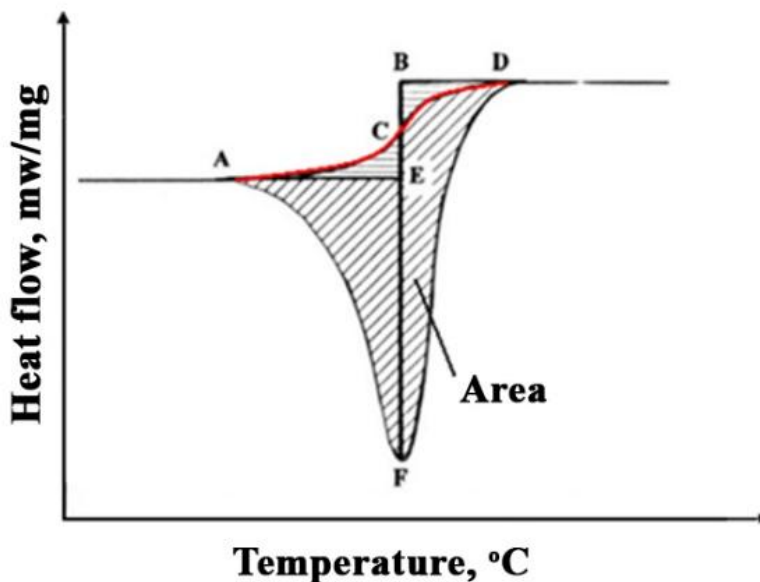


Figure 6. Area measurement using a sigmoidal baseline

In this case:

$$\text{ACDFA area} = \text{AEBDFA area} + \text{CBDC area} - \text{ACEA area}$$

Since the CBDC area \approx the ACEA area, then the ACDFA \approx AEBDFA. Using this type of baseline does not give the absolute area, but it is considered to give a closer value than using a linear baseline.

2. Working mode

In the laboratory, the critical temperatures specific to melting and solidification are determined from the DSC thermograms recorded during heating and cooling of the pure chemical elements: bismuth, indium, tin, zinc and mercury by the tangent and integral methods. The determination of the

Lab. 3. Determination of the critical transformation temperatures on a DSC thermogram using the tangent and the integral method. Determination of...

amount of heat absorbed/dissipated is performed using both a straight line and a sigmoidal baseline.

2.1. Determination of the start and end temperatures of melting and solidification by the tangent method. Determination of area using a linear and a sigmoidal baseline

To determine the critical transformation temperatures, follow these steps:

1. open the Proteus program
2. select File - Open - Open measurement files;
3. from Settings, select the X-Temperature option;
4. from Settings - Check Segments, select a heating and cooling segment

and press Ok;

Now the DSC thermogram appears in the program window in the coordinates Heat flux - Temperature. An endothermic minimum attributed to melting and an exothermic maximum attributed to solidification.

To determine the critical melting temperatures using the tangent method, proceed as follows

1. select the heating curve (click on the curve);
2. select Onset from the Evaluation menu;

3. move the vertical line to the left of the transformation until the line of the first derivative (dashed line) deviates from the linearity (as shown in Figure 7);

Then press Apply and Ok. The temperature T_s appears on the thermogram.

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To determine the temperature T_f by the tangent method, proceed in the same way with the difference that from the Evaluation we select End and the vertical line to the right transformation will be shifted to line of the first derivative deviates from linearity.

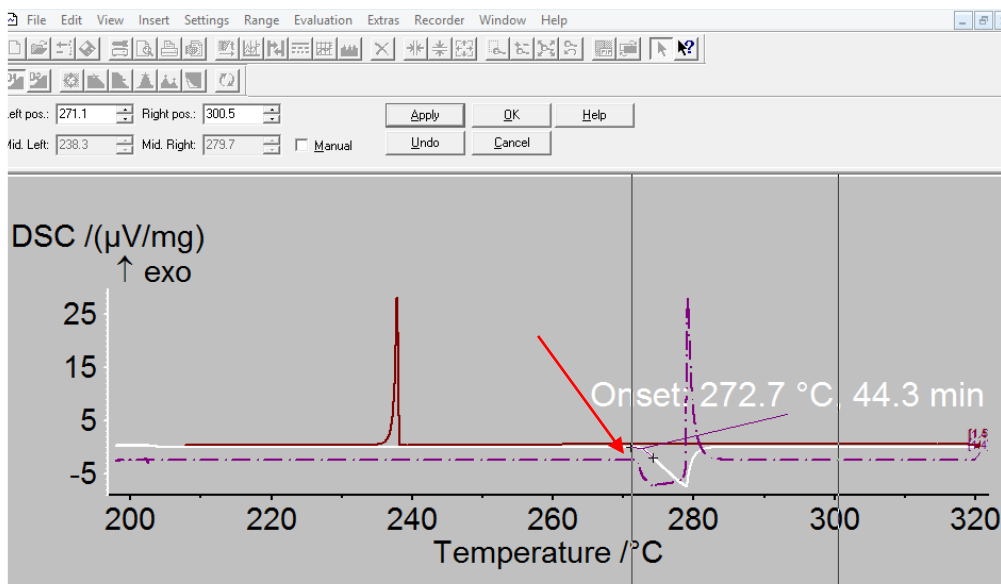


Figure 7. Determining the transformation start temperature using the tangent method

The T_{50} temperature is determined by selecting the Peak option from the Evaluation menu.

To determine the critical temperatures for the transformation from the liquid phase to the solid phase (crystallization), follow the same procedure as above, except that this time the higher temperature is the temperature at the beginning of the transformation and the lower temperature is the temperature at the end of the transformation.

To determine the area, perform the following steps:

Lab. 3. Determination of the critical transformation temperatures on a DSC thermogram using the tangent and the integral method. Determination of...

1. in the Evaluation menu, select 1st Derivative; the signal for the first derivative appears on the thermogram;

2. from the Evaluation menu, select the Area; the vertical lines are shifted to the left and right of the first derivative so that its linearity deviations are perfectly bordered;

3. from the top, select the type of baseline (Baseline tipe); the baseline will be selected as linear or sigmoid.

The obtained data are centralized in Table 1.

Table 1. Centralization of data obtained using the tangent method and a linear and sigmoidal baseline.

Sample	Temperature program	T_s [°C]	T_{50} [°C]	T_f [°C]	$\Delta H/m$ [kJ/kg]	
					Linear	Sigmoidal
Bismut	Heating					
	Cooling					
Indium	Heating					
	Cooling					
Staniu	Heating					
	Cooling					
Zinc	Heating					
	Cooling					
Mercur	Heating					
	Cooling					

2.2. Determine melting/solidification start and end temperatures using integral method

To determine the critical transformation temperatures using the integral method, follow these steps:

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- Select the heating curve (click on the curve);
- Select 1st Derivative from the Evaluation menu;
- In Evaluation, select Range; in the top left of the program window, select the "DSC integral curve" check box (see Figure 8);

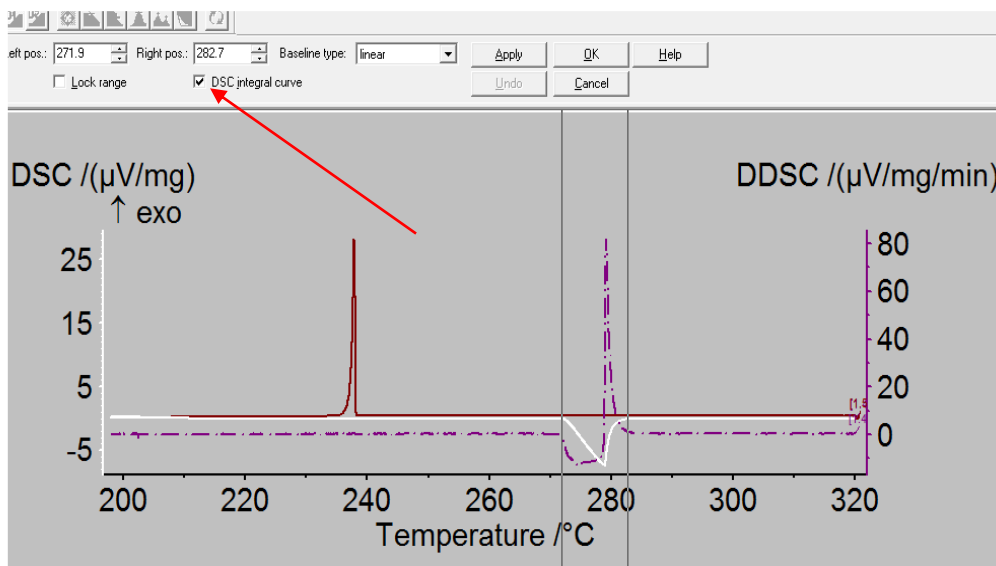


Figure 8. Selecting the integral method by activating "DSC integral curve"

- The vertical lines are moved to the left and right of the first derivative so that its linearity deviations are perfectly bordered;
- Press Apply and Ok. The integral appears on the thermogram together with the value for the area;
- Click on Integral; from Evaluation, select Set Value; a vertical line appears on the thermogram;
- move the vertical line until the desired percentage (10 or 90%) appears in the upper left window (Figure 9);
- press Apply and Ok.

Lab. 3. Determination of the critical transformation temperatures on a DSC thermogram using the tangent and the integral method. Determination of...

- The thermogram shows the values for the temperature $T_{s10\%}$, $T_{50\%}$ and $T_{f90\%}$.

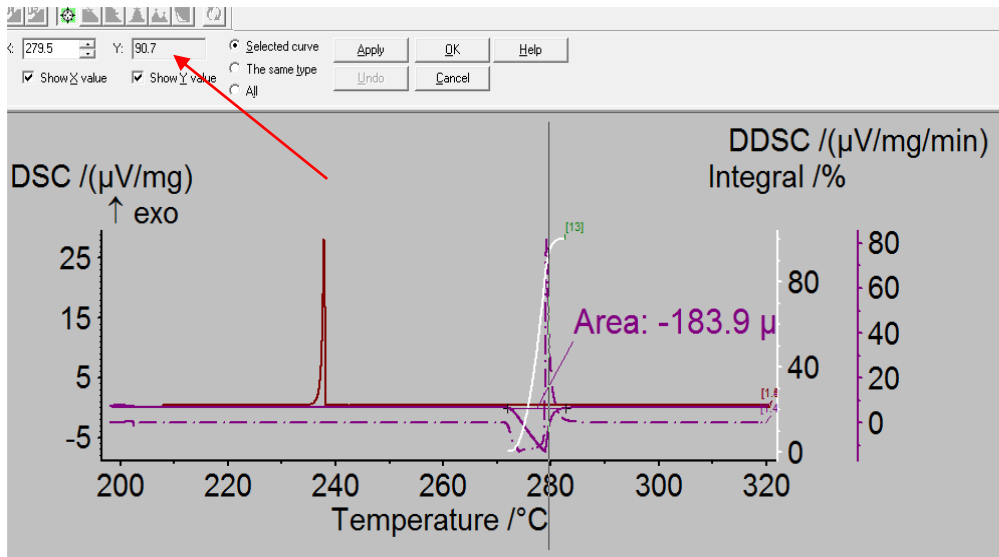


Figure 9. Determination of the critical end transformation temperature ($T_{f90\%}$)

The data obtained by the integral method will be centralized in table 2.

Table 2. Centralization of the data obtained using the integral method

Sample	Temperature program	$T_{s10\%}$ [°C]	$T_{50\%}$ [°C]	$T_{f90\%}$ [°C]	$\Delta H/m$ [kJ/kg]
Bismut	Heating				
	Cooling				
Indium	Heating				
	Cooling				
Staniu	Heating				
	Cooling				

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Zinc	Heating				
	Cooling				
Mercur	Heating				
	Cooling				

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Lab. 3. Determination of the critical transformation temperatures on a DSC thermogram using the tangent and the integral method. Determination of...

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Laboratory nr. 4

Obtaining and interpreting the DSC curves recorded during heating and cooling of a metallic alloy exhibiting phase transformations in the solid state

The objective of the lab is to familiarize students with the transformations that occur in a metallic alloy that undergoes phase transformations in the solid state, a NiTi shape memory alloy. In the laboratory, a sample of this alloy will be analyzed using the DSC calorimeter, which will be subjected to controlled heating to a higher reverse martensitic transformation temperature and then cooled to a lower direct martensitic transformation temperature.

1. Theoretical considerations

Shape Memory Alloys (SMAs) are a unique class of “smart materials” known for their unique thermomechanical properties, primarily the shape memory effect and superelasticity. These materials have the ability to return to their original shape when subjected to external stimuli. The first reported steps towards the discovery of the shape-memory effect were taken 4th decade (1932), when Olander discovered the Au-Cd alloy which had an elasticity of about 8% at room temperature, and exhibited a behavior called by Olander "rubber-type" [L.-G. Bujoreanu, 2002]. Subsequently, after 1951, other non-ferrous alloys were added to it, such as: Ni-Ti, Cu-Zn, Cu-Al-Ni, Cu-Zn-Al, as well as ferrous alloys: Fe-Mn-Si, Fe-Mn-Cr and Fe-Ni-C [N. Van Caenegem *et al.*, 2008]. Since the discovery of SMAs unique properties, they

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have been used for a wide range of applications. These alloys are currently used in various fields such as: aeronautical, mechanical, electrotechnical, medical and artistic industries [N.M. Lohan *et al.*, 2015]. Figure 1 shows the existing and potential applications of shape SMA in the automotive field.

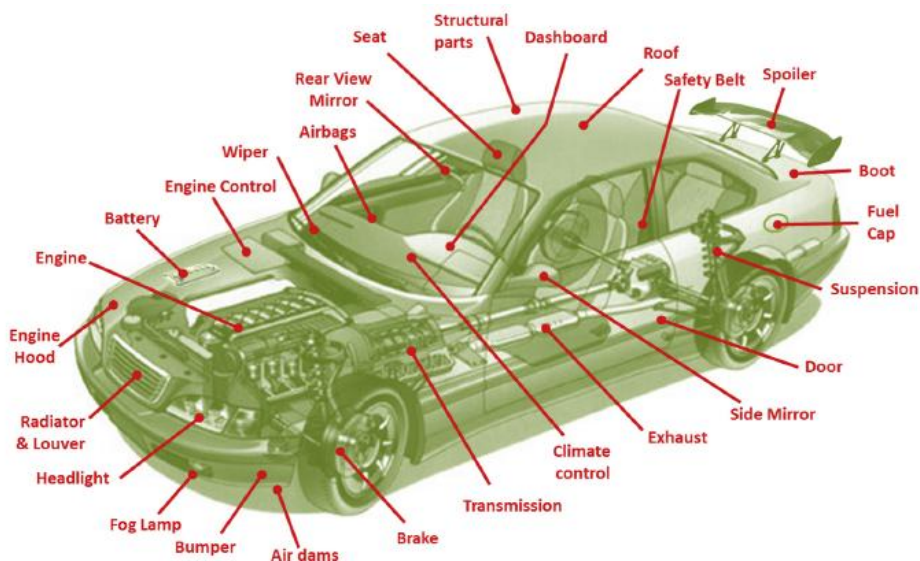


Figure 1. Existing and potential applications of SMA in the automotive sector
[J. Mohd Jani, 2014]

The NiTi alloy (also called Nitinol) is of notable interest in engineering with applicability in various technical and medical fields [J. Van Humbeeck, 2001]. The good combination of biocompatibility, ductility and hardness, with specific functional properties such as shape memory effect and superelasticity [A. Biesiekierski, *et all*, 2012] creates an exceptional material for various applications in fields such as [Mirjalili M *et all*, 2013, S.K. Wu, H.C. Lin, 2003, T.W. Duerig *et all*, 2000]: aerospace, biomechatronics or biomedical industries. Among the currently existing applications [W. Predki *et all*, 2008]:

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biomedical implants or medical devices, orthopedic and endodontic applications, actuators, robotic arms or microcontrollers (Figure 2).

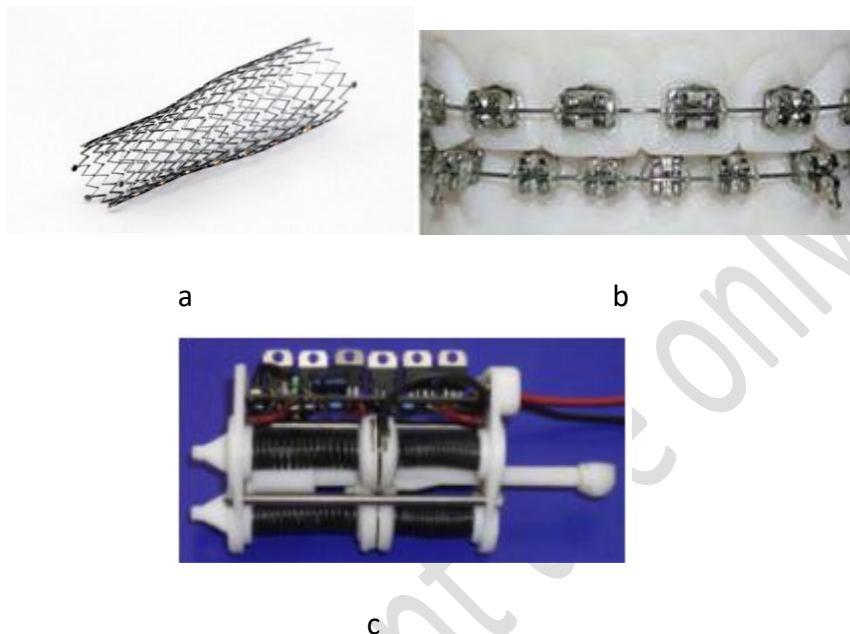


Figure 2. Applications of NiTi alloys: (a) stent, (b) orthodontic threads; (c) actuator [www.hzdr.de, www.totalmateria.com, J. Mohd Jani, 2014]

Currently, thin films of NiTi that are deposited on various substrates are also intensively studied, being new materials that can be used in the construction of micro devices.

The chemical composition of Nitinol varies between values close to the echiatomic concentration (50% at. Ni and 50% Ti). The functional properties of NiTi alloys are caused by a reversible martensitic phase transformation [A.R. Pelton *et al.*, 2012]. In general, during heating, the inverse martensitic transformation results between the monoclinic or orthorhombic crystal structure called *martensite* - M and the cantered face cubic type (cfc) crystal

Lab. 4. Obtaining and interpreting the DSC curves recorded during heating and cooling of a metallic alloy exhibiting phase transformations in the solid state

structure, called *austenite* - A [J. Olbricht *et al.*, 2013]. The chemical composition strongly influences the critical transformation temperatures. In some cases, after NiTi cooling, it is possible to observe the formation of an intermediate rhombohedral phase, between A and M, called the R phase [K. Otsuka, 1990]. The appearance of the R phase was explained by the presence of precipitates, mainly Ti_3Ni_4 [T. Fukuda *et al.*, 1997]. The R phase transition has been described as a kind of M (actually pre-martensitic) transformation with small thermal hysteresis [Y. Zhou *et al.*, 2006]. NiTi alloys exhibit a complex mechanical behavior, which depends on the chemical composition, heat treatment temperatures and production process.

The most efficient way to highlight phase transformations in a NiTi alloy is a DSC analysis [H. Mohamad, 2018].

Figure 3 shows the DSC thermogram of a heating/cooling cycle on a NiTi alloy in the temperature range between 10 ... 120 °C.

During heating, in the temperature range between 80 - 120 °C an endothermic transformation appears which is attributed to the M transformation in the parent phase, A (reverse martensitic transformation). During cooling, in the temperature range between 60 – 20 °C, two exothermic transformations appear: the first is attributed to the R phase and the second, to the A in M transformation (direct martensitic transformation).

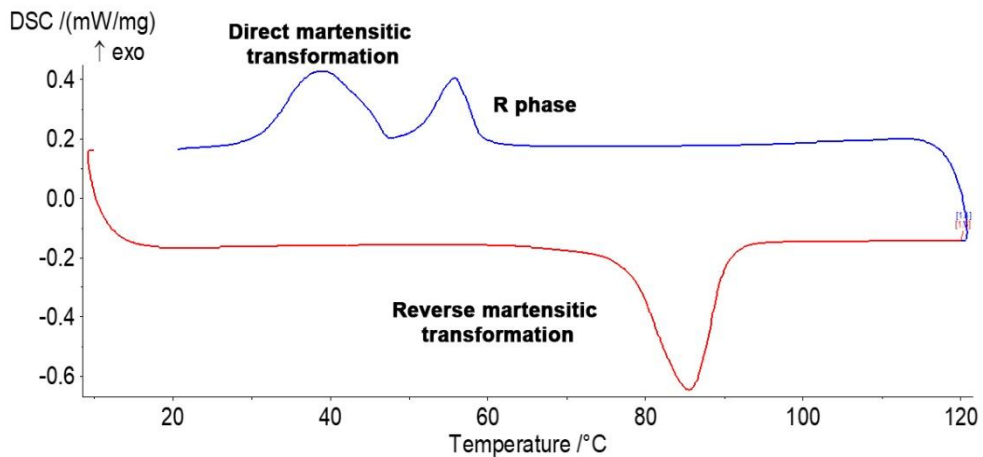


Figure 3. DSC thermogram recorded during heating/cooling of a NiTi alloy

2. Working mode

In the laboratory, an experiment will be carried out consisting of heating and cooling a NiTi SMA alloy in order to highlight the direct and reverse martensitic transformation. The sample that was first cut, cleaned and weighed will be placed in the crucible. The crucible will be placed inside the furnace and subjected to a temperature program consisting of:

- Heating from room temperature to 100°C at a rate of 10K/min;
- Cooling to 20°C at a rate of 10 K/min.

After recording the DSC thermogram, the critical temperatures of reverse martensitic transformation will be determined using the tangent method:

- A_s - austenite start temperature;
- A_{50} - austenite peak temperature;
- A_f - austenite finish temperature;

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- M_s - martensite start temperature;
- M_{50} – martensite peak temperature;
- M_f - martensite finish temperature.

The amount of heat dissipated and absorbed (ΔH) will be determined using a linear baseline.

The critical temperatures determined will be centralized in tables 1 and 2.

Table 1. Centralization of data obtained for the evaluation of reverse martensitic transformation temperatures

Sample	Heating rate [K/min]	A_s [°C]	A_{50} [°C]	A_f [°C]	$\Delta H/m$ [kJ/kg]

Table 2. Centralization of data obtained for the evaluation of direct martensitic transformation temperatures

Sample	Cooling rate [K/min]	M_s [°C]	M_{50} [°C]	M_f [°C]	$\Delta H/m$ [kJ/kg]

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Laboratory no. 5

Obtaining and interpreting DMA curves obtained in a heating / cooling metallic alloy with solid-state phase transformations

The aim of the lab work is to familiarize the students with the acquisition and interpretation of the results obtained by mechanical-dynamic analysis in the case of heating and cooling of a metallic material with solid phase transformations. The experiments will be carried out with the DMA 242 E Artemis dynamo-mechanical analyzer.

1. Theoretical Considerations

DMA analysis is a technique used to study and characterize materials (metallic and polymeric). The DMA analyzer can also be used for quality control and product development [Ebnesajjad S., 2006]. DMA analysis is a versatile technique that complements the information provided by more traditional TA techniques, such as DSC analysis.

The main moduli of solid materials are the stiffness or shear modulus (G) and Young's modulus (E). depending on the direction in which the stress is applied in the solid material they differ.

The storage modulus symbolized E' (for bending tests) or G' (for shear tests) is a measure of the elastic behavior of the sample.

The DMA analysis allows the determination of the storage modulus (E') and the loss modulus (E'') as well as the quantities derived from them. The

Lab. 5. Obtaining and interpreting DMA curves obtained in a heating / cooling metallic alloy with solid-state phase transformations

storage module or dynamic module (E') are commonly associated to the Young module. It is often associated with the "stiffness" of a material and determines how rigid or brittle a sample is. It can also be considered as a quantity that gives the ability of the analyzed material to store the applied energy. The loss modulus (E'') is the response of the viscous part of the materials and can be considered as a quantity that gives the tendency of the materials to dissipate the applied energy [Jawaid J., 2013]. The loss modulus is sensitive to different types of molecular motions, transformations, relaxation processes, morphology, and other structural heterogeneities.

The illustration of the two modules is shown in Figure 1.

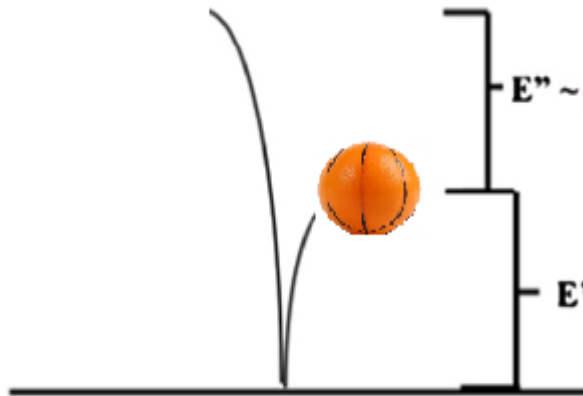


Figure 1. Illustration of loss and storage module

When a ball is dropped from a certain height, it will bounce to a lower final height. The size of the final height is determined by the elastic response of the material. This results in a certain amount of energy being dissipated and a certain amount of energy being stored.

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The ratio of dissipation to storage modulus is called $\tan \delta$ (Tan δ) and is referred to as damping capacity or internal friction, which is a dimensionless quantity. $\tan \delta$ is a measure of energy dissipation in the material.

The relationship between the loss modulus and the storage modulus is shown in Figure 2.

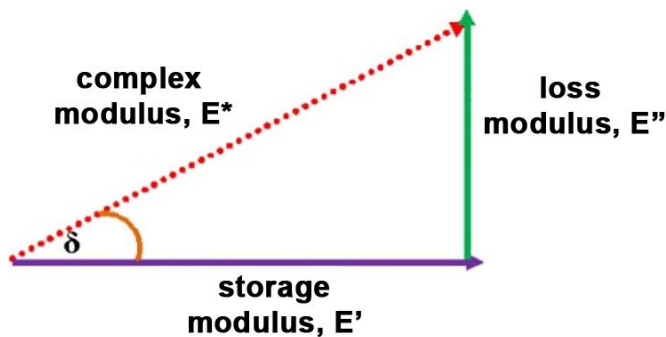


Figure 2. The relationship between E' , E'' and $\tan \delta$

From the figure above it follows that the storage module is:

$$E' = E^* \cdot \cos \delta;$$

The loss modulus is:

$$E'' = E^* \cdot \sin \delta;$$

Internal friction is:

$$\tan \delta = \frac{E''}{E'}$$

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The relationship between loss modulus, storage modulus, $Tan \delta$ and temperature in a DMA thermogram is shown in Figure 3. The resulting component is named the complex mode (shear mode), noted by (E^*). A high value of $Tan \delta$ indicates a material that has a high, non-elastic tension, while a low value indicates a high elasticity.

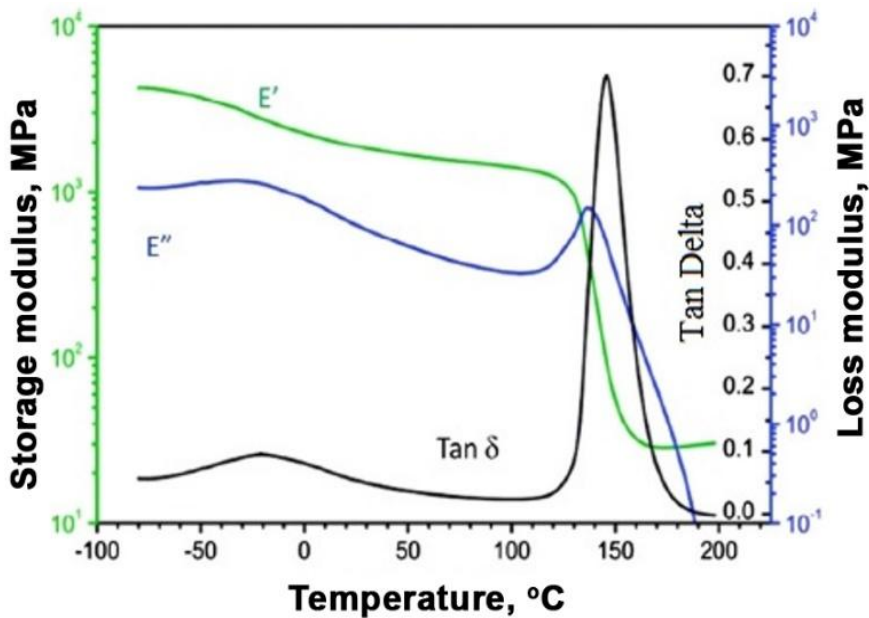


Figure 3. E' , E'' and $Tan \delta$ variation with temperature

$Tan \delta$ is the way in which energy is dissipated in a material subjected to cyclic deformation. It is a property of the material that consists in the ability to dissipate as efficiently as possible the energy accumulated by the material after a deformation. δ is 0° for purely elastic materials and 90° for purely viscous materials. Viscoelastic materials have a phase angle between these two ideal cases, depending on the rate of deformation (Figure 3).

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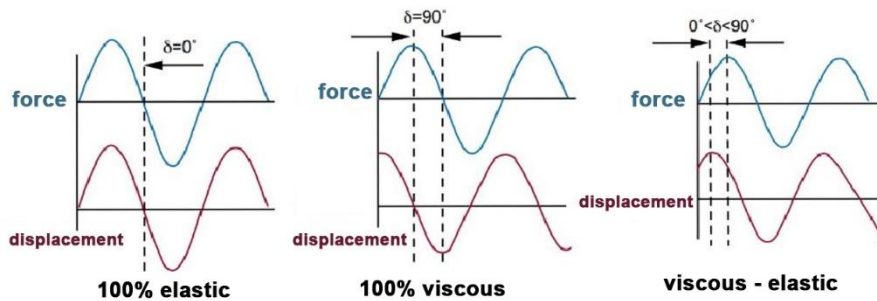


Figure 4. Illustration of elastic, viscous and viscous-elastic behavior
 [http://www.tainstruments.com]

DMA analysis consists of applying a sinusoidal strain to the specimen of known geometry. The sample can be subjected to controlled deformation or strain. When a known stress is applied, the sample will deform by a certain percentage depending on the stiffness of the sample. The deformation is sinusoidal and is applied by a motor that generates this oscillatory motion, which is transmitted to the specimen via a drive shaft.

Figure 4 shows the relationship between the applied sinusoidal force and the response of the material resulting in the phase difference, denoted by $\tan \delta$.

The viscoelastic parameters (E' , E'' and $\tan \delta$) can be measured as a function of strain amplitude, frequency, time and temperature.

The storage modulus determined by the DMA analyzer is different from the Young's modulus of the material. The Young's modulus is calculated from the initial part of the stress-strain curve and is conceptually similar to the storage modulus, but it is not the same.

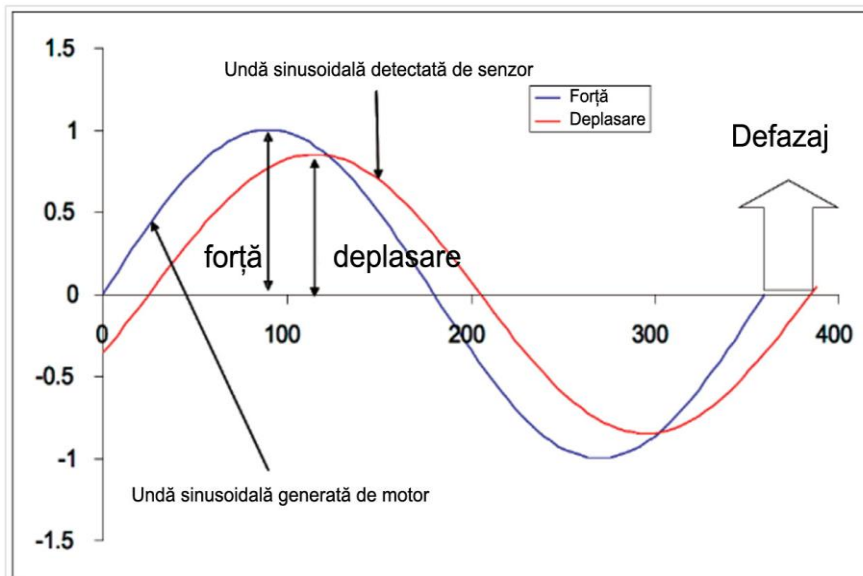


Figure 5. The relationship between the applied sinusoidal force and the reaction of the material [www.netzsch.com]

To obtain accurate results from DMA analysis, the following conditions must be met:

1. the instrument must be calibrated
2. the sample must be carefully prepared, taking into account the geometry required by the type of sample holder used;
3. elongations appropriate to the type of material must be used, as well as heating/cooling rates between 2 - 5°C, depending on the sensitivity of the transformation.

2. Working mode

An experiment will be performed in the laboratory consisting of heating an Fe-based SMA. The sample, which has been cut, cleaned and measured, is

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placed in the sample holder of the DMA analyzer. The parameters used in the experiment are:

1. protective atmosphere: argon;
2. type of specimen holder: three-point bending deformation;

Dynamic parameters used:

1. amplitude 20 μm
2. frequency: 1 Hz
3. dynamic force: 9 N

Temperature program:

1. heating up to 400 °C at 5 K/min
2. hold for 10 minutes
3. cooling to room temperature at a rate of 5 K/min.

After the experiment, the curves obtained are analyzed with Proteus software. Being an SMA, the reverse martensitic transformation appears during heating. After recording the DMA thermogram, the critical points of this transformation are determined. Figure 6 shows typical temperature variations of the storage modulus (E') and internal friction ($\text{Tan } \delta$) for an Fe-14Mn-6Si-9Cr-5Ni alloy (% mass). The transformation of martensite into austenite is always associated with a local maximum of $\text{Tan } \delta$.

Analyzing the thermogram in Figure 6, it can be seen that the decrease in storage modulus (E') is accompanied by two maxima of internal friction. In the Fe-Mn-Si SMA, on heating, the maxima ($\text{Tan } \delta$) are accompanied by a decrease in the storage modulus because the modulus of martensite ϵ -hc (compact hexagonal) is greater than that of austenite γ -cfc. If two maxima of internal friction occur during the heating of Fe-Mn-Si-based SMA, the first can

Lab. 5. Obtaining and interpreting DMA curves obtained in a heating / cooling metallic alloy with solid-state phase transformations

be attributed to the reversal of martensite α' -cvc (cubic with centered volume) in γ -cfc austenite, and the second, from high temperatures, to the reversal of ϵ -hc martensite in γ -cfc austenite [Mihalache E., 2017].

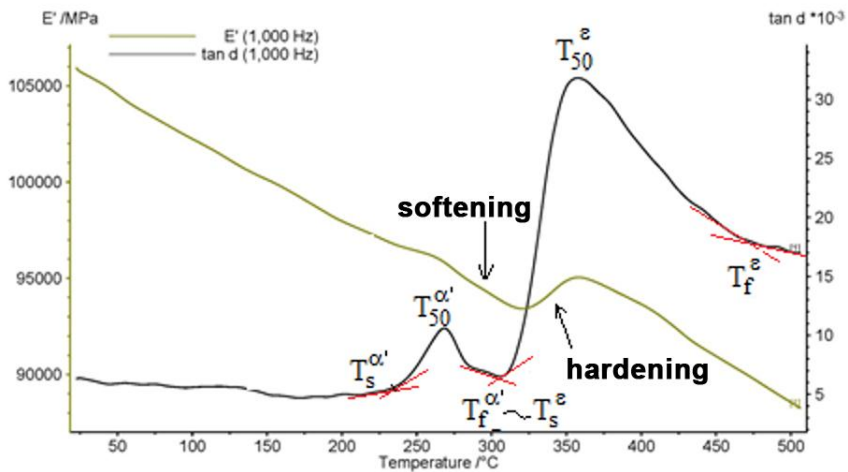


Figure 6. Variation of E' and $Tan \delta$ with temperature for an alloy Fe-14Mn-6Si-9Cr-5Ni (% mass)

In Figure 6, on the curve corresponding to the variation of $Tan \delta$ with temperature, the reverse martensitic temperatures were determined by using the tangent method:

- starting temperature of the transformation of α' martensite to austenite - $T_s^{\alpha'}$;
- peak temperature of a α' martensite in austenite - $T_{50}^{\alpha'}$;
- finish temperature transformation of α' martensite to austenite - $T_f^{\alpha'}$;
- start temperature transformation of martensite ϵ into austenite - T_s^{ϵ} ;
- peak temperature of ϵ martensite in austenite - T_{50}^{ϵ} ;
- finish temperature transformation of ϵ martensite in austenite - T_f^{ϵ} ;

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On the curve corresponding to the variation of storage modulus E' with temperature, a softening and a hardening can be observed, both phenomena correspond to the maxima recorded by the internal friction ($T_{50}^{\alpha'}$ and T_{50}^{ε}). Softening is associated with the transformation of the ε phase into γ during heating while hardening may be associated with the antiferromagnetic-paramagnetic transition of γ -cfc austenite that occurs during heating to Néel temperature T_{50}^{ε} [Mihalache E., 2017].

Based on these curves, the students will identify the transformations that take place and with the Proteus software they will identify the values of the start and finish temperatures, as well as the maximum of each transformation.

The data obtained will be included in Table 1 which, together with figure 6, will be the subject of analysis and discussion.

Table 1. Critical transformation temperatures

Sample	Transformation	Transformation temperatures [°C]		Storage module, E' [MPa]	Internal friction, $\tan \delta$
		T_s	T_f		
	martensite α' - austenite γ	T_s			
		T_{50}			
		T_f			
	martensite ε in austenite γ	T_s			
		T_{50}			
		T_f			

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