Fundamentals of the Differential Scanning Calorimetry application in materials science

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Until recently, methods testing the changes of the material properties as a function of time with temperature changes under specified measuring conditions were named the thermal analysis. However, in 1999, the International Confederation for Thermal Analysis and Calorimetry (ICTAC) introduced a new classification of research methods. Nowadays the Thermal Analysis (TA) should be understood as the technique which studies the properties of materials as they change with temperature/time conditions while the calorimetry as a method of measuring the heat. The different thermoanalytical research methods are distinguished depending on the measured properties of the sample. For example, when measurement concerns:

✓ *temperature difference* - there is a method of the DTA - the Differential Thermal Analysis,

✓ *heat capacity or heat of transformation* - depending on device construction we talk about calorimetry or Differential Scanning Calorimetry - DSC

✓ *weight change as a function of temperature* –there is a ThermoGravimetric Analysis TGA,

✓ *dimensional changes as a function of temperature* - this is defined as a method of ThermoDilatometric analysis - TDA

✓ *change in mechanical properties as a function of temperature* - ThermoMechanical analysis TMA.

These examples are only a part of the group of thermoanalytical methods. There is a much wider range of physical properties of materials that exhibit a dependence on temperature changes.

Depending on the sample heating method the different methods can be listed [1]:

✓ *static* – during the measurement the sample temperature suddenly changes and next it is held at that level until the sample components obtain the equilibrium state,

✓ *dynamic* – the measurement is carried out under the continuous conditions of temperature changes (mostly linear).

In practice, the combination of different methods is frequently used. Therefore, a further classification can be made [1]:

✓ *techniques at the same time* – a sample is investigated at the same time by two or more methods, such, for example, as DTA and TG;

✓ *simultaneously coupled techniques* – consist of a test sample by two or more techniques independently operating, but during the measurement the testing devices are connected to each other, such as: a combination of TG and mass spectrometry;

✓   *techniques periodically interact simultaneously* - consist of testing of a sample by two or more conjugated measuring techniques in which the second measurement is carried out in a discontinuous way, for example: DTA and gas chromatography.

Differential Scanning Calorimetry (**DSC**) relies on the measurement of the difference between the heat flow vs. temperature relation of the sample and the heat flow vs. temperature relation of a standard.

There are many types of calorimeters and the criteria for their classification. The classification of these devices can be made in respect of:

✓   *ranges of temperature and pressure range* – high temperature/pressure and low temperature/pressure;

✓   *type of the test process* – to measure the heat of mixing, heat capacity;

✓   *thermodynamic conditions* – adiabatic, non-adiabatic;

✓   *sample weight change during the measurement* – open (with the exchange of mass), closed (no mass transfer).

Due to the various applications and the type of test methods, calorimeters differ in design. For example, some of them have only one measuring chamber (called as appropriate calorimeter), whereas in the case of so-called differential calorimeter, in a common outer cover two identical measurement crucibles are placed (for the test sample and the reference sample) – Fig. 1. Irrespective of the type calorimeter a measured thermal effect is determined and automatically recalculated based on the directly measured value, which may be the temperature or the thermocouple thermoelectric power [2,3].
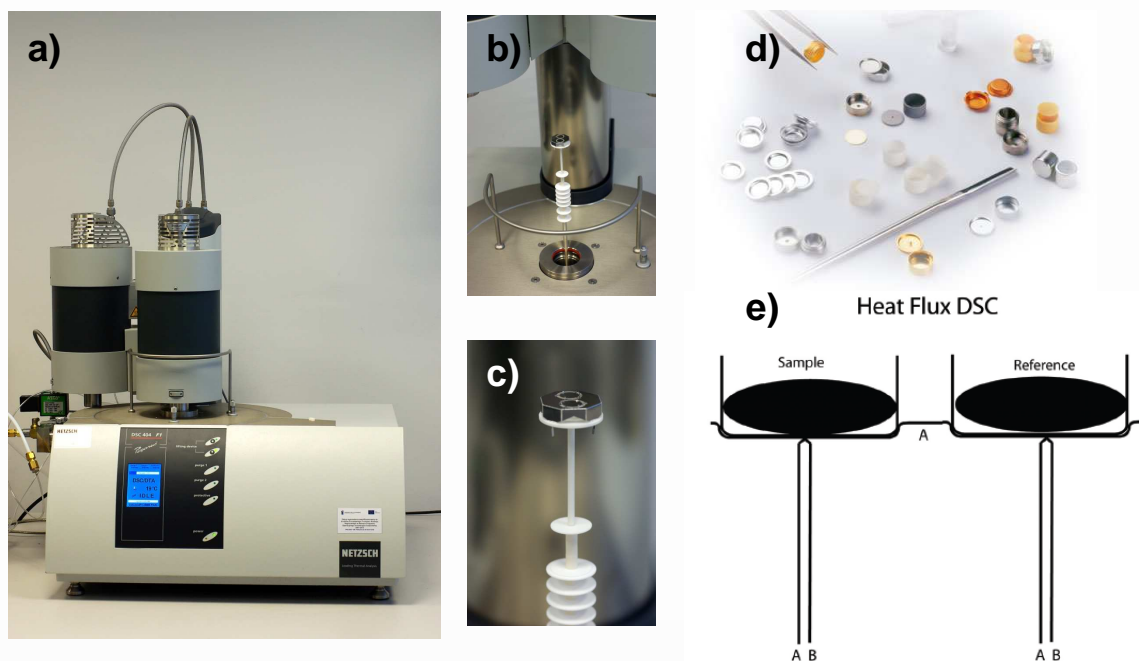

Fig. 1. Photos of the DSC 404 F1 Pegasus (Netzsch Company): a) overview, b), c) the DSC sample carrier; d) examples of the DSC crucibles; e) scheme of the DSC sample carrier cross section [4,5,6].

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Among the differential scanning calorimeters, two types of devices should be specified:
- ✓ *flow* (heat flux DSC),
- ✓ *compensation* (power compensation DSC).

In the case of heat flux differential scanning calorimeters, directly measured signal is a change in temperature between a test sample and a reference sample (Fig1a,b,c,e). This difference is proportional to the flow of the heat flux between the two samples and is automatically converted to the value of the heat flux using special software.

Compensating differential scanning calorimeters consist of two identical and isolated heaters located in the same temperature (in one heater a tested sample is placed and in the other - a reference sample). Temperature changes during the phase transformation or the reaction in the sample are compensated by varying the electrical energy supplied to the heater which is directly proportional to the heat absorbed during the process [1,7,8].

Differential Scanning Calorimetry (DSC), as it was mentioned above, is a method involving the measurement the difference of heat flow between a tested sample and a reference sample (standard, usually pure metals or sapphire), which is generated by the temperature control system. The melting point of the pure metals as well as their enthalpy vs. temperature relation are well known and therefore these information are used primarily for calibration.

The result of calorimetric measurements is a DSC curve shown as the temperature/time dependence on the heat flux (per time unit) - Fig 2. An endo- and exothermic peaks are recorded on these curves (Fig. 2), which result from the temperature differences between a tested sample and a reference sample, showing negative or positive deviations from the so-called "baseline", which is recorded at the time when no transformations/reactions occurs in the sample. The differences are caused by phase transformations and chemical reactions occurring in the material. If the temperature of a tested sample during the phase transformation/chemical reaction is lower than the reference temperature, the heat is absorbed. The situation is registered as the endothermic peak. Conversely, when the sample temperature is higher and there is separation of the heat, then this is marked as the exothermic effect on the DSC curve [1,7,9].
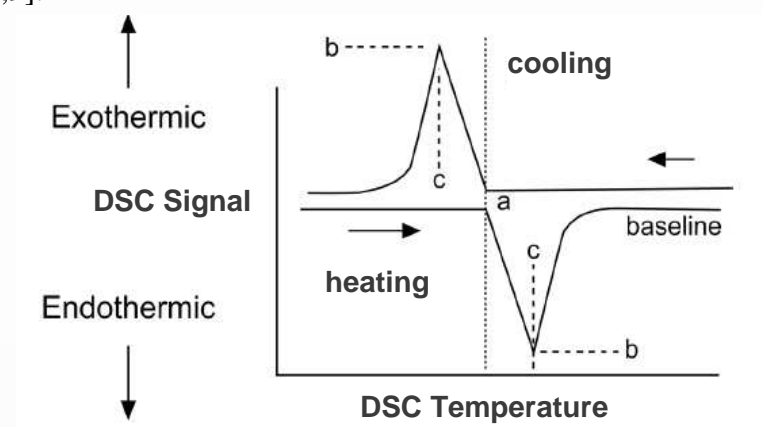

Fig. 2. DSC curves of heating and cooling cycles for pure metal: a - onset temperatures (the melting point for this example, T_M), b - peak signals, c - peak temperatures [6].

The measurements are performed in the controlled inert gas atmosphere for example: helium, argon or nitrogen of high purity. Before the proper measurement, the calibration of the device must be performed. The appropriate calorimeter calibration procedure allows to obtain a lot of information about the investigated material. The most popular measurements involve the determination of the liquidus and solidus temperatures [6] (Fig. 3a). Also, information about the temperatures as well as the heat of other phase transformations (marked as the peak area) can be obtained in the case of (Fig. 3):

- invariant reactions (eutectic, peritectic),
- the range of the thermal stability of the intermetallic compounds or solid solutions and the enthalpy of their phase transformations (for example: decomposition or degradation),
- martensitic transformation,
- recrystalization in the deformed materials,
- glass transition range (Fig. 3b),
- crystallization of a metallic glasses (Fig. 3b) with determination of their kinetics.

In order to determine the beginning of phase transition temperatures the extrapolated temperature (so-called T_{onset}, Fig. 3) of the peak should be marked as the point of intersection of the tangent drawn through the inflection point of the curve with the extrapolated baseline.
The differential scanning calorimetery is also dedicated to the precise measurements of heat capacity C_p determinate outside of the temperature range of the phase transformations.
These methods provide the possibility to determine a phase transition temperature and thermal stability of phases in the studied samples, which are important information for the determination of the phase diagrams, Fig. 4.

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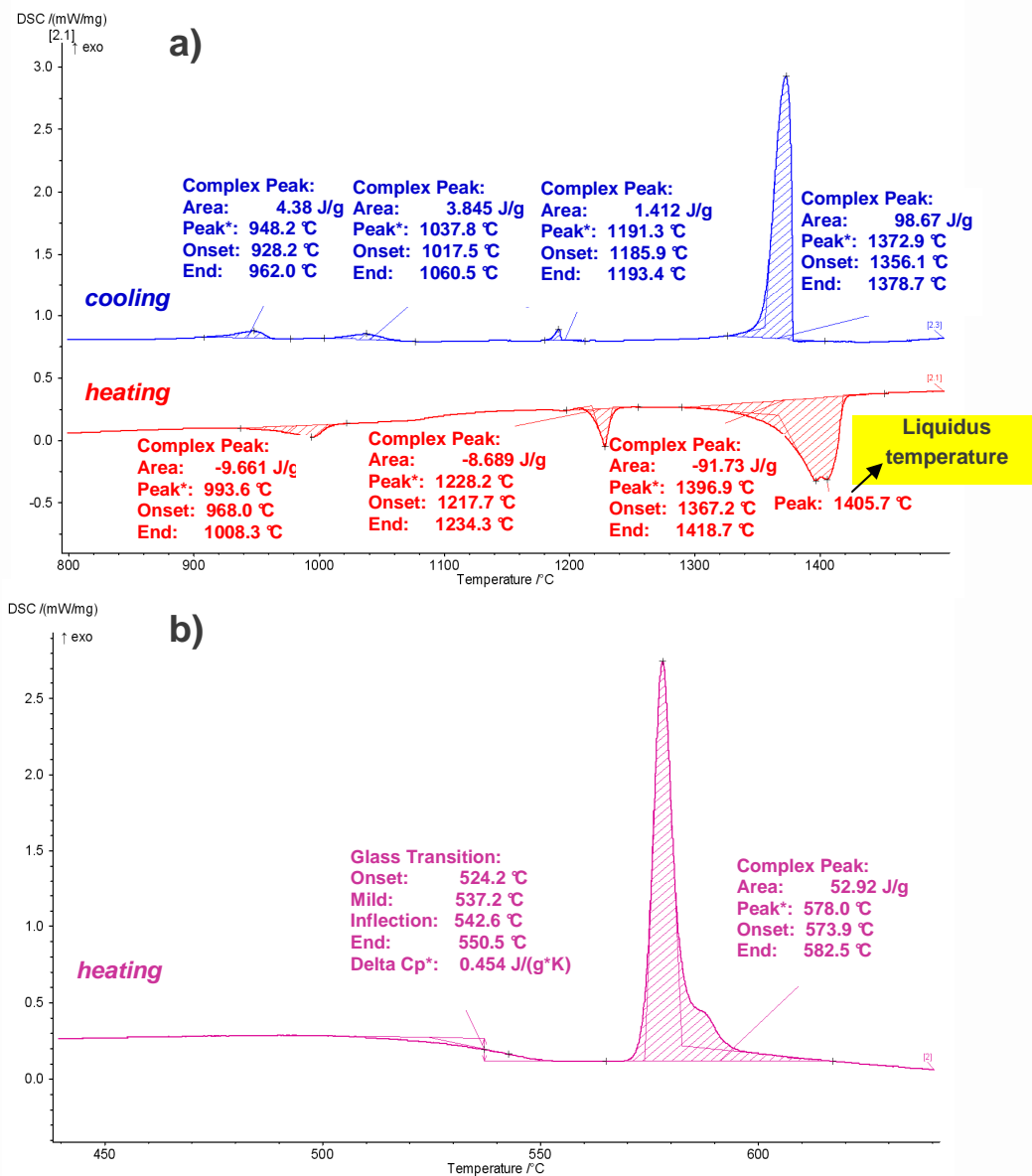
Fig. 3. Examples of the experimental DSC curves: a) peaks corresponding to the phase transformations in the multicomponent alloy obtained during heating and cooling with the constant rate, b) glass transition and crystallization peaks for the amorphous alloy registered in the heating cycle.

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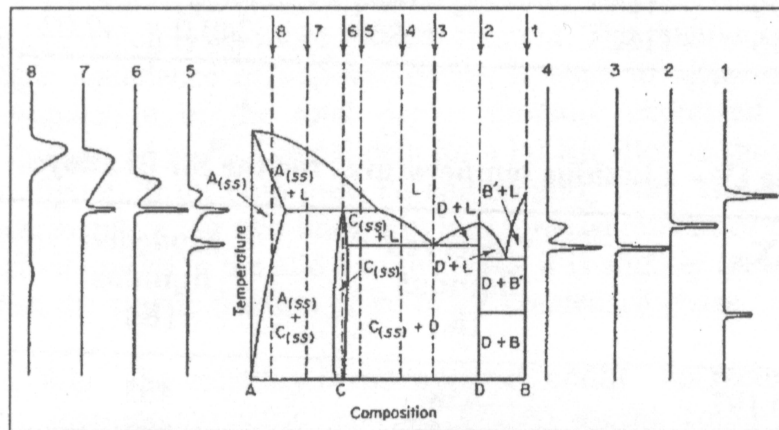
Fig 4. The hypothetical binary system A-B and DSC curves [10].

Moreover, it is worth to mention that there are also a number of other calorimetric techniques used for the determination for e.g. mixing enthalpy or formation. Exemplary methods include:

✓ calorimetric dissolution method,
✓ calorimetric method for the direct synthesis.

The calorimetric dissolution method is used to determine the enthalpy of dissolution, the change of enthalpy at the transition from a solid substance, liquid or gas into the solution. The material is dissolved in the bath (the solvent), and the thermal effect of this process is measured and recorded. The measurement of the thermal effect is based on the changes in temperature of the bath in which the sample is dissolved when the temperature of the block during the calorimetric measurement is constant. The main condition that must be fulfilled in this method is to dissolve the sample in a solvent bath rapidly and completely [3,11,12].

To determine the enthalpy of formation, the method of direct synthesis is used. The basis of this method is the measurement of the thermal effect which is accompanied by a direct reaction of the components of the substance at elevated temperature. Samples are introduced into the reaction chamber at room temperature [3,13].

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