

Jan 2010 José M. Córdoba Gallego, IFM  
Feb 2011 rev. Rickard Forsén och Jennifer Ullbrand, IFM

**TFYA21 Materialvetenskap/Physical Metallurgy  
Lab 3**

**LAB PM**

**Differential Scanning Calorimetry**

*-Investigating Phase Transformations*

# Contents

- 1 Introduction
- 2 Basic Thermodynamics
- 3 Typical Phase Transitions
- 4 Thermal Analysis Techniques
  - 4.1 Differential scanning calorimetry
  - 4.2 DSC curves
  - 4.3 Experimental equipment
- 5 Theory and Laboratory Procedure
  - 5.1 Melting/Freezing Aluminum Transformation
  - 5.2 Polymorphic Transformation (Martensite)
    - 5.2.1 Martensitic stainless steels
- 6 References

## 1 Introduction

In this laboration we are going to study phase transformations by differential scanning calorimetry (DSC). The amount of energy absorbed/released during a phase transformation and the temperature where it occurs can be determined. This information is useful when determining whether or not a transformation occurs and at what temperature.

We will study the melting and solidification temperatures of Aluminum and the austenite-pearlite phase transformation of steel. The temperatures and the enthalpies involved during the transformations will be determined.

The LabPM is organized by a short introduction to thermodynamic theory needed for the laboration followed by some examples of different phase transitions. The main chapter, 3 and 4 is dedicated to a description of the DSC and the material of interest respectively. In the end the exercises are stated.

## 2 Basic Thermodynamics

Thermodynamics describes a system (in this case our material and the absorbed or evaporated heat) by various macroscopic variables such as, energy, enthalpy and entropy using a statistical approach. This is very useful since no specific information of the microscopic properties of a material is needed to describe it.

In thermodynamics energy is ordered in to different kinds depending on its origin. Any system has an internal energy,  $E$ , due to the bonding state of the material. Work is transforming energy to heat and need to be accounted for e.g. at volume or pressure changes. The enthalpy is defined as the sum of the internal energy and the work done by the system. Here the work considered is only pressure-volume based. Hence,

$$H = E + W = E + pV$$

Entropy is another phenomenon that tells us the number of configurations,  $\Omega$ , a system can be in. A larger number of configurations give larger entropy. A gas phase has large entropy since the gas particles can be ordered in an almost infinite number of ways. A solid has a lower amount of entropy since the atoms can be ordered in fewer ways (and still remain in the same phase and composition). Usually the entropy increase with the temperature due to thermal vibrations. The entropy is defined as

$$S = k_B \ln \Omega$$

where  $k_B$  is the Boltzmann constant.

The Gibbs free energy is the energy that can be extracted from a material taking into account the already consumed energy by work.

$$G = H - TS$$

In the DSC we may determine the enthalpies of the phase transformation at a given temperature. The change in enthalpy is due to breaking or creation of bonds but could also be a result of work done by the system. If the material changes its volume due to e.g. a phase transformation, say, between liquid and gas the material performs work to keep the pressure constant. From the DSC data, we can determine the amount of energy required to raise the temperature of the material by e.g. one degree at constant pressure. This is known as the heat capacity of the material at constant pressure (can also be given at

constant temperature). Experimentally it is easier to keep the pressure than the volume of the system constant,

$$C_p = \left( \frac{dH}{dT} \right)_p$$

where H is the enthalpy, T is temperature and p is pressure. The *specific* heat capacity is the energy required to raise *a certain amount* of the material by 1 degree,

$$C_p = \frac{1}{a} \left( \frac{dH}{dT} \right)_p$$

where a can be number of grams or number of moles.

### 3 Typical Phase Transitions

At the phase transition point (for instance, boiling point for water) the two phases of water, liquid and vapor, have identical free energies and therefore are equally likely to exist. Below the boiling point, liquid-water is the more stable state of the two. At boiling point liquid and vapor are equally stable and above boiling point vapor is more stable than liquid state of water.

Phase transitions can occur between solid, liquid and gas, but there exist a large number of other phase transformations, some of them are listed below:

A **eutectic transformation**, in which a two component single phase liquid is cooled and transforms into two solid phases. The same process, but beginning with a solid instead of a liquid is called a eutectoid transformation.

A **peritectic transformation**, in which a two component single phase solid is heated and transforms into a solid phase and a liquid phase.

A **spinodal decomposition**, in which a single phase is cooled and separates into two different compositions of that same phase.

The transition between the ferromagnetic and paramagnetic phases of magnetic materials at the **Curie point**.

The **martensitic transformation** which occurs as one of the many phase transformations in carbon steel and stands as a model for displacive phase transformations.

Changes in the **crystallographic structure** such as between ferrite and austenite of iron.

The **emergence of superconductivity** in certain metals when cooled below a critical temperature.

It is sometimes possible to change the state of a system non-adiabatically in such a way that it can be brought past a phase transition point without undergoing a phase transition. The resulting state is metastable, i.e. not theoretically stable, but quasistable. See superheating, supercooling and supersaturation.

## 4 Thermal Analysis Techniques

Thermal analysis comprises a group of techniques in which a physical property of a substance is measured while it is subjected to a controlled and predefined heat treatment. In differential thermal analysis, which this lab will deal with, the temperature difference that develops between a sample and an inert reference material is measured as both samples are subjected to identical heat treatments. The technique which we will use during the lab is called *differential scanning calorimetry* and it relies on differences in the amount of energy that is required to maintain the sample and the reference material at identical temperatures.

### 4.1 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermo analytical technique in which the difference in the amount of heat that is required to increase the temperature of a sample and a reference material is measured as a function of temperature. Both the sample and the reference material are ideally maintained at the same temperature throughout the experiment. Generally the temperature program, i.e. how the temperature should vary with time during our experiment, is designed so that the temperature increases linearly with time. In order to determine the thermal response of the sample the reference sample should have a well-defined heat capacity over the range of temperatures that is about to be scanned. The main application of DSC is in studying phase transitions such as melting, glass transitions, crystallization, exothermic decompositions etc. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity. The technique was developed by E.S. Watson and M.J. O'Neill in 1960, and introduced commercially at the 1963 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

#### 4.1.1 DSC curves

The result from a DSC experiment is a curve of heat flux versus temperature or versus time. There are two different conventions, exothermic reactions in the sample are shown as either positive or negative peaks. By integrating a peak the enthalpy of its corresponding transition can be achieved. It can be shown that the enthalpy of transition can be expressed using the following equation:

$$\Delta H = K \cdot A$$

$\Delta H$  is the enthalpy of transition,  $K$  is the calorimetric constant, and  $A$  is the area under the curve. The calorimetric constant will vary from instrument to instrument and can be determined by analyzing a well-characterized sample with known enthalpies of transition.

## 4.2 Experimental equipment

The key features of a differential thermal analysis kit are as follows, Fig. 1.

1. Sample holder comprising thermocouples, sample containers and a ceramic or metallic block
2. Furnace
3. Temperature controller
4. Recording system (computer not shown in picture)

### Schematic

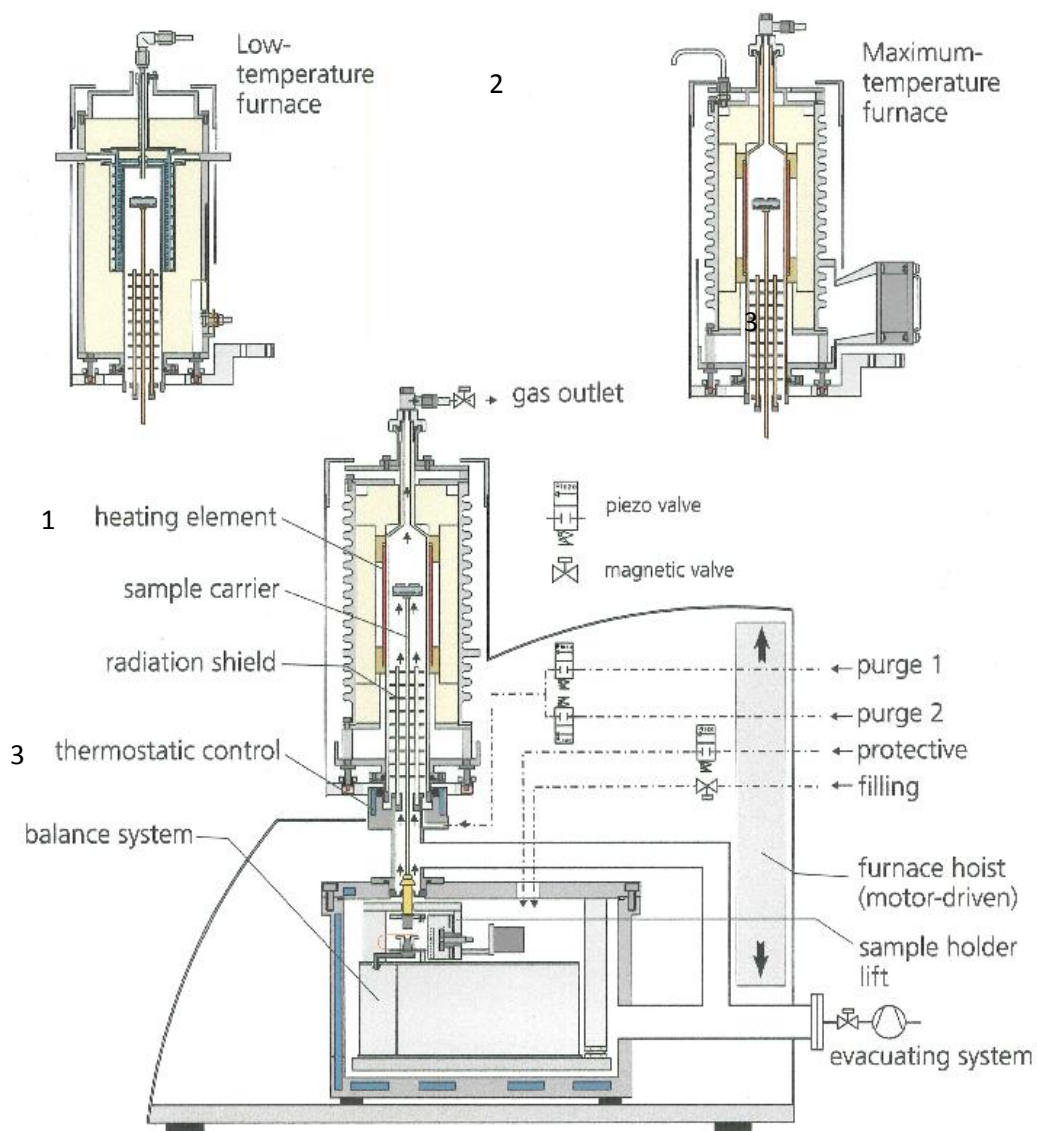


Figure 1

The essential requirements for the furnace are that it should provide a stable and sufficiently large hot-zone and must be able to respond rapidly to commands from the temperature controller. A temperature controller is essential in order to obtain constant heating rates. The sample holder assembly consists of thermocouples, one for each of the sample and reference material, surrounded by a block to ensure an even heat distribution. The thermocouples should not be placed in direct contact with the samples as to avoid contamination and degradation, although sensitivity may be compromised. Therefore the samples are contained in small crucibles, which may be made of materials such as Pyrex, silica, nickel or platinum, depending on the temperature range and nature of the test. To avoid oxidation during heating a protective atmosphere of helium or argon is sometimes used inside the chamber. One should also make sure that the sample is out-gassed in vacuum at some elevated temperature during several hours if for instance a powder is to be measured.

## 5 Theory and Laboratory Procedure

### 5.1 Melting/Freezing Aluminum Transformation

Aluminium is a silvery white and ductile member of the boron group of chemical elements. It has the symbol Al; its atomic number is 13. It is not soluble in water under normal circumstances. Aluminium is the most abundant metal in the Earth's crust, and the third most abundant element therein, after oxygen and silicon. It makes up about 8% by weight of the Earth's solid surface. Aluminium is too reactive chemically to occur in nature as a free metal. Instead, it is found combined in over 270 different minerals. The chief source of aluminium is bauxite ore. Aluminium is a soft, durable, lightweight, malleable metal with appearance ranging from silvery to dull grey, depending on the surface roughness. Aluminium is nonmagnetic and nonsparking. It is also insoluble in alcohol, though it can be soluble in water in certain forms. The yield strength of pure aluminium is 7–11 MPa, while aluminium alloys have yield strengths ranging from 200 MPa to 600 MPa. Aluminium has about one-third the density and stiffness of steel. It is ductile, and easily machined, cast, drawn and extruded. Corrosion resistance can be excellent due to a thin surface layer of aluminium oxide that forms when the metal is exposed to air, effectively preventing further oxidation. The strongest aluminium alloys are less corrosion resistant due to galvanic reactions with alloyed copper. This corrosion resistance is also often greatly reduced when many aqueous salts are present, particularly in the presence of dissimilar metals. Aluminium atoms are arranged in a face-centred cubic (fcc) structure.

#### *EXERCISE*

Plot energy/weight versus time and energy/weight versus temperature profiles and determine melting temperature of pure Al and the energy involved during the process. Also note the solidification temperature. Compare with literature. Why are the melting temperature and the solidification temperature not the same?

### 5.2. Polymorphic Transformation (Martensite)

Martensite most commonly refers to a very hard form of steel crystalline structure, but it can also refer to any crystal structure that is formed by displacive transformation. The martensite is formed by rapid cooling (quenching) of austenite which traps carbon atoms that do not have time to diffuse out of the crystal structure. This martensitic reaction begins during cooling when the austenite reaches the martensite start temperature ( $M_s$ ) and the parent austenite becomes mechanically unstable. At a constant temperature below  $M_s$ , a fraction of the parent austenite transforms rapidly, then no further transformation will occur. When the temperature is decreased, more of the

austenite transforms to martensite. Finally, when the martensite finish temperature ( $M_f$ ) is reached, the transformation is complete. One of the differences between the two phases is that martensite has a body centered tetragonal crystal structure, whereas austenite has a face center cubic (FCC) structure. The transition between these two structures requires very little thermal activation energy because it is a martensitic transformation, which results in the subtle but rapid rearrangement of atomic positions, and has been known to occur even at cryogenic temperatures. Martensite has a lower density than austenite, so that the martensitic transformation results in a relative change of volume. Martensite is not shown in the equilibrium phase diagram of the iron-carbon system because it is a metastable phase, the kinetic product of rapid cooling of steel containing sufficient carbon. Since chemical processes (the attainment of equilibrium) accelerate at higher temperature, martensite is easily destroyed by the application of heat. This process is called tempering. In some alloys, the effect is reduced by adding elements such as tungsten that interfere with cementite nucleation, but, more often than not, the phenomenon is exploited instead. Since quenching can be difficult to control, many steels are quenched to produce an overabundance of martensite, then tempered to gradually reduce its concentration until the right structure for the intended application is achieved. Too much martensite leaves steel brittle, too little leaves it soft.

### 5.2.1 Martensitic stainless steels

Stainless Steels, are iron-base alloys containing Chromium. Stainless steels usually contain less than 30% Cr and more than 50% Fe. They attain their stainless characteristics because of the formation of an invisible and adherent chromium-rich oxide surface film. This oxide establishes on the surface and heals itself in the presence of oxygen. Some other alloying elements added to enhance specific characteristics include nickel, molybdenum, copper, titanium, aluminum, silicon, niobium, and nitrogen. Carbon is usually present in amounts ranging from less than 0.03% to over 1.0% in certain martensitic grades. Corrosion resistance and mechanical properties are commonly the principal factors in selecting a grade of stainless steel for a given application. Stainless steels are commonly divided into five groups, and one of them is the martensitic stainless steels are essentially alloys of chromium and carbon that possess a martensitic crystal structure in the hardened condition. They are ferromagnetic, hardenable by heat treatments, and are usually less resistant to corrosion than some other grades of stainless steel. Chromium content usually does not exceed 18%, while carbon content may exceed 1.0 %. The chromium and carbon contents are adjusted to ensure a martensitic structure after hardening. Excess carbides may be present to enhance wear resistance or as in the case of knife blades, to maintain cutting edges.

#### *EXERCISE*

Plot energy/weight versus time and energy/weight versus temperature profiles and determine temperature of martensite transition and the energy involved during the process. Describe structure changes introduced.



## 6 References

1. Phase Transformations in Metals and Alloys, D.A. Porter and K.E. ed. Easterling (Chapman & Hall), 1992
2. Stoichiometry and thermodynamics of metallurgical processes, Y.K. Rao, ed. Press Syndicate of UC, 1985
3. Thermodynamics, Herbert B. Callen, ed. Wiley & Sons. , 1960.
4. Chemical Thermodynamics, Ilya Prigogine, R. Defay, ed. Longmans, Green & Co, 1954.
5. Thermodynamics: An Advanced Treatment for Chemists and Physicists, E.A. Guggenheim, 5th ed., ed. John Wiley & Sons (Interscience), 1967.
6. Basic Notions of Condensed Matter Physics, P.W. Anderson, ed. Perseus Publishing, 1997.
7. Differential scanning calorimetry, Günther Höhne, W. Hemminger, H.-J. Flammersheim, Second Edition, ed. Springer, 2003.
8. Modulated temperature differential scanning calorimetry, Mike Reading, Douglas J. Hourston, ed. Springer, 2006.
9. Wikipedia, 2010