SETSYS Evolution
Working under aggressive and corrosive atmospheres
Part 2: TG-DTA and TG-DSC modes

Introduction

In a part 1 (TN679), the working under corrosive atmospheres in TG mode was developed with the description of different options according to the atmosphere in the furnace. When connecting a DTA or DSC rod to the balance, the risk of damaging the detectors is higher as they are built with metallic parts. So it is needed to be very careful when the decomposition of the sample emits corrosive vapours or when a corrosive atmosphere is used in the test. The different situations where there is a risk of deterioration or corrosion can be listed as followed:

- emission of vapours coming from the sample decomposition: the material under study emits agressive vapours when decomposing. In this case, the vapours are diluted in the inert carrier gas and therefore the risk of pollution is:
  - limited to the crucible and the vicinity of the detector (DTA/DSC)
  - if there is some humidity in the furnace, risk of corrosion of the metallic part (bottom of the furnace) due to acid interaction
  - if the test is run under a gaw with a relative humidity, this effect will be enhanced

- investigation in an oxidative or reducing gas flow : the compatibility between the gas and the crucible/detector/thermocouple has to be checked and will be described in this note

- investigation in corrosive gas flow in dry conditions or wet conditions : with DTA and DSC, this type of applications is very limited due to the compatibility between the gas and the crucible/detector/thermocouple . This note will describe some solutions.

Working with both last situations (especially working under H_2, CO, corrosive gas) impose to apply specific safety conditions in the laboratory.

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Materials compatibility

In the TG-DTA and TG-DSC modes, the detectors suspended to the balance are made of different metals according to the temperature range (platinel, platinum rhodium, tungsten rhenium …). The crucibles used with the different detectors are made in aluminium, platinum, tungsten, graphite (figure 1). Special crucibles in zirconia, boron nitride can also be adapted.

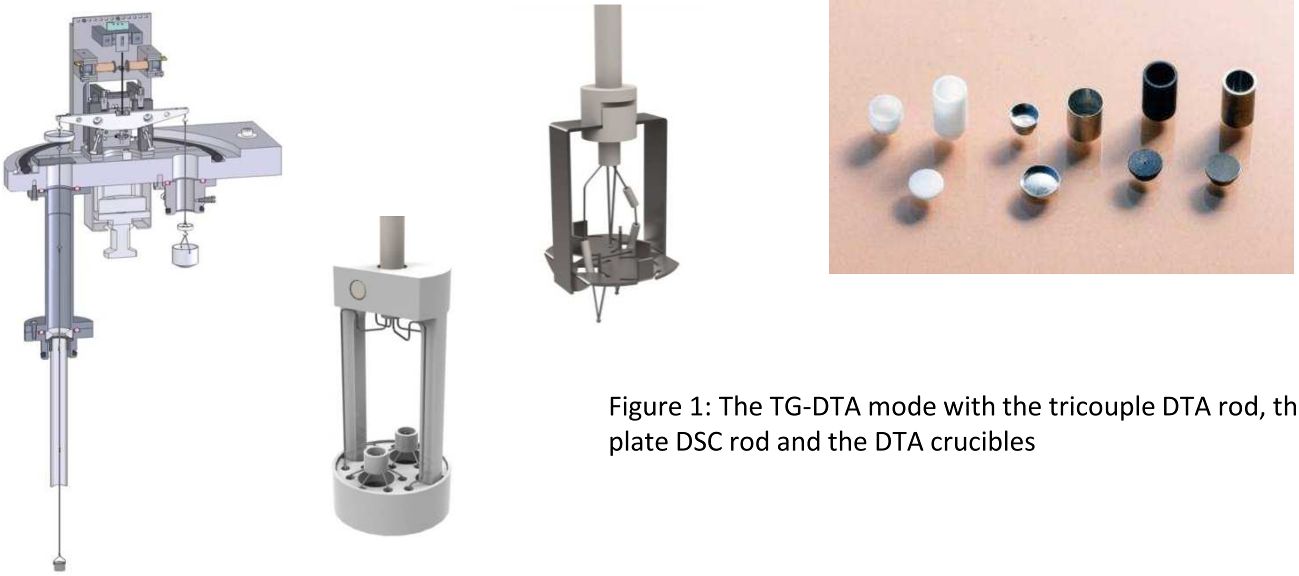

Figure 1: The TG-DTA mode with the tricouple DTA rod, the plate DSC rod and the DTA crucibles

The materials compatibility for the TG-DTA and TG-DSC rods is very similar to the description done in Technical Note 679. In the case of emission of agressive gas from the sample decomposition, each material has different limitations :

Platinum, as a metal, is very convenient for applications at high temperature (up to 1750°C) under inert and oxidising gases. It is used for the crucible and the thermocouples combined with Rhodium. However it is very sensitive to different types of gases and vapours.

- **Metallic vapour**

Among the metals, silicon (Si) is one of the most problematic as it is contained in silica (SiO2), SiC. The problem occurs especially above 1000°C. Among the other classical platinum poisons, it can be noticed phosphorus (P) , sulphur (S) coming from sulphides, lead (Pb), but also B, Zn, Sn, Ag, Au, Li, Na, K, Sb, Bi, Ni, Fe, As. In any case it is recommended to consider the corresponding phase diagram of Pt with the metal from the emitted vapour and check if there is a risk of eutectic formation. Here below the Pt-Si diagram (Figure 2).

In case of low emission of vapour, one way to prevent direct contact between the crucible and the metallic vapour, is to have the sample embedded in alumina powder.

Another trick: when SiO2 sample has to be investigated in a platinum crucible, an efficient way to prevent any interaction between sample and crucible, is to work under air or oxygen to prevent the dissociation of the silicon oxide, especially when it is needed to heat above 1000°C .

- **Hydrogen**

Platinum is also very sensitive to hydrogen above 1000°C. The wires of the PtRh thermocouples used in the DTA and DSC detectors become brittle and break. Another type of detector has to be used above 1000°C .

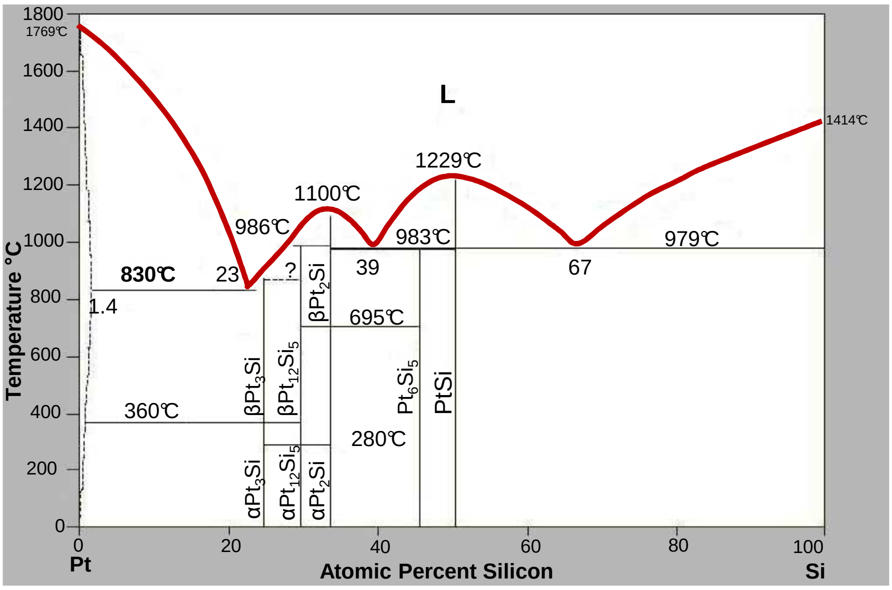

Figure 2: Pt-Si phase diagram

- **Other gases**

  Platinum is also stable in CO_2. But it will react with CO, SO_2, H_2S, chlorine. In general, platinum is not recommended to be used in reducing atmospheres.

Alumina, as a ceramic oxide, is highly suited for applications at high temperature (up to 1750°C) under inert and oxidising but has some limitations in reducing atmospheres. It is used for the crucible but also for the furnace inner tube and the thermocouple rods. However it is sensitive to some types of gases and vapours.

- **Hydrogen**

  Hydrogen is considered to be inert versus alumina on a very large range of temperature. However at high temperature, a reduction of traces of oxides (especially SiO2) in alumina can be observed.

- **Carboneous atmospheres (CO, CH4)**

  CO and CH4 are considered as reducing atmosphere. In the literature (Halmann and al., Energy 32 (2007) 2420–2427), it is reported that the reduction of alumina with CH4 may occur from 1500°C .

Graphite is a very convenient material for DTA crucibles for applications at very high temperature (up to 2400°C) but only under inert atmosphere. However nitrogen is not recommended as there is a risk of formation of cyanide.

Boron nitride is recommended for the investigation of molten metals in inert gas when alumina cannot apply. It can also be used as a liner in a standard crucible (alumina, platinum).

Tungsten is also dedicated to applications at very high temperature (up to 2400°C) under inert atmosphere. It is used to build the DTA detector (combined with Rhenium) and the corresponding crucibles. Oxidative atmospheres have to be forbidden.

- **Hydrogen**

  Tungsten is very well adapted for investigation in hydrogen atmosphere when platinum can not be used (above 1000°C). For such a test, tungsten or alumina will be used for the crucible.

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Solutions to work under corrosive conditions with TG-DTA mode

Compared to the TG mode, the solutions to work under corrosive conditions with the TG-DTA and TG-DSC modes are more limited. However here are some proposals to solve some problems in the TG-DTA.

Protected DTA rod (upper limit: 1750°C)

According to the materials and the atmosphere, different situations where a risk of corrosion of the DTA detector can be faced are the following:

- the interaction between corrosive emitted gas (coming from the sample decomposition) and the crucible and DTA detector
- the interaction between the corrosive gas flow (used for the reaction) and the DTA detector

Both situations can be solved by using the protected DTA rod (figure 3). In such a design, the thermocouples are embedded in the rod (using especially alumina cement). When an adapted crucible is fitted on the detector, no metallic part is visible from the emitted vapours or gas flow.

In the case of corrosive gas emission, it is recommended to use a carrier gas with a significant gas flow to limit the time of contact with the rod.

An adapted protected thermocouple, embedded in a ceramic sleeve, is also available for the temperature control in the furnace in such corrosive conditions. In case of emission of aggressive vapours, it is recommended to use a high carrier flow rate to limit the time of interaction between the vapour and the crucible/detector.

Figure 3: Cross section of the protected DTA rod and picture of the ceramic sleeve thermocouple

Solutions to work under corrosive conditions with DTA or DSC only

In the technical note TN679, different uses in TG only under corrosive conditions are described as it is not possible to find adequate materials for the DTA and DSC detectors that will resist in such conditions. However there are solutions if the two types of measurements are disconnected and no more simultaneous. The solution for DTA and DSC mode is to use a sealed crucibles. According to the temperature range different solutions are available and are described below.

Sealed crucibles with DTA or DSC only up to 1100°C

The sealed glass ampoule is a very convenient crucible to work without emission of corrosive vapours (especially metallic vapours). For such a test, the diameter of an open glass ampoule has to be selected in order to be contained in a standard crucible (alumina or platinum). After weighing the sample in the ampoule, it is sealed under vacuum and introduced in the corresponding crucible. Such an ampoule can be used up to 1100°C. it is suggested to insert the ampoule in an alumina powder bed in order to improve the heat exchange between the sample and the detector (figure 4).

Such a sealed glass ampoule can be used either with DTA or DSC detectors.

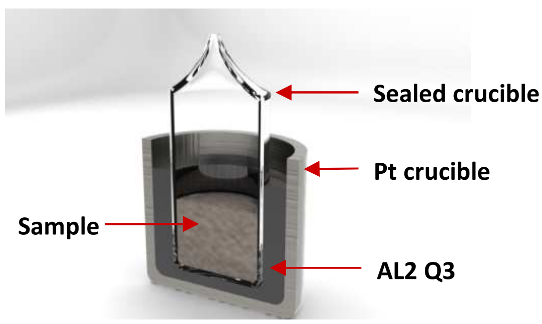

Figure 4: Description of the sealed ampoule contained in a platinum crucible

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Figure 5: Picture of the operation of tungsten crucible welding (from S. Ushakov, UC Davis, USA)

Sealed crucibles with DTA up to 1600°C

The only way to prevent any escape of a corrosive vapour out of the crucible is to sealed the corresponding crucible with an adapted cover. This can be done with metallic crucibles such as platinum and tungsten. In that case after weighing the sample, the cover is welded on top of the crucible. During this operation, it is needed to keep cold the bottom of the crucible to prevent the decomposition of the sample.

In such an experiment, the crucible cannot be reused.

For platinum crucible, an electrical welding can be convenient.

For tungsten welding it is needed to use a laser to perform such an operation (figure 5) *(see Sergey V. Ushakov, Alexandra Navrotsky, J. Mater. Res., Vol. 26, No. 7, Apr 14, 2011)*

Gas compatibility table

The following table gives a brief summary of the compatibility of the main parts of the TG-DTA/DSC analyzer according to the most used gases.

The table considers the following parts:

- The crucible
- The inner tube in the furnace defining the experimental chamber
- The DTA and DSC detectors
- The temperature control (T/C) thermocouple

	Tube			Crucible			Thermocouple/Detector			
	Alumina	Vitreous carbon / Graphite	Silica	Alumina	Platinum	Tungsten	Platinel	Pt/ Pt-Rh10%	Pt-Rh6% / Pt-Rh30%	W5
Inert	1750°C	2400°C	1000°C	1750°C	1750°C	2400°C	1000°C	1600°C	1750°C	2400°C
Reducing										
H_2	1750°C	600°C	1000°C	1750°C	1000°C	2400°C	1000°C	1000°C	1000°C	2400°C
CO	1750°C	600°C	1000°C	1750°C	1000°C	1750°C	1000°C	1000°C	1000°C	NA
Oxydative										
Air	1750°C	NA	1000°C	1750°C	1750°C	NA	1000°C	1600°C	1750°C	NA
O_2	1750°C	NA	1000°C	1750°C	1750°C	NA	1000°C	1600°C	1750°C	NA
CO_2	1750°C	700°C	1000°C	1750°C	1750°C	NA	1000°C	1600°C	1750°C	NA

NA: not applicable

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