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Pressure Cell for DSC with Diamond-Like-Carbon Coating

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Thermoanalytical techniques, such as differential scanning calorimetry (DSC), are routinely applied to determine basic safety data for process risk assessments (PRA) in the chemical industry as well as for storage and transport of bulk chemicals (Stoessel F., 2008; TRAS 410). Since DSC measurements are performed with sample materials in amounts of milligrams, the legitimate question is always, whether the measured data is representative for the large-scale unit operation or not (scale-up problem). One aspect which must be considered in this context is the interaction of the sample material with the crucible material of construction.
During the many years of practical experience in the field of calorimetry for PRAs, many examples of critical material combinations where observed in the laboratories of TÜV SÜD Process Safety, i.e. formerly Swissi. In this presentation some examples are given, where the interaction between sample and crucible material of construction was significant and therefore the measured data was not representative for the process of concern and thus could not be used for scale-up purposes.
These observations demonstrate again the possible lack of information when only a single method is applied for safety data evaluation and the need for complementary, alternative testing methods respectively (Grewer T., 1994). It also highlights the necessity for information exchange between plant (process owner) and safety lab, to define testing conditions as representative as possible.

1. Introduction

Microcalorimetric Lab Tests, like Differential Scanning Calorimetry (DSC) are widely used to characterize the thermal behaviour of substances, and reaction mixtures. These data are a standard basis for thermal risk assessment (Brown M.E., 2004).
In Microcalorimetry, very small samples (5-50 μl) are enclosed in crucibles. They are heated either with a constant temperature increase rate or exposed to a constant elevated temperature for a certain time. It is monitored whether the samples absorb heat (for example for melting) or release it (exothermic reaction).
The reactivity of chemicals can be significantly changed by contact with other materials, namely iron and steel. As the samples are so small surface interaction with the wall material may become dominant and the observed behaviour may not be representative for the bulk sample material. This can be illustrated based on the ratio of the area, i.e. sample surface which is in contact with the material of construction to the sample mass (see Table 1). This ratio is about 1000 times higher in a DSC steel crucible compared to a 1 m^3 reactor.
Examples of unwanted surface interactions in microcalorimetry:

- Samples containing water or alcohols may not be tested in aluminum crucibles, because a reaction between aluminum and polar solvents results in exothermic signals.
- The decomposition of hydrogen peroxide is catalyzed by iron or steel (see Figure 4).
- An exothermic reaction occurs between samples containing chlorine ions and steel crucibles

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Table 1: Typical surface to mass ratios for different containers

Container type	Area/Mass [$mm^2 \cdot mg^{-1}$]
Steel crucible (20 µl)	3.7
Gold plated crucible; sample mixed with 10 % steel-powder (considering only contact area of sample to steel)	1.5
steel reactor (1 m^3)	0.005

Therefore, about 30 years ago, sample vessels were developed, which are coated with gold, because this surface is less reactive than steel. But even gold-plated surfaces are not fully inert. Indeed, gold has proved to be an effective catalyst for many reactions (Stephen et al., 2006). However, in microcalorimetry applications these reactions are often unknown and are therefore not identified, which may result in incorrect measurements or misinterpretations of the measurements.
As an alternative, glass ampoules may be used. Closing these ampoules with micro burner, however, is a difficult task and jeopardizes the validity of data due to undesired heating of the samples before the experiment. Due to the difficulty to close glass ampoules without destroying the sample, a rather high ampoule design is chosen, typically 15 mm, such that the temperature in the ampoule is not homogeneously distributed anymore and a kind of reflux boiling can occur during the test (compare Figure 1a).
Special equipment must be used to produce small glass ampoules without destroying the sample (see Figure 1c).

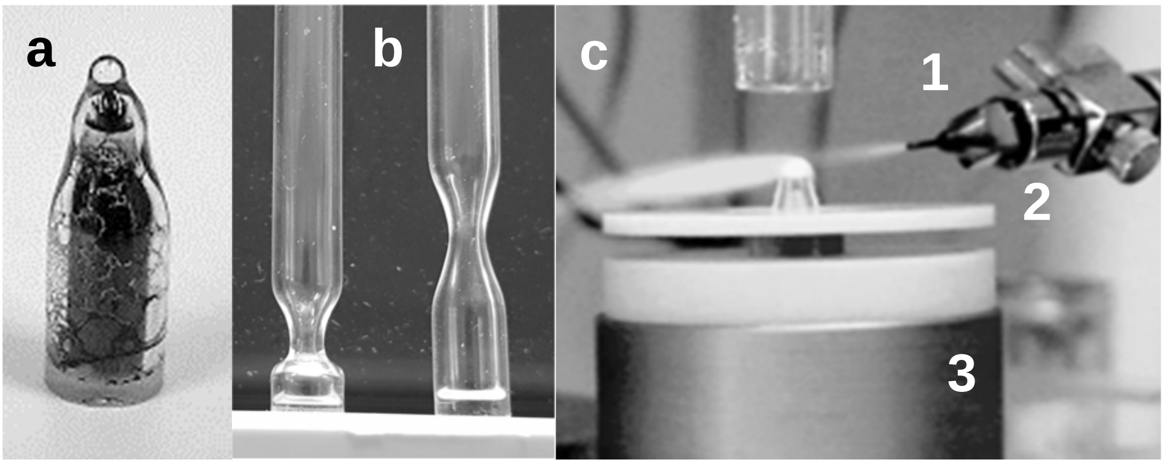

Figure 1: a) Sample in high ampoule after a DSC run: Traces of reflux can easily be identified. b) small and standard size ampoule. c) special equipment for sealing small ampoules: 1: Micro burner; 2: Radiation shield; 3: Cooling element

2. New Approach: Coated Crucibles

2.1 Diamond-like Carbon

Diamond-like carbon (DLC) is a glassy-amorphous coating consisting of carbon atoms, that are deposited by evaporation on a supporting surface. This material is highly inert against many chemicals. It is widely applied in numerous technologies, e.g. tooling components, high performance motors, various medical applications like implants.

2.2 The DLC Crucible

A new type of DSC crucible has been developed, which has the same dimensions and closing mechanism as the widely used steel crucibles (M20) but is coated inside with a layer of Diamond-Like-Carbon. This glass-like coating is chemically highly resistant and allows testing of aggressive media like acids or peroxides. Thus, the advantages of the standard pressure crucible and the glass ampoule or are combined in this new sample cell.

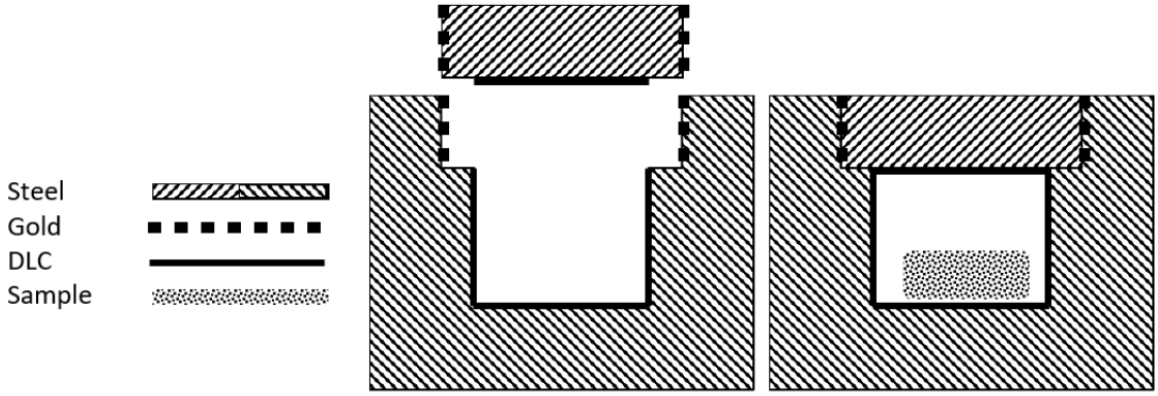

Figure 2: Design scheme of the DLC coated high pressure crucible

Figure 3: Left: Standard gold-plated crucible M20; right: DLC coated crucible, notice the coating on the inside of the cover

3. Results and Discussion

Test runs with some high-energetic material were carried out in a Mettler-Toledo DSC 3, using dynamic heating rates of 4 K/min in the temperature range between ambient and 400 °C. The sample weight was between 5 and 10 mg. The curves are shown in Figures 4-7.

The comparison of dynamic DSC measurements with Hydrogen peroxide 31% in different crucibles is shown in Figure 4. The onsets in the DLC coated crucible and the glass crucible are significantly higher than those in steel or gold-plated crucible.

The measurements with Heptyne are shown in Figure 5. The catalytic effects of the metal surface especially of the gold surface is clearly shown. The respective onset temperatures of the measurement in the gold-plated crucible is about 85 °C lower than in DLC coated crucible. This effect is explained by the destabilization of the alkine π-System on the gold surface (Stephen et al., 2006).

The measurements with Chloropentyne, as shown in Figure 6, do not show such a strong effect of the gold surface. On the contrary, in the gold-plated crucible the respective onset temperature was the highest. The signal of the measurement in the glass ampoule shows again considerable noise caused by reflux boiling.

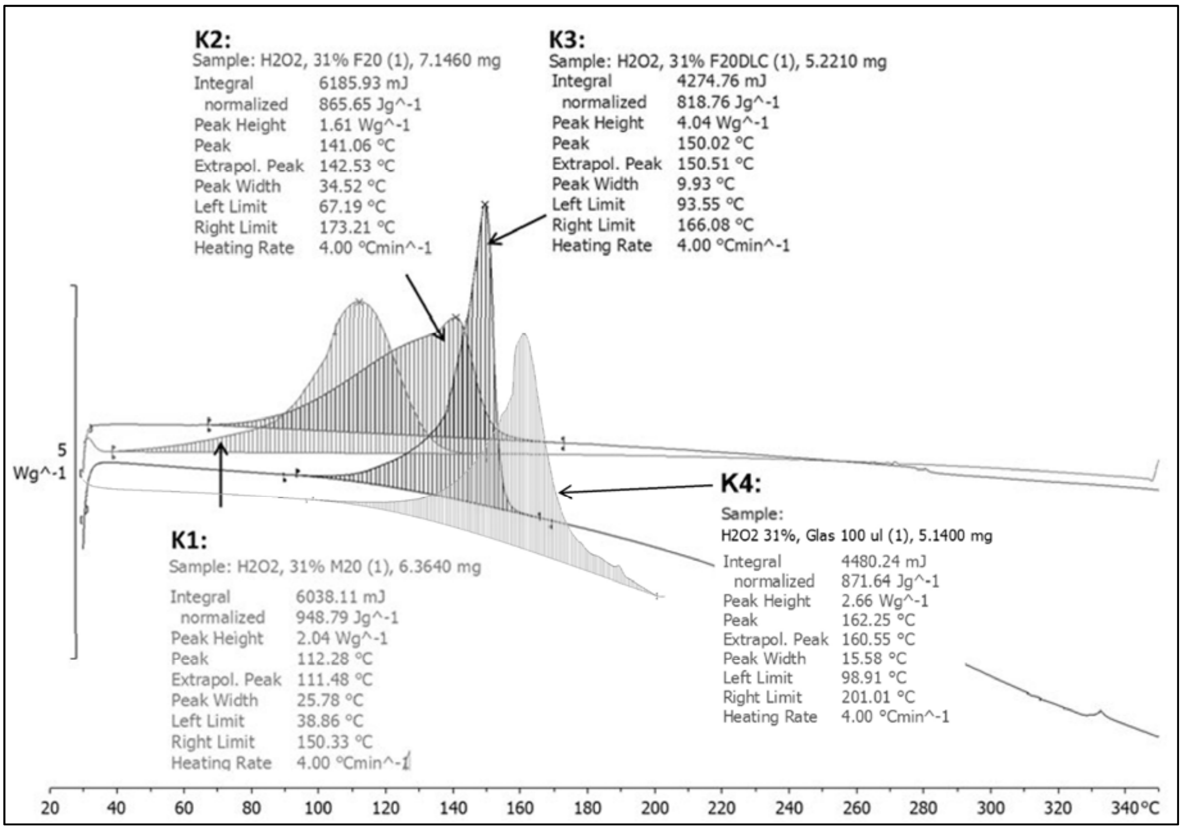

Figure 4: Comparison of dynamic DSC measurements with Hydrogen peroxide 31 % in different crucibles (gold-plated crucible K1, steel crucible K2, DLC coated crucible K3, glass ampoule K4)

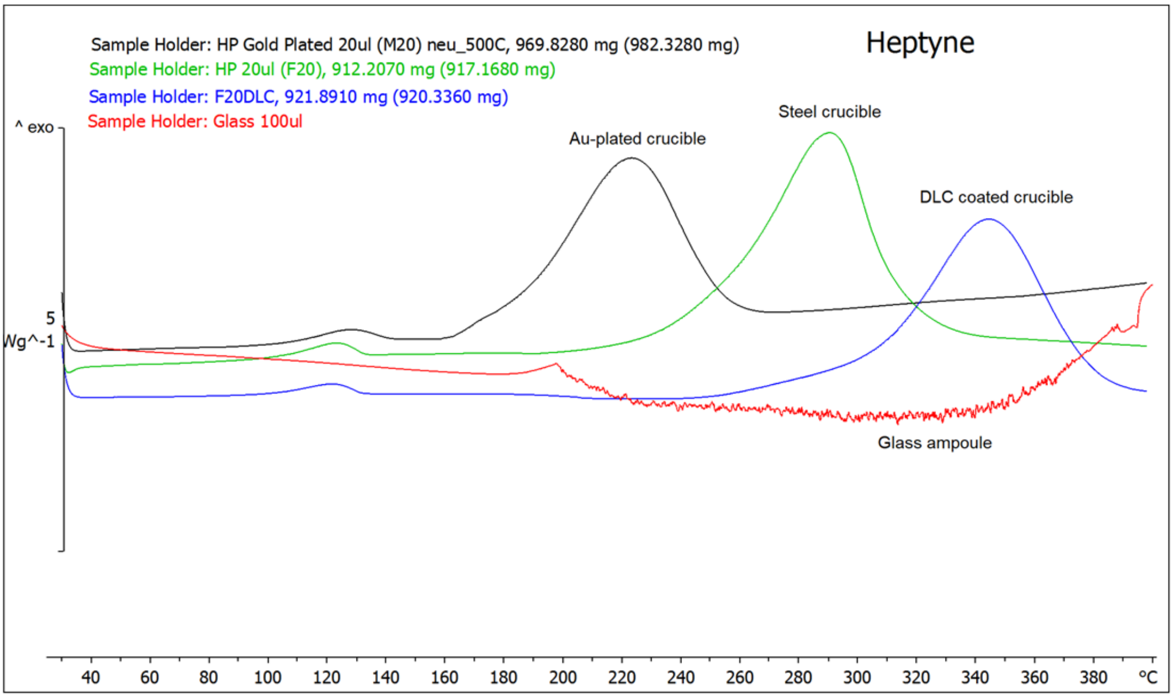

Figure 5: Comparison of dynamic DSC measurements with Heptyne in different crucibles

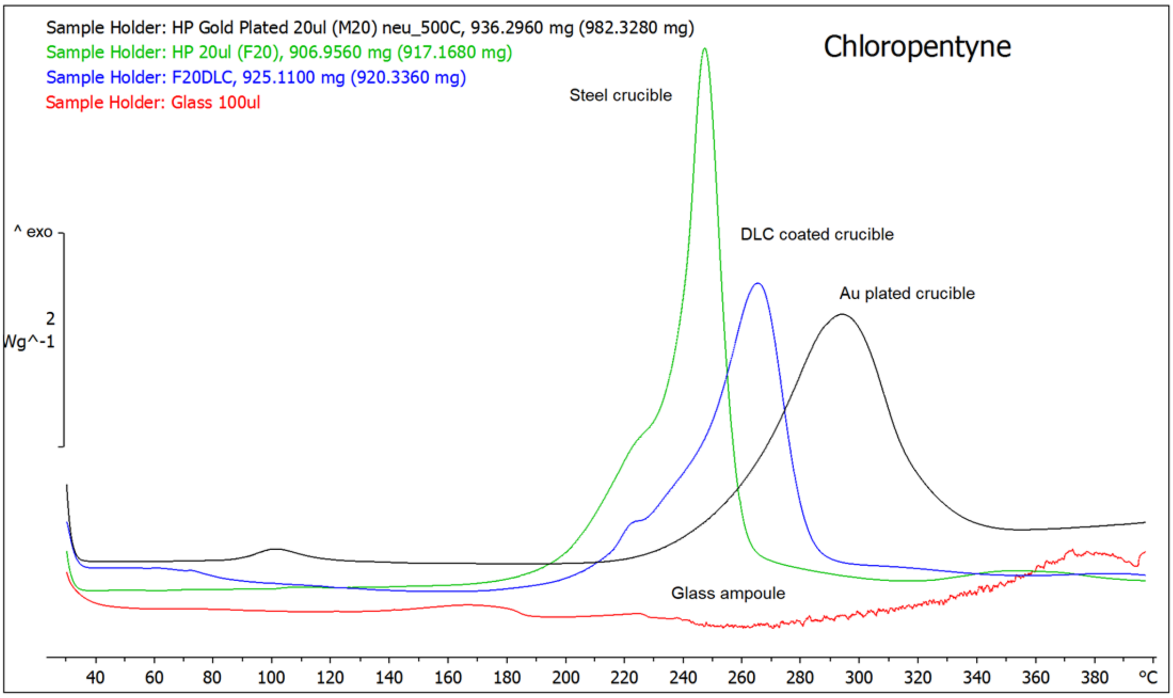

Figure 6: Comparison of dynamic DSC measurements with Chloropentyne in different crucibles

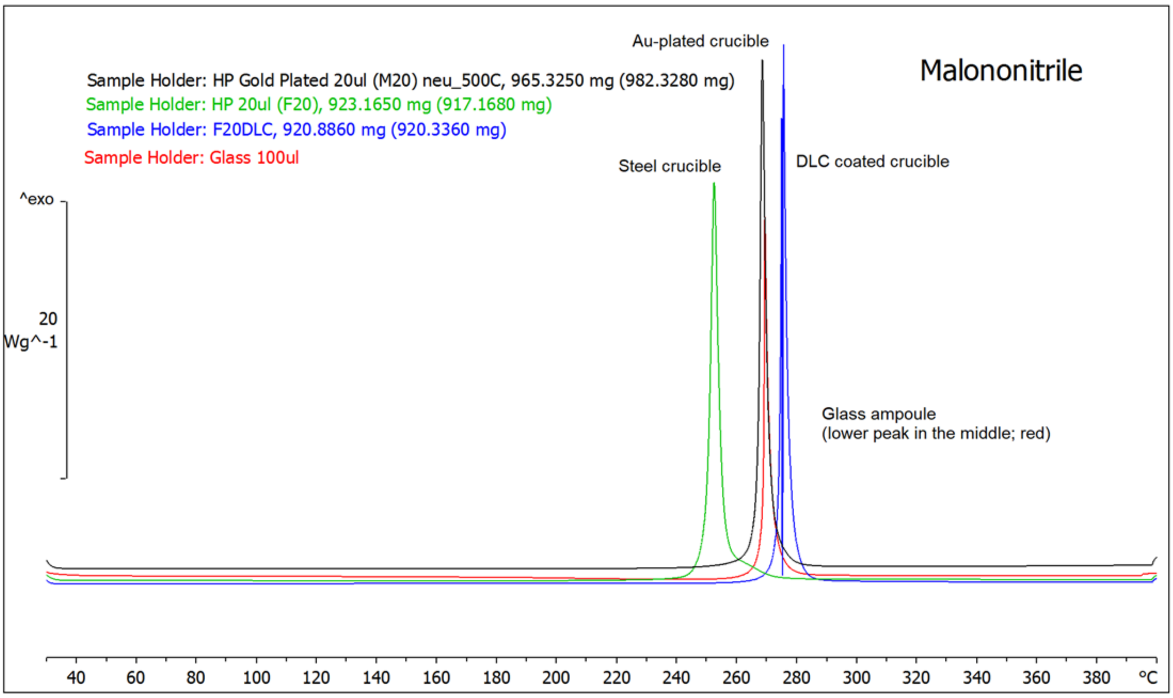

Figure 7: Comparison of dynamic DSC measurements with Malononitrile in different crucibles

From the measurements with Malononitrile, as shown in Figure 7, the onset temperature in the DLC coated crucible is again higher than in all other crucibles. For the measurement in the glass ampoule the decomposition energy obtained by integration of the heat flow signal is only about 50 % of the published value. This is due to the fact that part of the material was evaporated and condensed in the upper part of the ampoule (inserted).

4. Conclusions

The interaction of samples with the surface of the crucible material of construction may have a significant effect on the results of DSC measurements, namely on the onset temperature of the decomposition reactions. Metal surfaces are known to either undergo reactions with many chemicals or to have catalytic effects on the decomposition reactions. This may lead to completely worthless test results dramatically overestimating the risks of thermal instability and thus to much too conservative interpretations. Glass is, except for the well-known reaction with fluorine atoms, much less reactive. However, the correct use of small glass ampoules requires special skills to close them correctly in order to get useful measurements.
DLC coated crucibles combine the advantages of standard metal crucibles, which are rather simple to handle, i.e. to close, still having a high pressure resistance of at least 200 bar when properly sealed, with the low reactivity of glass ampoules.

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