

THE EFFECT OF CRUCIBLE TYPE ON DIFFERENTIAL SCANNING CALORIMETRY (DSC) MEASUREMENTS

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It has been found that different thermal stability screening methods can show significant differences between results on the same samples, depending on the test cell used. Certain materials of construction (including gold) of test cells have been found to catalyse reaction/decomposition of the test sample. This paper documents an investigation of the effect of using different crucibles on the thermal stability of various materials using Differential Scanning Calorimetry (DSC).

INTRODUCTION

Within Syngenta, the various safety functions around the world utilise both commercially available equipment such as the Mettler RC1, DSC and equipment developed in-house. For thermal stability screening the concepts of Time to Maximum Rate (TMR_{AD})¹ derived from DSC data, and “Onset Temperature” derived from data generated from Carius Tube, temperature-pressure-time testing² are both utilised. Whilst DSC crucibles are available in various materials, for hazards testing high pressure gold-plated stainless steel crucibles are generally used due to the alleged chemically inert nature of gold. Small samples of materials of reactor construction (e.g. mild steel, stainless steel, cast iron, Hastelloy) can be added to test their effect. Carius tubes are made from glass, to which the relevant materials of reactor construction can also be added for the test.

During development of novel routes to two compounds at a number of Syngenta sites across the world some thermal stability screening of the compounds was carried out using the different methods. Whilst direct comparison of data from Carius tube tests and DSC tests can be problematic, owing to differences in sample size, equipment sensitivity and modes of operation, comparison of the results indicated significant differences in the thermal stability predicted from small scale tests. Initially, it was thought that the differences may have been due to the effects of materials of construction of the test cells. An investigation of these effects was therefore undertaken. In order to eliminate the effects of scale, test sensitivity and mode of operation, the following work was carried out using the same calorimeter, and test cells made of stainless steel, gold plated stainless steel and glass.

EXPERIMENTAL/RESULTS

The following experiments were carried out using a Mettler DSC 30, operating on the Mettler Toledo STAR[®] System software.

All dynamic tests were carried out using the following conditions:

Scan Rate	–	5 K/min
Scan Range	–	30 to 450°C
Purge Gas	–	Nitrogen, 75 ml/min
Reference	–	Empty crucible

All isothermal tests were carried out using the following conditions:

Scan Temperature	–	230°C
Purge Gas	–	Nitrogen, 75 ml/min
Reference	–	Empty crucible

DYNAMIC THERMAL STABILITY TESTING OF A NITRO ACID CHLORIDE SOLUTION

Material: 30% w/w solution of a nitro acid chloride in benzonitrile.

IN HIGH PRESSURE STAINLESS STEEL CRUCIBLE

A complex exotherm was observed starting from ca 60°C with an initial peak at 145.14°C and several other peaks, subsiding at ca 320°C. A further small exotherm was observed between ca 350°C and 450°C (see Figure 1).

IN HIGH PRESSURE GOLD PLATED STAINLESS STEEL CRUCIBLE

A complex exotherm was observed starting from ca 128°C with an initial peak at 181.7°C and several other peaks, not completely resolved up to test end at 450°C (see Figure 2).

IN SEALED GLASS CRUCIBLE

A complex exotherm was observed starting from ca 190°C with an initial peak at ca 260°C and several other peaks, not completely resolved up to test end at 450°C (see Figure 3).

DYNAMIC THERMAL STABILITY TESTING OF A CHLORINATED THIAZOLE

Material: A chlorinated thiazole.

IN HIGH PRESSURE STAINLESS STEEL CRUCIBLE

A complex exotherm was observed starting from ca 60°C with an initial peak at ca 148°C and several other peaks, not completely resolved up to test end at 450°C (see Figure 4).

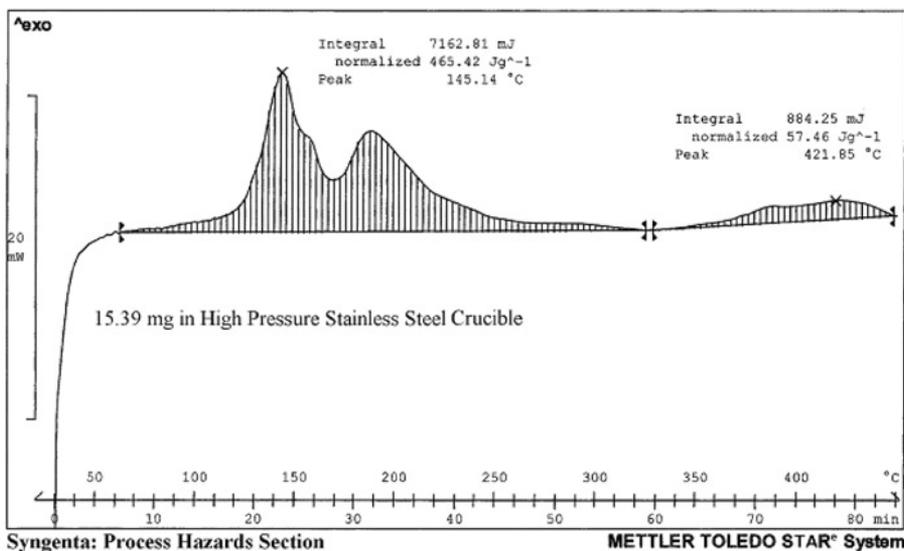


Figure 1. 30% w/w nitro acid chloride in benzonitrile

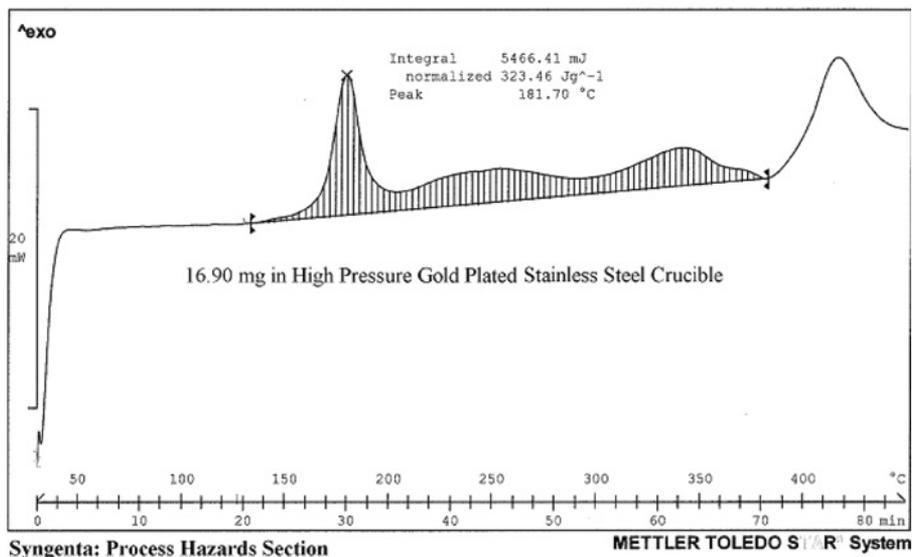


Figure 2. 30% w/w nitro acid chloride in benzonitrile

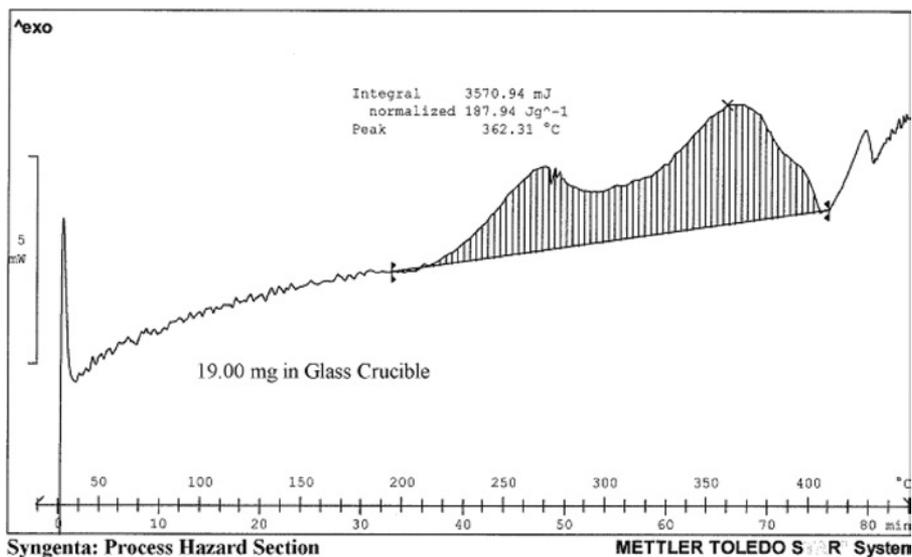


Figure 3. 30% w/w nitro acid chloride in benzonitrile

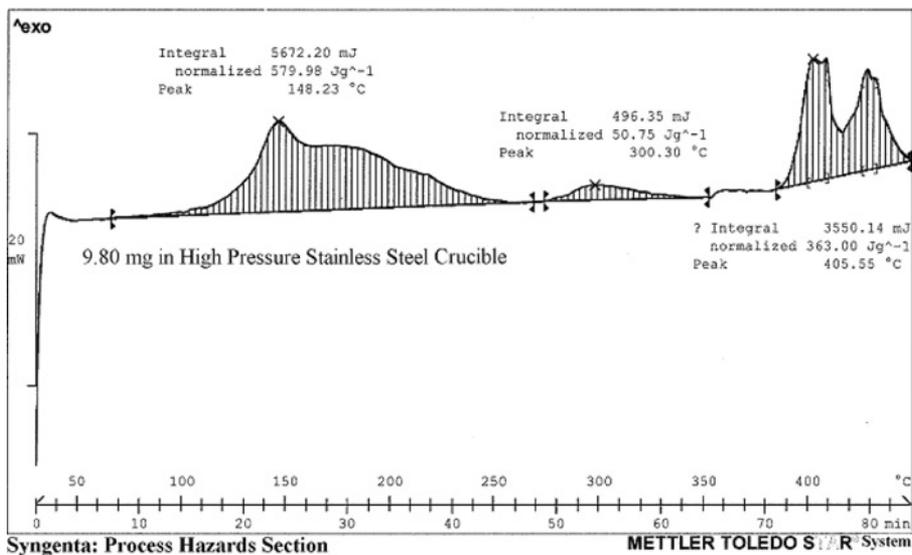


Figure 4. Chlorinated thiazole

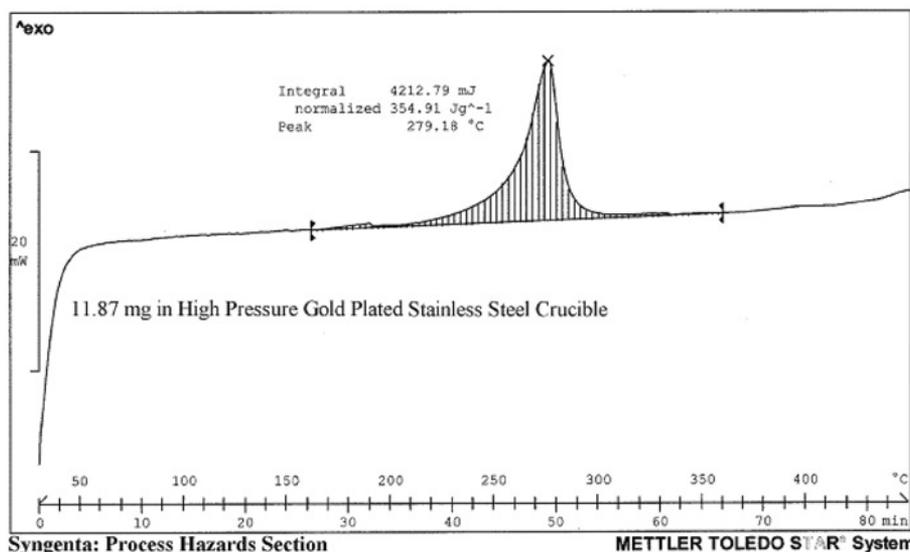


Figure 5. Chlorinated thiazole

IN HIGH PRESSURE GOLD PLATED STAINLESS STEEL CRUCIBLE

An exotherm was observed starting from ca 160°C peaking at 279.18°C returning to baseline at ca 360°C. Possible further exothermicity, starting from ca 400°C, incomplete by test end (see Figure 5).

IN SEALED GLASS CRUCIBLE

An exotherm was observed starting from ca 185°C peaking at 284.67°C returning to baseline at ca 365°C. Possible further exothermicity, starting from ca 405°C, incomplete by test end (see Figure 6).

ISOTHERMAL STABILITY TESTING OF A CHLORINATED THIAZOLE

Material: A chlorinated thiazole.

IN HIGH PRESSURE STAINLESS STEEL CRUCIBLE

Heat released immediately in a single peak at 230°C, substantially subsided within ca 6 minutes, and completely returned to baseline by ca 25 minutes. No further heat release over 300 minutes (see Figure 7). A dynamic test on the same sample following

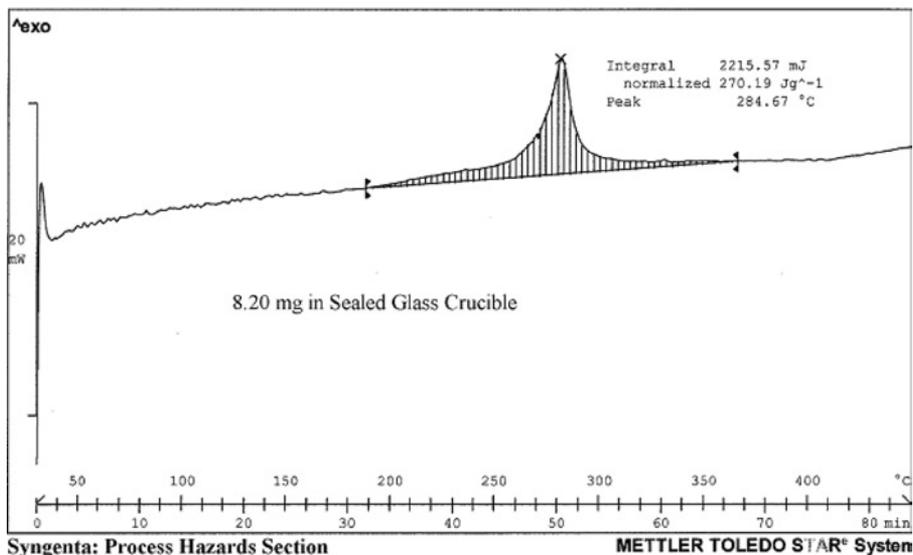


Figure 6. Chlorinated thiazole

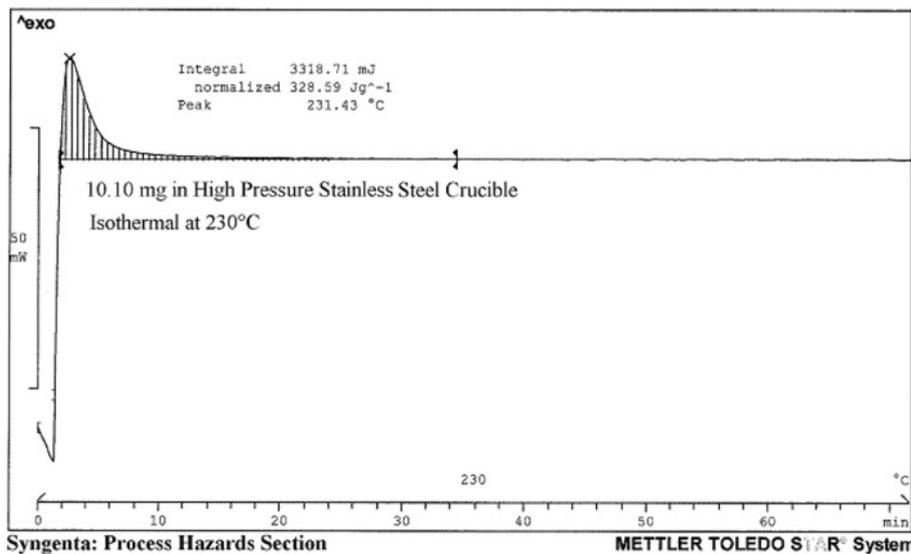


Figure 7. Chlorinated thiazole

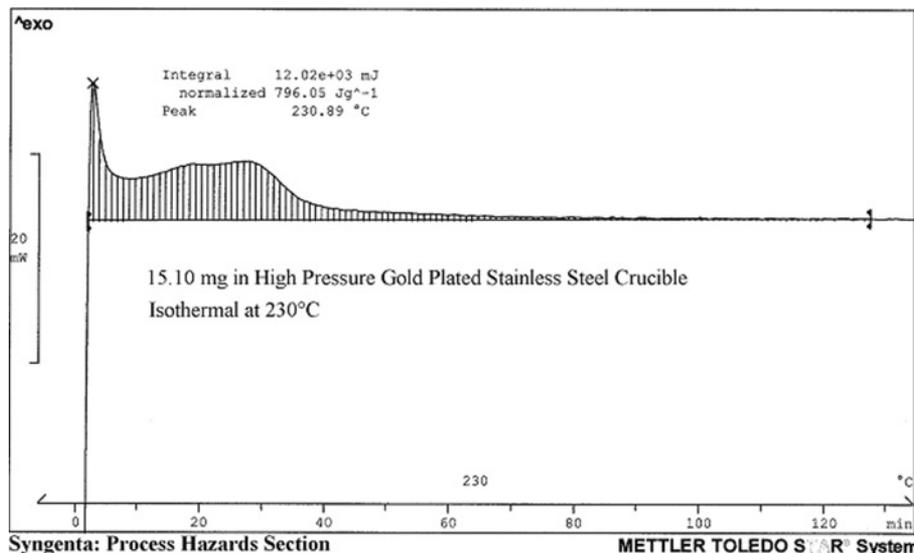


Figure 8. Chlorinated thiazole

the isothermal hold found that the exothermicity observed above 270°C in test 4.1 (see Figure 4) was still present.

IN HIGH PRESSURE GOLD PLATED STAINLESS STEEL CRUCIBLE

Heat released immediately in a complex exotherm at 230°C. Initial sharp peak substantially subsided within ca 6 minutes, after which the heat output increased again showing conjoined peaks at ca 18 and 30 minutes, completely returning to baseline by ca 120 minutes. No further heat release over 300 minutes (see Figure 8). A dynamic test on the same sample following the isothermal hold found significant complex exothermicity observed above 280°C.

IN SEALED GLASS CRUCIBLE

Heat released immediately in a complex exotherm at 230°C. Initial sharp peak substantially subsided within ca 1 minute, going into a second sharp peak after which the heat output subsided substantially and increased again into one wide peak at ca 48 minutes, subsiding slowly and completely returning to baseline by ca 170 minutes. No further heat release over 300 minutes (see Figure 9). A dynamic test on the same sample following

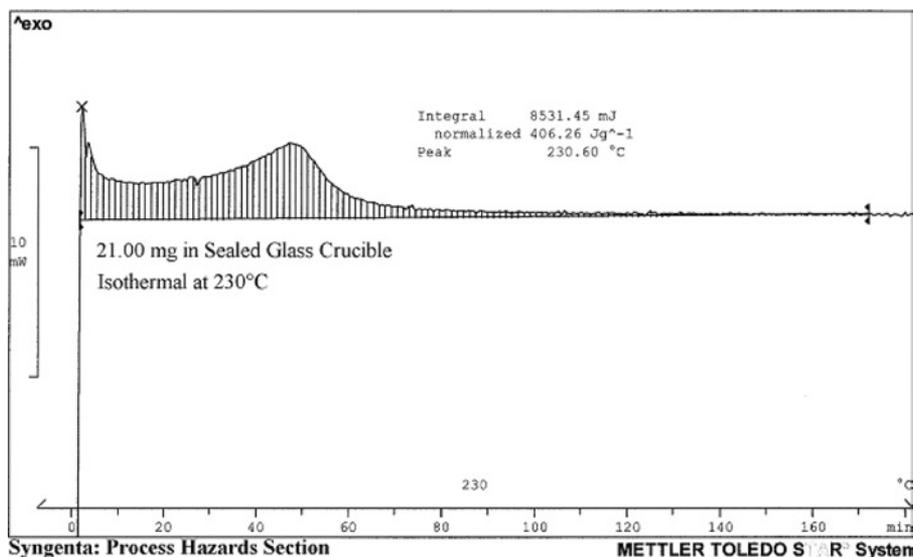


Figure 9. Chlorinated thiazole

the isothermal hold found a large sharp exotherm observed from ca 233–240°C, quickly subsiding to baseline with no further significant exothermicity observed up to 450°C.

DISCUSSION

THERMAL STABILITY OF THE NITRO ACID CHLORIDE SOLUTION

The DSC traces for the dynamic tests of the nitro acid chloride in all three crucible types are superimposed in Figure 10. This comparison clearly shows the decomposition reaction to be catalysed, most significantly, by stainless steel and, to a lesser extent, by gold, with onset of exothermicity occurring at lower temperatures than in the glass crucible.

From the chemistry, it should be expected that the acid chloride would corrode the steel crucible, possibly forming products, which are likely to catalyse the sample decomposition and reduce the onset temperature of exothermicity. Therefore, it is unlikely that this type of material would be used in an unlined steel reactor.

However, it would not necessarily be expected that this effect would also be observed with a relatively inert material such as gold. Allowing a suitable safety margin for scale-up from the observed onset temperature in the test, it may be predicted that the onset of exothermicity would occur close to ambient temperature if operated on large-scale plant. This would only occur in reality in a gold plated reactor! However, the predicted “low” onset temperature could preclude the development of the process to large-scale manufacture.

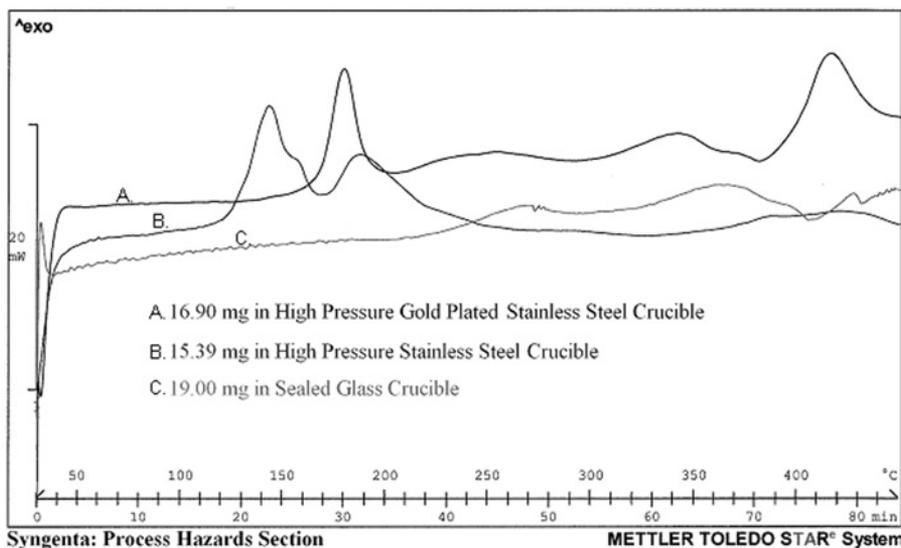


Figure 10. Comparison of nitro acid chloride dynamic tests

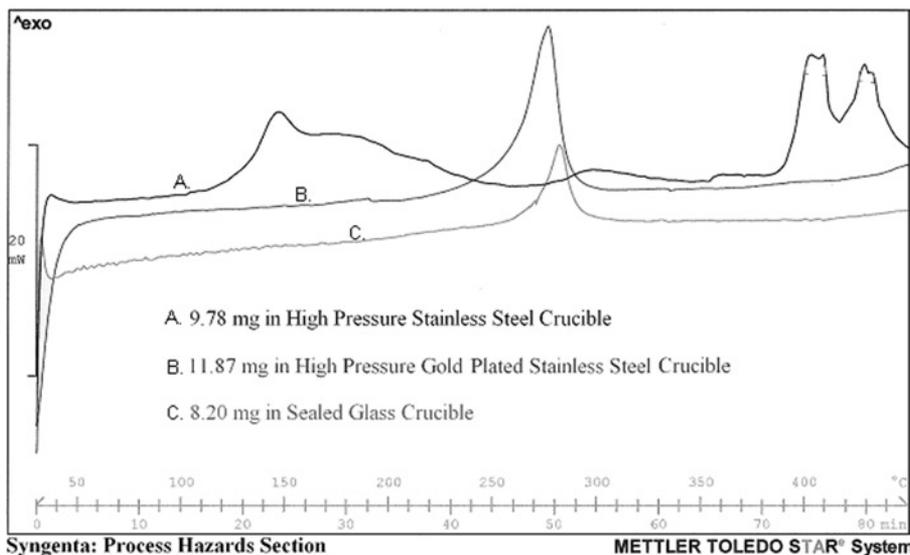


Figure 11. Comparison of chlorinated thiazole dynamic tests

THERMAL STABILITY OF THE CHLORINATED THIAZOLE

The DSC traces for the dynamic tests of the thiazole in all three crucible types are superimposed in Figure 11. This comparison again clearly shows the decomposition reaction to be catalysed by stainless steel, but the comparative effect between gold and glass is not so well defined. Therefore, isothermal testing was carried out to determine if thermal history exacerbated the effect.

The three isothermal tests are superimposed in Figure 12. At 230°C, the temperature chosen for the testing, some initial exothermicity was seen in all three samples, although this was relatively minor in the glass crucible, the peak power output observed after ca 48 minutes. In the gold plated crucible the peak power output was observed in the initial exotherm and was much greater than in the glass crucible. Further exothermicity was observed as a conjoined double peak at ca 18 and 30 minutes. As the initial rate of power output at various isothermal temperatures can be used to determine TMR_{AD} , again the result determined in the gold crucible test may be expected to have a significant effect by reducing the calculated TMR_{AD} . Again, this may preclude development of a large scale manufacturing process.

CONCLUSIONS

It has been clearly shown that both stainless steel and gold can catalyse certain decomposition reactions. The reaction between steel and a number of materials is expected, and

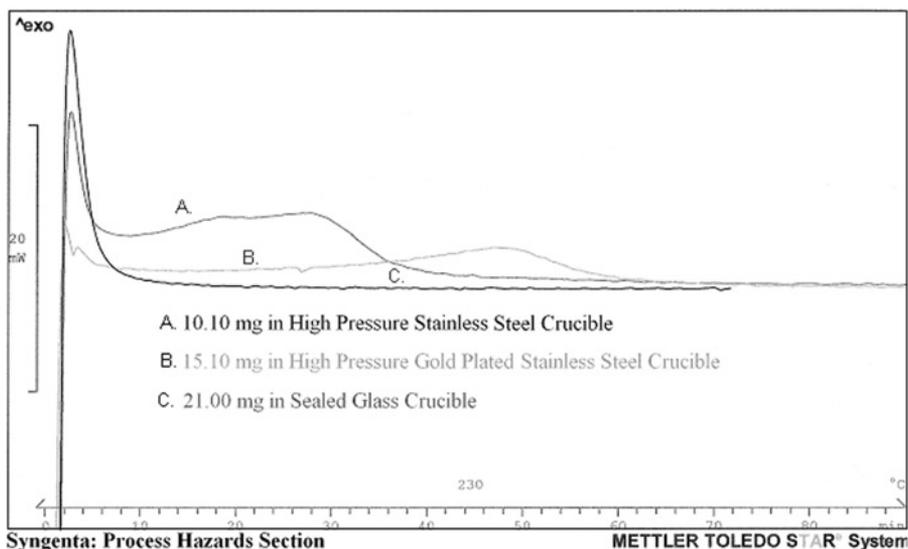


Figure 12. Comparison of chlorinated thiazole isothermal tests

protected against in practice, but gold is generally accepted to be relatively chemically inert, hence its almost universal use for DSC crucibles in safety testing. Whilst this observed effect with gold may not give rise to a chemical reaction hazard in practice — unless severe contamination with gold occurs, which is unlikely — it may preclude the development of a viable chemical manufacturing process.

It is recommended that care is exercised in the choice of test cell material in any form of thermal stability testing; the assumption that a material is inert in a particular application should be tested.

REFERENCES

1. Gygax, R., 1988, Thermische Prozess-Sicherheit, ISCRE 10.
2. Gibson, N., Rogers, RL., Wright, TK., 1987, Chemical Reaction Hazards: An Integrated Approach, Hazards from Pressure. IChemE Symp Ser No 102: pp. 61–84.