A novel hermetic differential scanning calorimeter (DSC) sample crucible

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Abstract

The design of a novel differential scanning calorimeter (DSC) sample crucible that allows for the analysis of liquid and solid materials (the solids can also be wetted with a liquid) at high temperatures is described. The sample to be analyzed is placed within a thin walled stainless steel tube, which is then sealed by tungsten inert gas (TIG) welding. The stainless steel tube is 8.8 mm (0.35 in.) long, has an outer diameter of 3.14 mm (0.125 in.) and a wall thickness of 0.015 mm (0.006 in.). Placing the flattened end of the tube in the jaws of a large copper block (heat sink) allows for the sealing of the tube by TIG welding without heating the sample excessively. The utility of the sample crucible is demonstrated by a study of the kinetics of the thermal decomposition of di-*t*-butyl peroxide (DTBP), where an activation energy of 140 kJ mol^{-1} and a frequency factor of 5.30×10^{13} s^{-1} was obtained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Differential scanning calorimeter; Novel sample crucible; Thermal decomposition; High temperature; Kinetics

1. Introduction

Techniques using non-isothermal calorimetry have been widely used in academic and industrial laboratories [1,2]. They are routinely used to study the thermal properties of a wide variety of materials, from polymers to pure metals. In a typical differential scanning calorimetry (DSC) experiment, the difference in power required to heat a reference pan and sample pan is monitored as a function of temperature at a fixed temperature sweep rate. This procedure allows for the examination of both exothermic and endothermic events and the determination of their heats.

Typically, DSC sample pans are made of aluminum, but gold, platinum, and stainless steel have been used for specific applications requiring higher temperatures or pressures. To analyze air-sensitive or volatile samples crimped versions of the above holders have been developed. Our experience with crimped aluminum sample pans is that they often leak when a liquid sample is exposed to elevated temperatures during study due to the generation of high pressures. This issue has been addressed by a number of commercial manufacturers, TA Instruments and Mettler Toledo, who have developed sample systems based on glass capillaries or high pressure sealing [3,4]. One difficulty with the glass capillary approach is that the system requires oxygen (for the flame) to seal the glass capillary. Much of our work involves air-sensitive samples comprised of both liquid and solid phases that require manipulation and sealing in DSC sample

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crucibles entirely within an inert atmosphere of a glove box. The glass capillary sealing system is not compatible with inert atmosphere requirements. Furthermore, the glass capillary system is relatively expensive, with a cost of about US$ 6 per run.

The cost of an experiment using the Mettler high pressure crimp crucibles nears US$ 40 per run. Experiments using Mettler's high pressure crucibles equipped with a screw top and metal gasket have a cost of about US$ 6 per run, but if temperatures above 350 °C are required, the cost per run increases to near US$ 60.

To overcome the limitations described above, we have designed a novel DSC sample crucible based on welded thin-walled stainless steel tubing. The sample crucibles can be welded closed in ambient air, or within an inert atmosphere glove box. A large copper heat sink is used during the welding operation to prevent excessive heating of the sample. The thin-walled tubing is relatively inexpensive, the welder is an ''off-the-shelf'' low power unit, so the entire facility for making such DSC samples is relatively inexpensive compared to other options. Our experience shows that the cost is about US$ 0.25 per run. Furthermore, the initial capital cost of the complete system is comparable to the other high pressure DSC solutions.

Here, we describe the new sample crucibles, demonstrate that they give reliable measurements for the endotherm associated with the melting of tin, and allow the extraction of reaction kinetics for the thermal decomposition of di-*t*-butyl peroxide (DTBP) that are in good agreement with literature values. Furthermore, the samples do not leak, as demonstrated by their unchanged mass from the start to the end of the experiment.

1.1. Crucible design and preparation

The new DSC sample crucible consists of a 3.14 mm (0.125 in.) outer diameter stainless steel, type 304 seamless tube having a wall thickness of 0.015 mm (0.006 in.) (MicroGroup, Medway, MA). The stainless steel tubing was cut into 8.8 mm (0.35 in.) long pieces, but these can be longer if desired. These new sample crucibles are inexpensive (25¢ each). The sample crucibles are cleaned and have one end flattened. The flattened end is then welded shut by tungsten inert gas (TIG) welding using a Miller Maxstar 91 ARC welder, equipped with a Snap Start II high frequency ARC starter. Sample crucibles shown at several stages of the procedure as well as a conventional hermetic seal Al DSC pan are shown in Fig. 1. The welding of the sample tube is performed with the sample contained within a large copper block as a heat sink. Fig. 2 shows the sample within the confines of the copper block. The slot at the top of the block is just large enough to accommodate the crucible within a recess with thin jaws (1 mm thick) at the top. The jaws of the block are then clamped together to ensure good contact to the heat sink (copper block) as shown in Fig. 3 and the crucible is ready to be welded. The TIG welding is performed under a flow of Ar and essentially melts the end of the tube together. Typical welding conditions were dc currents between 2 and 5 A at voltages below 15 V, once the arc was started. Typical weld times were under 2 s.

With one end of the sample crucible sealed, the desired sample was placed into the tube. Although, the new sample crucible has a higher mass (100 mg) than a typical Al pan (55 mg), it has the capacity to hold up to 40 mg of material. The crucible can contain liquid, a solid or a combination of both. When the sample had been loaded, the tube was crimped and welded shut.

Calculations assuming that the crucible will burst when the hoop stress equals the yield stress of 304 stainless steel, suggest that the burst pressure will be about 2000 atm. This neglects high stress regions around the crimp and weld, but suggests high pressures should not be a problem. Heating water to 310 °C gives an internal pressure of 100 atm, and our crucibles have been tested with water within to 310 °C without bursting.

The welding of the sample tube has raised a few concerns (to the ''doubting Thomases'') about the generated temperatures during welding, which may affect the sample. To address these concerns we calculated the temperature that would be generated at the jaws of the heat sink during a ''worst case'' scenario. We assume that all the electrical power supplied by the welding supply is added as heat to the end of the sample tube that protrudes above the jaws. This neglects the fact that some power will be dissipated to the atmosphere and that the welding process is not 100% efficient. Fig. 4 gives a sketch of the heat flow during the weld operation. The welding of the sample tube at a maximum of 15 V and 5 A, for a total power of 75 W, for a duration of

Conventional Al Pan

Welded Pans

Before Filling

Before DSC

After DSC

Fig. 1. Comparison between conventional hermetic Al DSC pans and the new stainless steel welded DSC pans. A Canadian 10¢ piece showing the famous "Bluenose" is shown for size comparison.
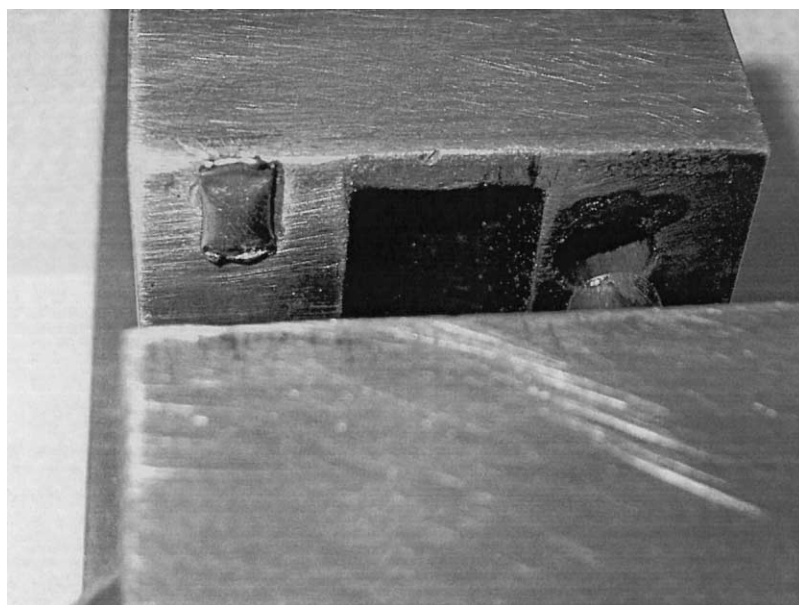
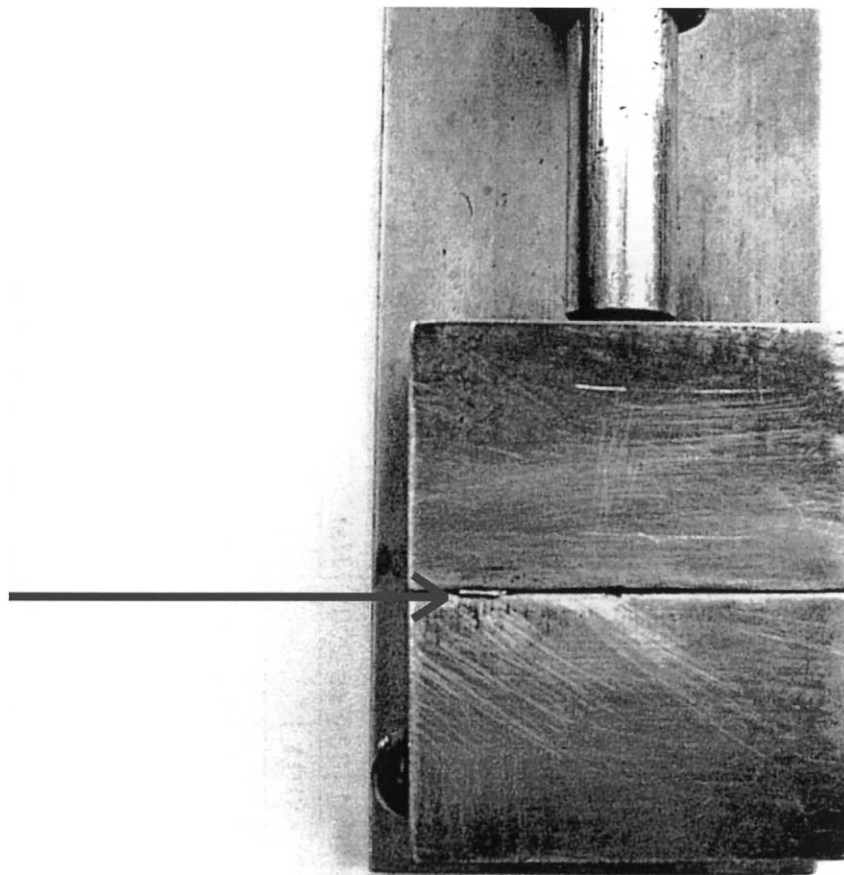Fig. 2. Sample pan placed in the pocket of the large copper block (heat sink) prior to welding.

Fig. 3. Sample pan clamped in the jaws of the copper heat sink.

approximately 2 s. Using a simple equation for thermal conduction through a bar of length Δx and cross-sectional area, A:

$$\Delta T = \frac{\Delta x}{kA} I, \qquad (1)$$

where k is the thermal conductivity of the bar and I is the thermal current, the temperature increase during welding can be calculated [5]. We assume a steady-state condition with 75 W being input at the sample side of the jaws, and the block side of the jaws at room temperature. This is a very generous estimate because the weld time is only 2 s. Using the dimensions given in Fig. 4 and the room temperature thermal conductivity of copper (401 W m^{-1} K^{-1}), a temperature increase of

about 35 K would be predicted for the sample in a "worst case" scenario. Thus, the sample holder will certainly remain below 60 °C during welding.

Air-sensitive and thermally unstable solids, liquids or wetted materials that can not be analyzed at high temperatures in typical Al DSC sample pans, due to the inability to contain the internal pressure, can now be analyzed effectively. Air-sensitive materials are easily studied since the welding (in our case) is performed under inert gas conditions in a glove box, whereas glass capillaries require an oxygen environment for sealing, giving rise to problems in studies of air-sensitive material.

Once sealed, the sample crucible was weighed and analyzed in the DSC with no special adapters or holders
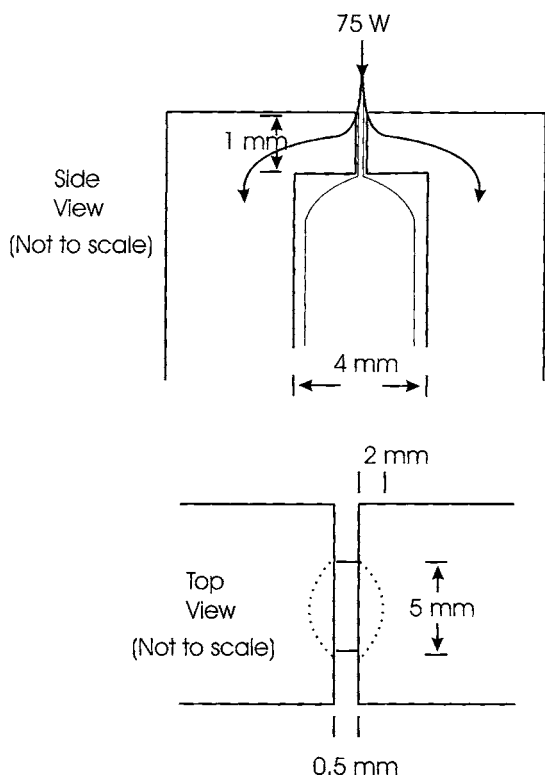
Fig. 4. Sketch of heat sink block design showing the direction of heat flow during the welding step (not to scale).

required. The stainless steel sample crucibles, shaped like a miniature pillow, sit on the same spots in the DSC head as the previous sample crucibles. To verify there were no leaks in the sample crucible, its mass was determined before and after analysis. Only those runs showing no weight loss were used for data analysis.

1.2. Testing of the welded DSC crucible

The thermal conductivity of stainless steel is much lower than that of Al [6]. This lower thermal conductivity facilitates the welding of the sample crucible without heating the sample, but might also cause changes in the DSC signal due to inefficient heat transfer at the programmed heating rate. It is important to use thin walled tubing to ensure minimize thermal resistance, and that is the reason we selected 150 μm walled tubing. The thermal resistance, R, of the crucible wall was calculated from the thickness of the sample crucible metal, l, and the thermal conductivity,

k, of the crucible as $R = l/k$. For the conventional Al hermetic pans, we find $R = 0.013$ K cm^2 W^{-1}, while for the new welded crucibles $R = 0.051$ K cm^2 W^{-1}. This may limit the application of these crucibles to low heating rates.

To test the effect of the stainless steel pan on the response of the DSC, a typical standard for high temperature work, tin, was used. A 10 mg sample of tin (99% pure, Aldrich) was placed in an Al sample pan and then hermetically sealed. The sample was then heated at 10 K min^{-1} to above its melting temperature, to record the shape and location of the endotherm. The experiment was then repeated, after cooling to room temperature, but at 2 K min^{-1}. The same type of experiment was performed but in the newly designed stainless steel DSC sample crucibles where 13 mg of tin was used. The results of the two experiments are shown in Fig. 5. The results for the two sample crucibles are practically identical and thus we believe that the lower thermal conductivity of the stainless steel does not significantly affect the response of welded DSC at least up to 10 K min^{-1}.

These new sample pans are most useful when analyzing solids or liquids that decompose or partake in reactions that produce gaseous products at high temperature, since these systems produce high pressures that are difficult to contain. To demonstrate the performance of these new sample crucibles, a small portion of di-t-butyl peroxide (DTBP, Aldrich) was sealed in stainless steel sample crucibles and analyzed
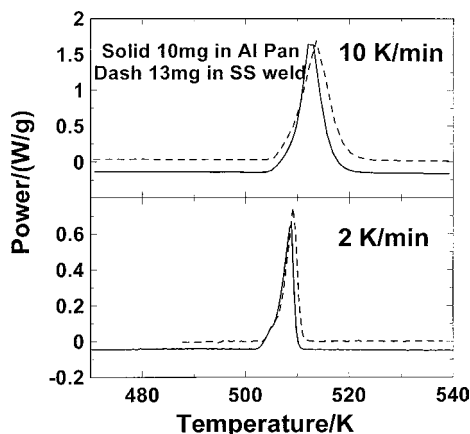

Fig. 5. Comparison between the endothermic melting peaks of Sn measured in the welded stainless steel sample pan (dashed line) and in a conventional hermetic Al DSC pan (solid line).
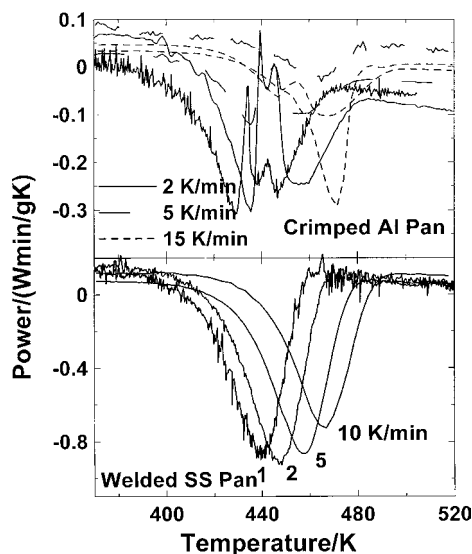
Fig. 6. Comparison of the thermal decomposition of di-*t*-butyl peroxide (DTBP) measured in hermetic Al DSC pans and in welded stainless steel pans at various heating rates (2, 5 and 15 K min⁻¹, for Al pans and 1, 2, 5 and 10 K min⁻¹ for SS pans). Evolved power has been divided by the heating rate to present the results clearly on the same axis.

under a variety of heating rates. These profiles were then compared to samples of DTBP, sealed in hermetic Al DSC pans, under the same conditions. The results of these experiments are shown in Fig. 6. All of the profiles for the samples contained within the hermetic Al DSC pans, except one, contain sharp upward (endothermic, indicating evaporation) peaks, which indicate the liberation of the generated gases from the decomposition of DTBP. Indeed the mass of the crucibles before and after the DSC run in Al pans

had changed. The samples measured in the welded stainless steel tubes exhibit only one peak that moves in a fashion typical for non-isothermal DSC experiments at various heating rates [7]. The sample holders did not leak. Fig. 6 demonstrates the clear advantage in using welded sample containers for DSC analysis of thermally unstable liquid specimens.

Di-*t*-butyl peroxide has been widely studied as a cetane improver in diesel fuels [8]. These cetane improvers are used to improve the ability of the fuel to autoignite in the combustion chamber of a diesel engine and thus the thermal decomposition of DTBP has been studied extensively [9]. A wide variety of kinetic parameters have been determined depending on the method used for analysis but all have concluded a first-order decomposition mechanism [10]. A summary of Arrhenius parameters from the literature for DTBP is given in Table 1.

In a DSC experiment, the generated power per unit mass for a first-order decomposition is

$$P = H\gamma \exp\left(\frac{-E_a}{k_B T}\right)(1 - \alpha), \tag{2}$$

where H is the total heat generated by the reaction per gram of reactant, α the fractional degree of conversion of the reactant, γ the frequency factor, E_a the activation energy, k_B the Boltzmann constant and T is the temperature. Using the data of Fig. 6 for the welded stainless steel pans, we were able to perform a least squares fitting of the four data sets (at different temperature scan rates) to obtain the best-fitted Arrhenius parameters [11]. The results of this fitting to the normalized power is shown in Fig. 7. The analysis gives an activation energy of 140 kJ mol⁻¹ and a

Table 1
Summary of the Arrhenius parameters reported for di-*t*-butyl peroxide

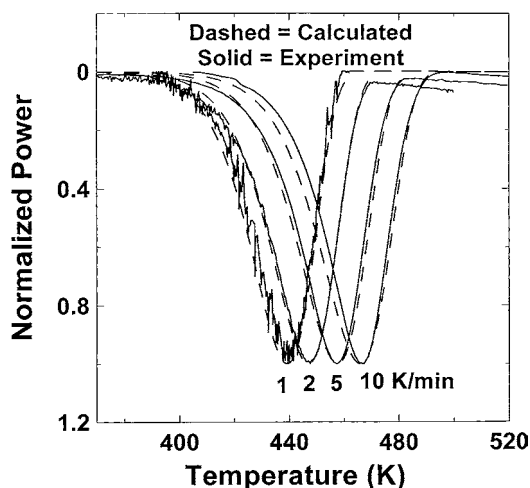| E_a (kJ mol⁻¹)	A (s⁻¹)	Conditions	Reference
144–151		Cumene solution	[12]
148	1.40×10^{16}		[13]
163	2.80×10^{16}	Gas phase	[14]
154	1.30×10^{15}	DSC, mineral oil	[2]
158	2.30×10^{16}	ARC, mineral oil or toluene	[2]
122	3.20×10^{11}	DSC, 725 psi	[15]
158	6.47×10^{15}	Gas phase "best" literature average	[16]
136	7.36×10^{12}	0.1 M in diesel fuel	[17]
148	7.39×10^{14}	Neat	[8]
140	5.50×10^{13}	Neat	This study

Fig. 7. Comparison of calculation (dashed line) and experiment (solid line) for the thermal decomposition of di-*t*-butyl peroxide (DTBP) at the indicated heating rates (1, 2, 5 and 10 K min^{-1}). Evolved power has been normalized to present the results clearly on the same axis.

frequency factor of 5.50×10^{13} s^{-1}, which is in good agreement with the results published in the literature as listed in Table 1.

The welded stainless steel tubes used as sample crucibles for DSC, have been "cloned" in larger sizes for use as low mass accelerating rate calorimeter (ARC) sample bomb. These new ARC sample bombs are 39.1 mm (1.54 in.) long and 6.35 mm (0.250 in.) in diameter. To test the reaction kinetics obtained from the analysis of DSC data, ARC self-heating rate profiles were calculated and compared to experimental data.

In an ARC experiment, the self-heating rate is given by

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{h}{C_{\text{tot}}} \frac{\mathrm{d}\alpha}{\mathrm{d}t}, \tag{3}$$

where h is the total heat which can be evolved by the sample due to the reaction (J) and C_{tot} is the total heat capacity of the reactants and the sample bomb (J K^{-1}). The h/C_{tot} corresponds to the temperature rise, ΔT, from the onset of the exotherm to the end of the exothermic behavior because

$$\int_0^\infty \frac{\mathrm{d}T}{\mathrm{d}t} \, \mathrm{d}t = \Delta T, \tag{4}$$

$$\int_0^\infty \frac{h}{C_{\text{tot}}} \frac{\mathrm{d}\alpha}{\mathrm{d}t} \, \mathrm{d}t = \frac{h}{C_{\text{tot}}} \Delta\alpha = \frac{h}{C_{\text{tot}}}, \tag{5}$$

since $\Delta\alpha = 1$ for the complete consumption of the reactant, thus

$$\Delta T = \frac{h}{C_{\text{tot}}}. \tag{6}$$

Here, a 29 mg portion of DTBP was added to a 950 mg ARC sample bomb and then sealed by TIG welding. Using an average heat of reaction of 916 J g^{-1} $\pm$ 12% from the four DSC runs (1, 2, 5 and 10 K min^{-1}), a specific heat of 2.3 J K^{-1} g^{-1} [15] for DTBP over the range of temperature involved and a specific heat of 0.46 J K^{-1} g^{-1} [6] for stainless steel type 304, a temperature rise of 52.7 K is predicted. The 12% uncertainty in the heat of decomposition for DTBP is due to the weighing of this sample in an inert atmosphere glove box, where the accuracy of the balance is only $\pm$0.001 g. Fig. 8a shows the calculated ARC profile using the kinetics determined from the DSC. Clearly, the calculated profile has a larger temperature rise than the experimental data, but the shape of the ARC profile is accurately reproduced. Fig. 8b shows the calculated ARC profile for same kinetics, but with a temperature rise of only 51°. A very accurate reproduction of the decomposition kinetics can be achieved. The accurate reproduction of both ARC and DSC data with the same reaction kinetics gives a high degree of confidence in the obtained parameters.
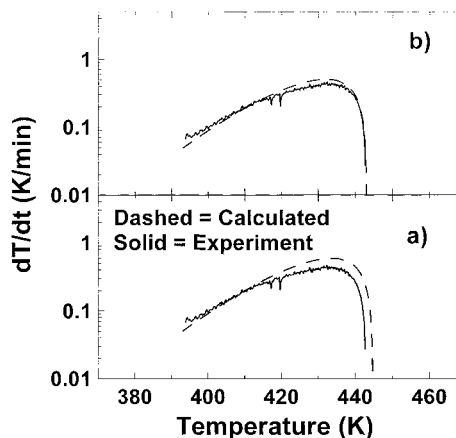

Fig. 8. Comparison of the calculated (dashed line) and experimental (solid line) self-heating rate profiles for 29 mg of DTBP. Panel (a) gives the predicted profile for the calculated temperature rise of 52.7 K, while panel (b) shows the prediction for a temperature rise of 51 K

This stainless steel tubing/TIG welding thermal analysis procedure has been extended to the analysis of air-sensitive, thermally unstable battery electrode materials [18]. In addition, the method has been used to synthesize high temperature products that are air-sensitive or prepared from air-sensitive reactants [19]. These tubes provide a completely sealed and inert environment that can be heated in excess of 1000 K.

2. Conclusion

A new welded sample crucible for DSC analysis has been described. The stainless steel crucible has sufficient thermal conductivity so samples can be analyzed reliably at heating rates at least as high as 10 K min^{-1}. Liquid samples such as di-*t*-butyl peroxide can be studied without leaking. The sample crucibles are inexpensive and can be used with air-sensitive materials. The new sample crucibles were used to accurately measure the Arrhenius constants for the first-order decomposition of di-*t*-butyl peroxide. The measured activation energy of 140 kJ mol^{-1} and frequency factor of 5.30×10^{13} s^{-1} agree well with literature values and could accurately reproduce both ARC and DSC profiles. The methods described in this paper could be applied to thin walled-tubing made of other materials, if there is chemical incompatibility with stainless steel, provided that a reliable weld can be made.

Acknowledgements

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