J Therm Anal Calorim (2012) 109:495–499
DOI 10.1007/s10973-011-1748-6

Deformation of sample pans used in differential scanning calorimeters

S. A. Malik · L. Wang · M. A. Paget ·
F. Biddlestone · G. F. Fernando

Received: 19 April 2011 / Accepted: 15 June 2011 / Published online: 2 July 2011

Abstract The authors have previously reported on an optical technique to enable the simultaneous and non-contact acquisition of spectral, thermal and physical information of a sample in a differential scanning calorimeter (DSC). This was achieved using a simple bifurcated fibre optic probe to link the DSC to a conventional Fourier transform infrared spectrometer and an optical spectrum analyser. The fibre optic probe was located over the sample and reference compartments of the DSC. In the current study, a series of experiments were designed to investigate the stability of DSC pans during heating from ambient to 230 °C. During the first heating cycle, the base of the aluminium pans used in these experiments was found to deform in a non-linear manner. The deformation characteristics of pans manufactured from copper and steel were also investigated. Annealing the aluminium pans was found to improve significantly the deformation or expansion characteristics.

Keywords Differential scanning calorimetry · Thermo-mechanical analysis · Annealing · DSC pans · Optical TMA

Introduction

Differential scanning calorimetry is an established technique for characterising the thermal properties of materials. Experiments involving a differential scanning calorimeter (DSC) generally involve the use of aluminium pans that are placed in the sample and reference compartments. The primary function of the metal pan is to contain the test specimen and to enable intimate contact with the furnace. Previously it has been demonstrated that a DSC can be linked to a Fourier transform infrared spectrometer (FTIRS) via a simple bifurcated fibre optic probe [1, 2]. The feasibility of extracting data (non-contact) on the thermal expansion or contraction of the sample in the DSC, as a function of temperature, was also demonstrated [3]. Here, single-mode optical fibres were integrated into a fibre optic probe, and white-light interferometry was used to interrogate the distance from the surface of the sample and the tip of the optical fibres [4]. During the development of the optical thermo-mechanical analyser (OTMA), it was observed that the thermal expansion characteristics of the aluminium pans used in the DSC were variable. A conventional thermo-mechanical analyser (TMA) was also used with the DSC pans to provide independent confirmation of the non-linear and variable deformation. With reference to conventional DSC and TMA analyses involving the use of aluminium pans, any small deformations in the pan, as a function of temperature, may not be significant as good thermal contact is generally retained between the sample contained in the pan and the furnace. However, uncontrolled expansion can have a major influence on the optical-based hyphenated analytical techniques associated with the DSC. Therefore, a brief study was undertaken to investigate the reasons for the observed variability when aluminium pans were used in the DSC [4].

In the current study, a conventional TMA was used to characterise as-received and annealed DSC pans. A flat aluminium disc was also used to study the thermal expansion characteristics of as-received and annealed aluminium pans. Finite element modelling was used to verify

S. A. Malik · L. Wang · M. A. Paget · F. Biddlestone ·
G. F. Fernando (✉)
Sensors and Composites Group, School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
e-mail: g.fernando@bham.ac.uk

the deformation characteristics of the aluminium disc where a good correlation was observed between the predicted and experimental results.

Experimental

TMA experiments and annealing

TMA experiments

A schematic illustration of the experimental setup involving a DSC pan and the TMA probe is presented in Fig. 1. A thermo-mechanical analyser (TMA) (Pyris-TMA7, Perkin Elmer) was used to characterise the thermal expansion characteristics of the DSC pans. To ensure the contact between the probe and the specimen, a force of approximately 1 mg was applied. The effects of the force on the pan-deformation were studied by reducing the applied force to 50% (0.5 mg); however, no noticeable change in the expansion or contraction was recorded. The pans were heated at 5 K/min from 30 to 250 °C and then cooled to room temperature. The experiments were carried out using aluminium, copper and stainless steel pans from specified suppliers. The copper and stainless steel pans were used in their as-received states.

Annealing

The aluminium pans were annealed at 300, 400 and 500 °C for 2 h. After cooling to room temperature, the annealed pans were stored in a desicator until required. Five individual aluminium pans were tested at each of the above-mentioned temperatures.

Finite element modelling

An independent verification of the thermal expansion of an aluminium disc with a diameter of 1.6 mm and a thickness of 1.4 mm was carried out by finite element analysis (FEA). Commercially available code ANSYS version 11 was used to perform the FEA. The mesh was generated using Solid-90 elements which had 20 nodes. Each node had a single degree of freedom, i.e. temperature. The boundary conditions were similar to that used in the TMA experiments. The sample was heated at 5 K/min, and a time-dependent (transient) analysis was performed.

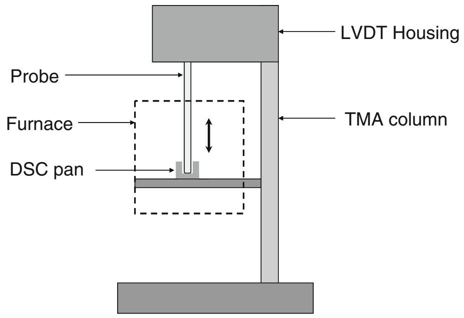

Fig. 1 Schematic illustration of a TMA with a sample; an LVDT (linear voltage displacement transducer) was employed to measure the expansion of specimen

Results and discussion

As-received pans

Typical deformation characteristics, as a function of temperature, for two as-received aluminium pans, from two suppliers, are shown in Fig. 2. In the case of Sample-1, a small contraction is observed up to approximately 100 °C after which a faster rate of contraction in the pan is observed. On the other hand, Sample-2 (from a different supplier) displays a small steady contraction up to 225 °C followed by a rapid decrease when the experiment was terminated at 250 °C. This general trend was observed for a batch of five samples tested from each of the two suppliers. Upon cooling from 250 °C to ambient, the two types of pans displayed a similar behaviour.

The deformation behaviour of a steel pan used in this study is shown in Fig. 3, where during the first heating cycle the sample contracted by 0.163 μm in the range 30–80 °C and then it expanded. However, when it was heated for the second and third time, it expanded and contracted in a liner manner, without exhibiting any significant hysteresis. The implication here is that residual stresses in the pans, introduced during their manufacture via a metal-stamping process, are responsible for the non-liner deformation characteristics during the first heating/cooling cycle. Figure 4 shows the TMA trace obtained

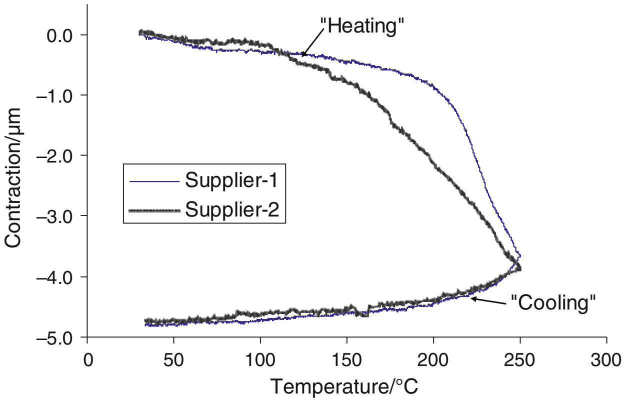

Fig. 2 TMA data showing the deformation characteristics for aluminium pans from two suppliers during heating and cooling

from copper pans. The coefficient of thermal expansion for the copper is 17 µm/K. Therefore, the deformation characteristics for pans manufactured from copper is unexpected but these can also be attributed to the residual fabrication strains in these pans.

Annealed pan

The deformation characteristics of the aluminium pans that were annealed at 300 and 400 °C for 2 h are shown in Fig. 5; the data for the as-received aluminium pans are reproduced here to enable ease of comparison.

The data presented in Fig. 5 clearly show that the magnitude of the deformation of the as-received pan is reduced significantly when using annealed pans. The contraction of the pan annealed at 400 °C was lower in magnitude when compared to that annealed at 300 °C (Table 1).

Figure 6 shows the deformation characteristics for an aluminium pan that was annealed at 500 °C for 2 h. Here, the pan was subjected to three consecutive heating and cooling cycles from ambient to 250 °C, where after the third cycle, the hysteresis in the heating/cooling cycle is minimal. This clearly demonstrates that the fabrication stresses in the aluminium pans can be relieved by annealing. It is seen that annealing the aluminium pans leads to a significant reduction in the inward bending during the first heating cycle.

Figure 7 shows the expansion characteristics of a flat aluminium disc with a diameter of 6 mm and a thickness of 1.5 mm. The TMA traces for an as-received and an annealed pan have also been included in Fig. 7; here, the aluminium disc was placed in the aluminium pan.

With reference to Fig. 7, it is seen that thermal expansion of the aluminium disc is linear up to 250 °C when the experiment was terminated. In this instance, the aluminium pan was annealed at 500 °C for 2 h. As observed previously, the expansion characteristics of the as-received aluminium pan deviated from linearity after approximately 150 °C. The annealed pan on the other hand showed a linear thermal expansion up to 200 °C, after which a small deviation from linearity was observed. This deviation may be due to constrained expansion of the aluminium disc that was located in the aluminium pan or the retention of some residual fabrication stresses in the pan. The coefficient of thermal expansion for the aluminium disc was estimated to be 23.14 µm/K; this correlated well with that reported in the literature for a similar aluminium alloy in the form of a sheet (23 µm/K) [5]. The coefficient of thermal expansion when the aluminium disc is housed in an un-annealed pan over the temperature range 30–250 °C is 22.64 µm/K. This error can be minimised using annealed aluminium pans.

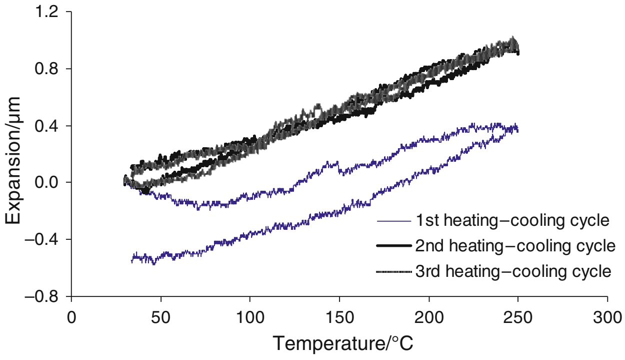

Fig. 3 TMA traces for stainless steel pans for three successive heating and cooling cycles from ambient to 250 °C

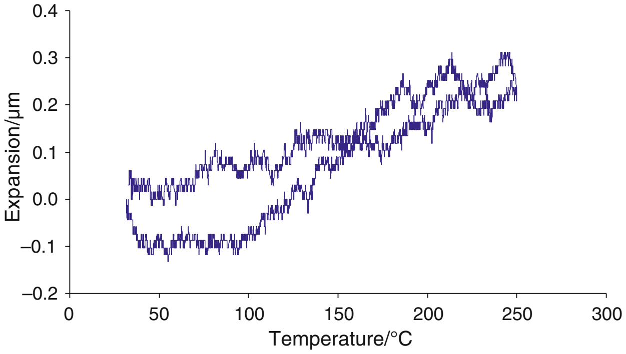

Fig. 4 TMA traces for a copper pan during heating and cooling

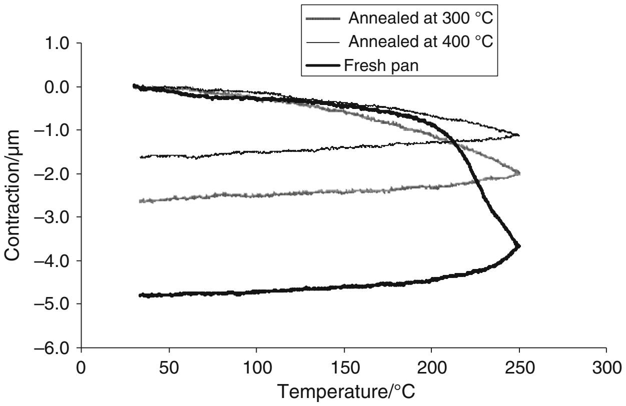

Fig. 5 The deformation characteristics for aluminium pans annealed at 300 and 400 °C for 2 h. The data for an as-received or fresh pan are also included

Admittedly, the deformation characteristics observed for the as-received aluminium pans are small and these are unlikely to influence data generated from conventional DSCs. However, the unpredictable deformation of DSC pans can have a significant influence when optical measurement techniques are interfaced to the calorimeter. Therefore, it is recommended that as-received aluminium pans be annealed before use with optical hyphenated

Table 1 Deformation of DSC pans as calculated from Fig. 5

TMA trace/sample type	As-received aluminium pan	Annealed at 300 °C	Annealed at 400 °C
Contraction at 100 °C/µm	0.281	0.266	0.148
Contraction at 250 °C/µm	3.642	1.984	1.125
Total deformation/µm	3.361	1.718	0.977

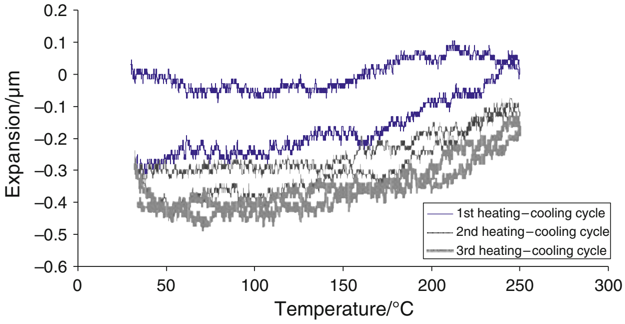

Fig. 6 TMA traces for an aluminium pan that was subjected to three heating and cooling cycles after annealing at 500 °C for 2 h

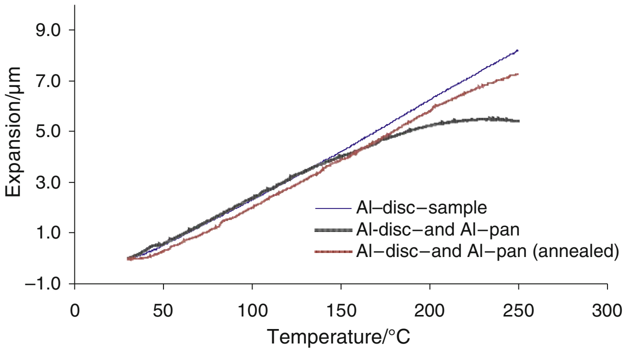

Fig. 7 TMA traces for an aluminium disc (see Fig. 8). The traces when the aluminium disc was located in an annealed and as-received pans are also included

analytical techniques. This brief study has also demonstrated that aluminium pans secured from specified suppliers also have different deformation characteristics over the temperature range 30–250 °C.

The thermal expansion of an aluminium disc was modelled using FEA. The experimental (TMA) and predicted data are presented in Fig. 8 where a good correlation is observed between the two data sets. The data presented in Figs. 7 and 8 give further evidence to indicate that the induced measurement errors associated with the deformation characteristics of aluminium pans can be minimised by annealing at 500 °C for 2 h. The slight deviation after 220 °C between the predicted (FEA) and measured expansion (TMA) may be due to the imperfections in the disc specimen that were not generally considered in the finite element modelling.

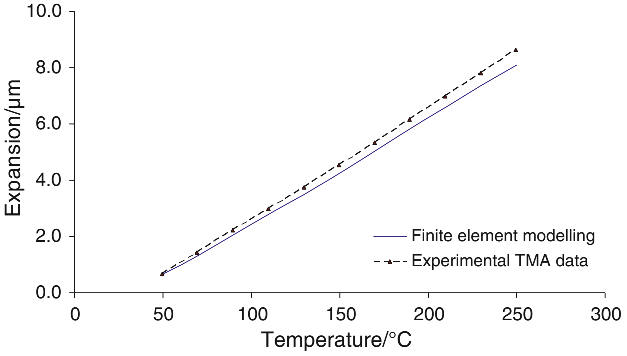

Fig. 8 Comparison of experimental and FEA of the expansion of an aluminium disc (diameter of 1.6 mm and thickness of 1.4 mm) from 50 to 250 °C

Conclusions

The study has shown that the as-received aluminium pans used in DSCs deform when heated to 250 °C; this behaviour is attributed to residual stresses imparted to the aluminium pans during their manufacture via a stamping process. These residual stresses can be relieved by annealing the pans at 500 °C for 2 h. In situations where DSC pans are used to contain samples for optical-based experiments within the DSC chamber, it is recommended that the DSC pans be annealed to relieve the residual fabrication stresses. A good correlation is observed between the experimental results and a FEA of the deformation of an aluminium disc.

Acknowledgements The authors wish to thank the Engineering and Physical Sciences Research Council and the Technology Strategy Boards for financial support for projects TS/G000387/1, AB135A and BD072K. GFF wishes to acknowledge the financial support provided by the Royal Society. The technical assistance given by Professor Brian Ralph is duly acknowledged.

References

1. Dumitresu O, Crosby PA, Fernando GF. Thermal and spectral analysis of an epoxy/amine resin system. Presented at Cea de-a XI-A Conferinta Internationala, de Chimie si Inginerie, Chemica, Romania, 30 Sept–2 Oct. 1999.
2. Dumitrescu OR, Doyle C, and Fernando GF. Extending differential scanning calorimetry to include non-contact vibrational spectroscopy. 30th annual conference, North American thermal analysis society, 23–25 Sept 2002.

3. Degamber B, Winter D, Tetlow J, Teagle M, Fernando GF. Simultaneous DSC/FTIRS/TMA. J Meas Sci Technol. 2004;15(9):L5–10.
4. Degamber B, Fernando GF. Fibre optic dilato-spectroscopic sensor: simultaneous thermal, spectral and physical analyses of materials. J Smart Mater Struct. 2006;15:1054–8.
5. Shackelford JF, Alexander W, editors. CRC materials science and engineering handbook. 3rd ed. New York: CRC Press; 2000.