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Note

LONG-TERM CYCLING OF PHASE CHANGE THERMAL ENERGY STORAGE MATERIAL: A DSC STUDY

P.E. ARNDT, J.G. DUNN and R. WILLIX

School of Applied Chemistry, Western Australian Institute of Technology, Perth, Western Australia 6102 (Australia)

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Phase Change Materials (PCMs) offer a number of advantages over "sensible" systems for the storage of thermal energy from the sun. The thermal energy is stored under essentially isothermal conditions and, if the temperature swing is not too large, they offer considerable savings in terms of energy densities.

In the selection of an appropriate PCM a number of considerations should be made [1]. The material should be cheap, chemically stable, non-corrosive and non-toxic, have a large latent heat for the phase change, and melt and cool congruently within a fairly narrow range at the desired temperature. Additionally, an essential characteristic of the material is that it should maintain its properties after continual heat/cool cycling.

The purpose of this study is to describe the use of a computer interfaced DSC system, utilising automatic data processing, for the determination of long-term thermal cycling effects on PCMs. The particular PCM chosen for the study is naphthalene. While naphthalene possesses a slight toxicity [2], it has been suggested by a number of authors [3] as a candidate PCM. In addition, a number of other materials such as various waxes are currently undergoing long-term cycling tests in our laboratory.

EXPERIMENTAL

Apparatus

A Dupont Thermal Analyser (Model 990), equipped with a standard DSC cell (Model 900600-902) and interfaced to a DEC PDP 11-20 (28 K core) computer by means of a Datel digital voltmeter, a BCD-Binary converter and a DEC DR-11C general input—output device, was used for all measurements. The details of the interfacing are outlined in a previous communication [4]. The output for the computer was displayed on a Model 43 hardcopy teletype. Automatic onset and offset for data collection was achieved using temperature triggers incorporated in the programme. Peak integration was performed using variance from a projected baseline to trigger the onset and a differential between consecutive signals to trigger the offset. Peak integration values were relative to a baseline drawn between the offset and onset temperatures.

Within the temperature range (30—120°C) and the scan rate (10°C min^{-1}) used, controlled cooling based upon natural convection could not be achieved. Initial attempts to alleviate this problem using a coolant gas caused cell vibration resulting in an excessively noisy baseline. Controlled cooling was achieved, however, by the construction of a simple metal cooling jacket as outlined schematically in Fig. 1.

The jacket was engineered by lathing a solid aluminium cylinder of 8 cm diameter to the appropriate shape. Iced water from a cryogenic bath was circulated via a pump to the jacket which fitted over and contacted the walls of the cell. The entire jacket was covered by a PVC sheath to eliminate water condensation problems. This arrangement may also be used for subambient temperature cycling if the iced water is replaced with a dry ice—ethanol mixture.

Procedure

A sample (2.54 mg) of L.R. grade naphthalene was weighed into an aluminium pan using a microbalance. The sample was then sealed using a hermetic press and placed in the DSC cell. The cooling jacket was placed over the cell

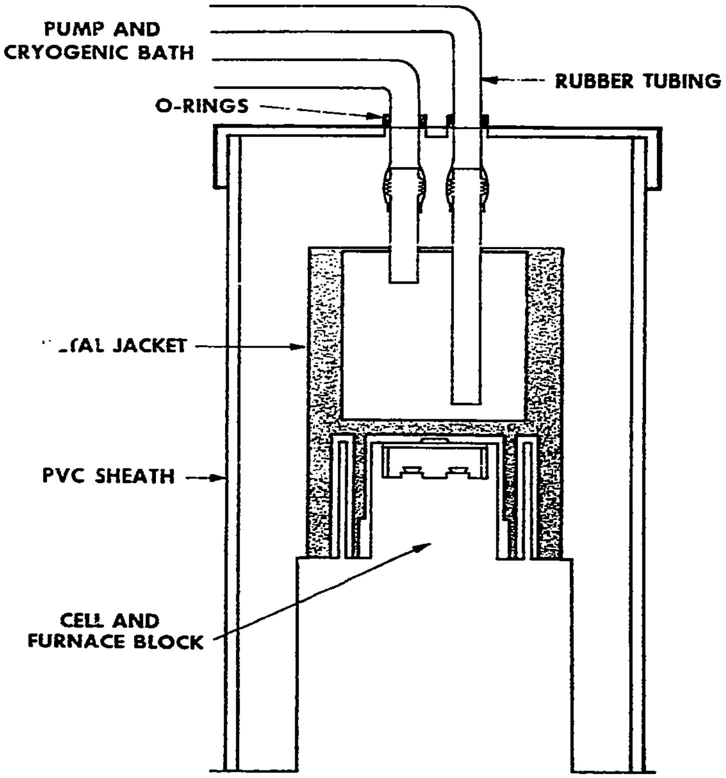

Fig. 1. Controlled cooling apparatus.

and controlled cycling between 30 and 120°C commenced. A heating rate of 10°C min^{-1} was used and the sample was maintained under a flowing nitrogen atmosphere of 100 ml min^{-1}. While there are no restrictions to the extent of cycling, materials were typically subjected to around 200 cycles.

The peak area was calibrated by repeating the above procedure on an indium standard of known calorific value.

RESULTS AND DISCUSSION

The DSC scan obtained for naphthalene is illustrated in Fig. 2. The naphthalene had a melting onset temperature of 81°C and melted within an 11°C range. In the cooling scan there was some supercooling with the onset temperature for the solidification occurring at 67°C. The melting temperature remained constant for the entire 220 cycles.

Figure 3 illustrates the heat of fusion for the various melting cycles that the sample underwent. It is evident that there is no significant decrease in the value of the heat of fusion for naphthalene (148 Joules g^{-1} averaged over the 220 cycles as compared with 147 Joules g^{-1} cited in the literature [5]), with the line of best fit having a slope of —0.011 and a standard deviation of

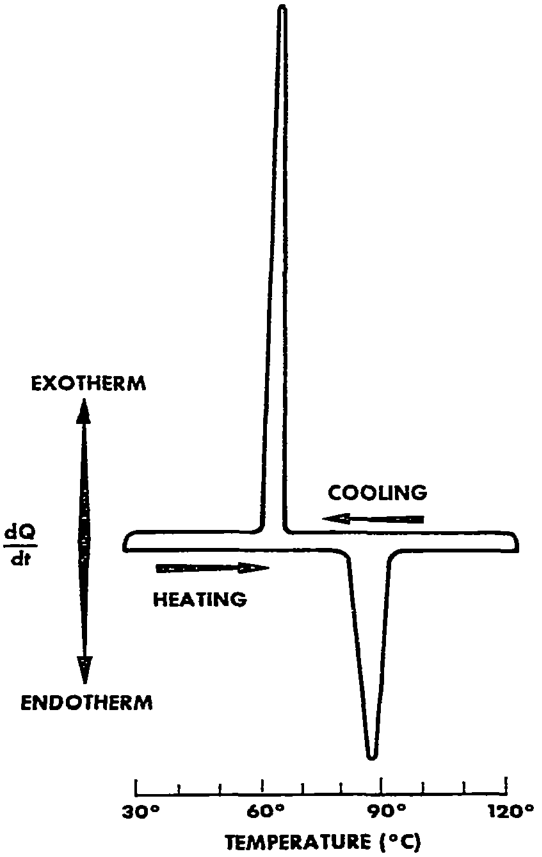

Fig. 2. DSC scan for naphthalene.

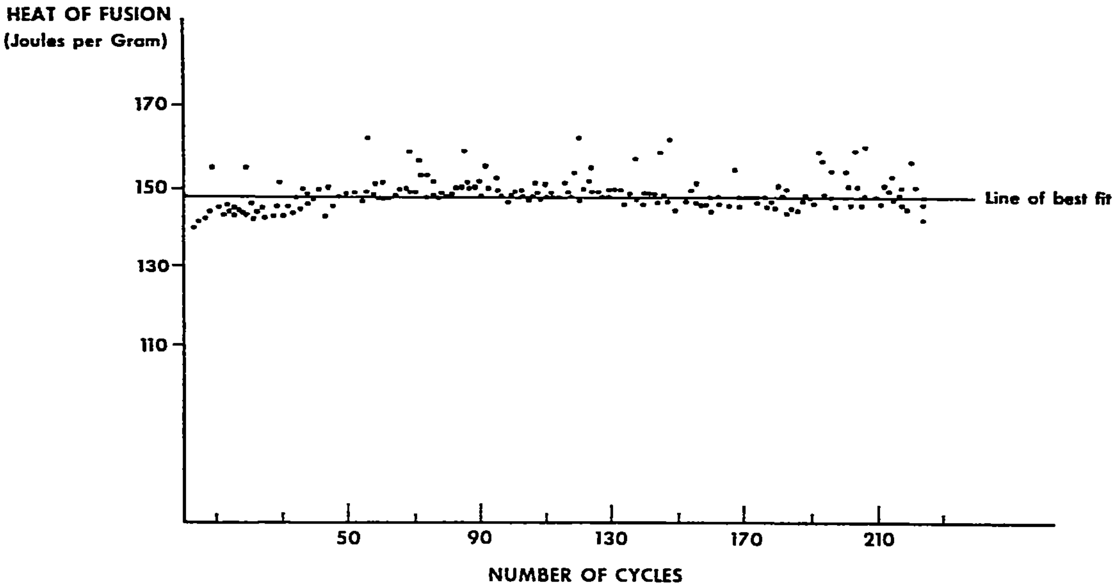

Fig. 3. Effects of thermal cycling on heat of fusion for naphthalene.

—0.016. The scatter of points obtained for the peak area results from small vibrations in the baseline causing fluctuations in the onset and offset integration temperature triggers.

The system described allows the thermal stability of a candidate PCM to be assessed on the equivalent of one years cycling in a solar storage system in one week of testing in the laboratory. The value of this screening procedure is that materials which degrade are unlikely to be suitable for solar storage applications.

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