A NEW METHOD OF DTA: THEORY AND PRACTICE

N. H. SZE and G. T. MEADEN*

Research Centre of National Iron and Steel Mills Ltd.
Republic of Singapore, 22; *Artetech International, Bath, BA2 5DWR, England

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A novel differential thermoanalytical technique is described and discussed with regard to function, operation, performance, theory and application. Information is provided about the nature of the internal processes taking place at the time of absorption or release of energy. Notable features of the technique include high sensitivity and independence of a reference sample.

Over the years, since the pioneering work of Roberts-Austen [1, 2] Le Chatelier [3, 4], and others [5] at the turn of the century, DTA has been put to extensive and varied use in science and industry. From the technical standpoint much attention has been directed at increasing the sensitivity and reproducibility of the method, and this has led to the development of elaborate and sophisticated automatic recording techniques. The fundamental principle of comparison with a reference material has been maintained throughout this period. Nevertheless there are certain difficulties which are unavoidable with this technique. On the one hand there are problems associated with the selection of a suitable reference material and on the other hand with the requirement that both the substance and the reference should be exposed to identical environmental conditions. This requirement necessitates that, ideally, there should be insignificant temperature gradients across the specimens and between them. These basic difficulties are met by the new approach to DTA presented here.

In this method, because the test sample itself is used as its own reference, no separate reference material is necessary. The requirement for eliminating temperature gradients disappears because by contrast with conventional DTA, a deliberately-imposed temperature gradient along the sample is obligatory. Moreover, by means of this technique, a new type of effect taking place at first-order phase transitions is revealed. A distinctive thermoanalytical curve characteristic of the method is produced, and its analysis gives physical information about internal microscopic processes which are new to thermal analysis. The method should be of particular value when used in conjunction with conventional DTA as a means of obtaining more complete differential thermal information about the physical and chemical processes occurring within materials. Brief descriptions of the new
method have been announced in publications elsewhere [6–8]. The present paper provides a more complete mathematical and physical account and includes much additional material (see also reference [9]).

**Technique**

As with conventional DTA, the sample to be investigated is mounted either in a furnace or in a cryostat containing a heater, whose power adjustment allows the sample and its environment to be raised or lowered in temperature at a controlled rate.

![Diagram of heater and thermocouples](image)

**Fig. 1. Disposition of the heater and thermocouples for (a) solid samples (S₁), (b) powdered or liquid samples (S₂). H = heater, C = container of poor thermal conductivity, T = upper thermocouples, ΔT = differential thermocouples.**

Samples of any shape may in principle be studied, but there is a practical convenience in working with cylindrical samples. A typical sample might be a solid rod such as S₁ (in Fig. 1(a)), or a powder or liquid such as S₂ (in Fig. 1(b)) held in a tube C made from a material of poor thermal conductivity, such as pyrophyllite or polyethylene. The sample is mounted vertically with a small wire-wound resistance heater H firmly secured to its upper end. The means of attachment varied according to the sample and the temperature range of investigation, but for the various solid substances that we have studied (metals and nonmetals) spot-welded, soldered, or epoxy-resined joints were satisfactory. For liquid or powder samples the heater support passed through the wall of the container and into the sample itself.