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DTA USING SINGLE PARTICLES

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A DTA sample holder for single particles was constructed using three thermocouples to hold the sample and reference material, respectively. The arrangement can be used to multiparticle samples too by setting a spherical-section sample holder on the three thermocouple junctions.

As part of an investigation of effects of mechanical deformation, differential thermal analysis of single particles weighing a few milligrams was needed because of the obvious irreproducibility of the strained state in a polymeric material [1]. This procedure is quite different from choosing to use very small samples for some apparent or fancied advantage in small samples. In this use of small samples, the information sought is the difference from particle to particle.

Measuring the temperature of a single particle imposes some special problems [2]. The use of a sample pan would isolate the specimen from the thermocouple and introduce an additional heat capacity. Both effects tend to spread out peaks. For the planned purpose, ease of placing the specimen was essential because, in one of the studies planned, some rearrangement could be expected even at ambient temperatures. The time required for mounting the specimen carefully on a single thermocouple was too long. The most effective sample support is a three-point support and, rather than introduce an unnecessary heat leak, each of the three points was a thermocouple bead.

Apparatus

For the major part of the work, because no atmosphere control was needed, the furnace itself was an inverted pot furnace capable of reaching 800° at no less than 10°/min. The sample support can be easily adapted to any furnace configuration. In this use it comprised a thermal insulating support, six two-hole alumina tubes and six Chromel-Alumel thermocouples. (In a later model, two six-hole alumina tubes were used to position the thermocouples. There is little advantage.) The thermocouples for the sample extended about 4 mm above the end of the tube so that they could be bent outward or inward as needed to accommodate larger or smaller particles (Fig. 1). The wires are sufficiently resilient that irregular particles could be held firmly by spring tension. The wires were joined to like wires from the reference thermocouples to form a series circuit (after the method of Lodding and Sturm) [3].

The thermocouple wires were 0.25 mm in diameter and the junctions were small and uniform in shape and mass of bead. Prior to use, they were bent as needed to retain the particle by three-point support, none of the thermocouple wires touching the specimen except through the junction. In practice, the gaps

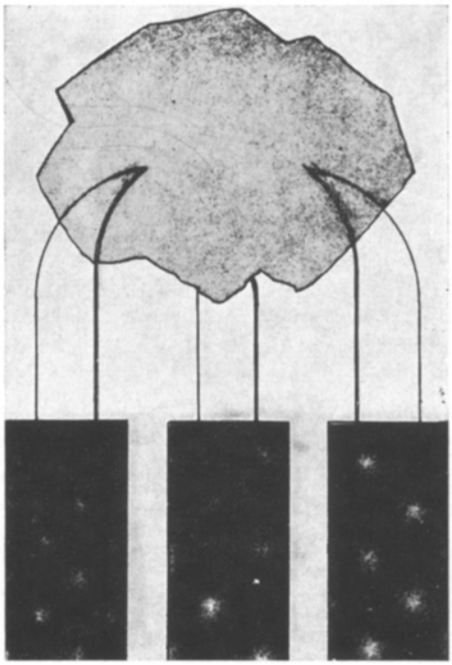

Fig. 1. Three-point sample support for single particles

between the junctions could be reduced to less than 0.1 mm or enlarged to more than 3 mm without undue stress on the wires. Both sample and reference sets were adjusted and a particle of coarse alumina or silicon carbide was set in the reference set. (Fine wire thermocouples not in contact with some other body can show spurious fluctuations of several microvolts because of convection currents.)

Results

To test the sample arrangement with a known material, a single hydrothermally grown crystal of quartz was mechanically crushed. Several particles in the 2 – 8 mg range were tested one by one by heating at 8°/min through the quartz transition (573°), cooling to ca. 520° and again heating through the transition. In each case, irregularities were observable on the first heating from ca. 540° to the transition. Also in each case, these irregularities did not appear on the second heating. Typical first-heating curves are shown in Fig. 2a. In another test, a particle was heated to 700° and dropped into liquid nitrogen. The results of thermal stress are shown in Fig. 2b.

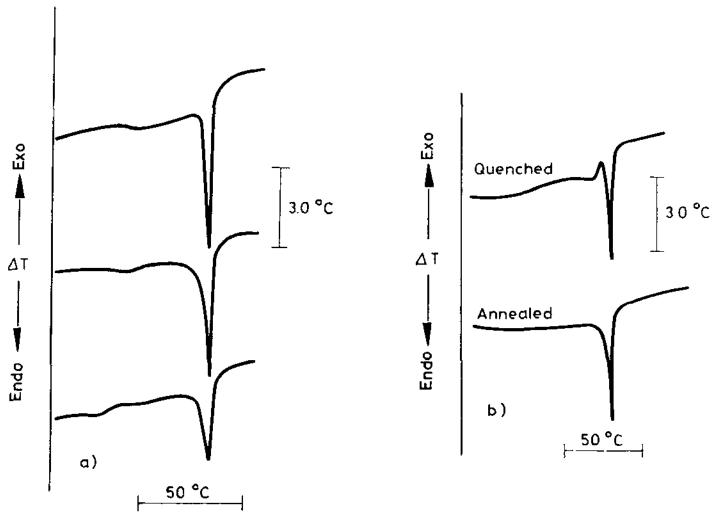

Fig. 2. DTA curves for (a) mechanically and (b) thermally stressed samples

Simple transitions behave as they would in any other sample holder. The peaks are sharp and suggest good homogeneity within particles. This would be anticipated because there is no heat source or sink in contact with the particles. Irregularities in behavior were seen using the potassium nitrate tested in the First International Test Program [4]. An example is shown in another publication [5]. The variation in behavior has been traced to the strain in these polycrystalline particles.

Use for multiparticle samples

In the course of the investigation, the experimental arrangement was tested to ascertain whether or not it could provide better measurement of temperature than the uncertain contact between a sample pan and either a flat support or a ring of thermocouple wire. While no clear superiority has been established, a spherical-section sample holder, set upon the three junctions, has been used successfully. The experimental question mark was the effect of the metal pan on the electrical measurement of T and ΔT. Using platinum cups, no interference was detected. The resistance between the cup and any thermocouple was greater than 1 KΩ

because of the oxide coating on the already used Chromel-Alumel thermocouples. The resistance along the thermocouple wire is only a few ohms, so the shunting through an oxide coating is normally of no consequence. This electrical shunting might be serious with new thermocouples and irreproducibly varying as the junction became oxidized. Nonetheless, when the need arises, the arrangement is useable and useful.

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