Dilatometry

The dilatometric method utilises either transformation strains or thermal strains; the basic data generated are in the form of curves of dimension against time and temperature.

Thermal Expansion

The coefficient of linear expansion, also known as expansivity, is the ratio of the change in length per °C to the length at 0°C. The coefficient of volume expansion for solids is approximately three times the corresponding linear coefficient. The coefficient of volume expansion of a liquid is the ratio of the change in volume per degree, to the volume at 0°C. The value of the coefficient varies with temperature. The coefficient of volume expansion for a gas under constant pressure is nearly the same for all gases and temperatures, and is equal to 0.00367.

If l_0 is the length at 0°C, then the length at a temperature T can be written:

$$l_T = l_0(1 + e_1 T + 2_2 T^2 + \ldots) \tag{1}$$

The expression is usually terminated after the second term; the same form of equation can be used to represent volume expansion.

The thermal expansion is a consequence of the nature of interatomic forces, and solid–state theory predicts a simple relationship between specific heat capacity at constant volume (C_V) and the coefficient of linear expansion. Thus, Gruneisen has demonstrated that e_1 is proportional to C_V, and this relationship can be exploited in dilatometry; Curie transitions in metals are associated with an anomaly in the specific heat capacity, and can therefore be detected by dilatometry through the accompanying change in e_1.

The sample should be free to move, *i.e.* without any mechanical constraints which would limit accuracy. The length changes should not be transmitted through a second material upon whose expansion coefficient depends the evaluation of the test material. These conditions rule out the use of most push–rod type dilatometers. A dilatometer capable of meeting the requirements is described in the Journal of Scientific Instruments, 2, 515 (1969).

Study of Vacancies

Dilatometry, combined with precision X–ray lattice parameter measurements may be used to determine the concentrations of point defects in metals (R. O. Simmons and R. W. Balluffi, Physical Review 117, 1960, 52–61) . They showed that the the ratio of vacancies to lattice sites, c_v, is given by

$$c_v = 3\left(\frac{\Delta l}{l} - \frac{\Delta a}{a}\right) \tag{2}$$

where l is the length and a the lattice parameter of a material with a cubic lattice. The presence of point defects must alter the volume of the sample, but the lattice parameter should not be affected, apart from certain changes due to relaxation, to be discussed later. In comparing lengths at different temperatures, subtracting $\Delta a/a$ removes changes due to thermal expansion, leaving only the effect of point defects.

This subtraction is not necessary in isothermal experiments. The lattice parameter measured is a mean value which includes the effect of local relaxations around a point defect. Subtracting $\Delta a/a$ from the length change therefore also removes the influence of local relaxations, leaving only the contribution to Δl of new lattice sites formed or lost in creating the defects. During isothermal annealing of defects, lattice parameter measurements provide a measure of the lattice relaxation due to the defects and permit the determination of the absolute defect concentration.

Vacancy clusters can lead to a misinterpretation of results. Fortunately, the concentration of such clusters is expected to be relatively small. Note that it is the *excess* concentration of vacancies that is revealed because interstitials can cancel some of the effect of the vacancies.

Push–Rod Dilatometer

The push–rod dilatometer can only be used for studies of length changes in solid materials. The sample rests between the tips of a fixed quartz rod and a similar frictionless sensing rod in the centre of a high–frequency induction furnace. Length changes are transmitted through the frictionless rod to an electronic transducer which in turn drives the recording system. The thermocouple is spot welded to the sample, and referenced at 40°C by means of a constant temperature bath. Quenching gas enters the chamber, passes through the hollow cylindrical sample and escapes through the openings.

It may not be possible in conventional dilatometers to conduct experiments in which the specimens require very fast heating or cooling rates, because of the high thermal inertia of the furnaces involved. In a high–speed dilatometer, the specimen is positioned along the axis of a cylindrical heating coil, which is connected to a radio–frequency power generator. During operation, the magnetic field around the coil induces currents in the specimen, causing it to warm up. The induction coil itself is only mildly heated through resistive effects, but is in any case water cooled, Hence, the response of the system depends on the thermal characteristics of the specimen rather than those of the furnace. Fast quenching rates can therefore be achieved by directing high–pressure jets of gas through the centre of a hollow specimen; quench rates of up to 5000°C/s can be obtained in favourable circumstances.

Helium is used as the quenching gas in high cooling rate experiments because its thermal conductivity is about six times that of nitrogen. Large thermal gradients can develop in the specimen during the quench, which may cause difficulties in the interpretation of the observed changes in specimen dimensions. The system should ideally be arranged to stabilise at the isothermal temperature concerned before the onset of any transformation.

The specimen can be enclosed in a vacuum, but it is more usual to use an inert atmosphere; in the case of steels, an inert atmosphere results in a smaller degree of decarburisation. The specimen chamber should be evacuated before triggering the quench gas; otherwise, the build up of pressure in the chamber retards the quench, and may cause the lid of the dilatometer chamber to be blown off! The pumping system must be isolated before triggering the quench.

Specimen Design

Specimens for use in high–speed dilatometry are usually in the form of hollow rods, with internal and external diameters of 1.5 and 3.0 mm respectively; the length is limited by the extent of the furnace to a maximum of about 3 cm. These dimensions are somewhat arbitrary, but experience suggests that they satisfy the following requirements:

1. The specimen should be sufficiently thick to prevent free surface effects from altering

transformation kinetics. The tests should reflect what happens in equivalent bulk samples. Nickel plating the specimens (to a thickness of about 0.08 mm) helps to reduce surface nucleation. Contrary to popular belief, this is not an effective way of preventing decarburisation in steels. To reduce decarburisation, the specimen should be copper plated; carbon is only sparingly soluble in copper. The plating material should be chosen so as not to interact with the sample, for example by penetration into the grain boundaries of the substrate.

2. The specimen dimensions must be small enough to allow rapid changes in temperature.

The specimen should obviously be representative of bulk material. Its ends should be ground flat and parallel to give a true cylindrical shape. Otherwise, slip at the specimen–quartz interface can lead to erroneous interpretation especially under the influence of the high–pressure quench–gas jets.

It is normal to isolate the specimen from the RF coil with a length of quartz tubing, not only to avoid contaminating the coil, but also to guard against the potentially disastrous consequences of accidental specimen melting.

High–speed dilatometers generally do not have long term electronic or mechanical stability. Equipment like this cannot be used for tests lasting more than a few hours. Prolonged holding at high temperatures can also lead to slag–forming reactions between the specimen and quartz retaining–rods. A certain amount of pressure is always necessary to hold the specimen between the quartz retaining rods and to remove backlash, so care should be taken to ensure that any resulting creep effects are negligible.

Calibration

The temperature calibration is similar to that of differential scanning calorimeter and is not discussed further. However, for the calculation of thermal expansion coefficients, and for the purposes of absolute dilatometry, it may be necessary to calibrate the magnification of the displacement transducer.

There are two ways of doing this:

1. A pure platinum specimen with known expansion characteristics is heated at a sufficiently slow rate over the temperature range of interest. The magnification M is then given by
$$M = \frac{\Delta l}{\Delta T l_{Pt} e_{Pt}} \tag{3}$$
where Δl is the deflection of the length recording pen, ΔT is the difference between the initial and final temperatures T_1 and T_2 respectively of the test, l_{Pt} is the length of the Pt specimen at T_1, e_{Pt} the linear expansively of Pt (obtainable from standard handbooks). This method can be accurate, but does not take account of the expansion of the part of the quartz rods within the furnace assembly.

2. A micrometer attachment on the dilatometer allows the transducer to be stimulated independently of specimen movement. The magnification is then simply Δl/micrometer movement. Having calculated the magnification the additional expansion to be expected from the quartz rods, $l_Q e_Q$ can be obtained from :
$$\Delta l = M(l_{Pt} e_{Pt} + l_Q e_Q) \tag{4}$$

Interpretation of Transformation Curves

Dilatometric data are plotted as graphs of relative length change versus time. These plots are usually sigmoidal in shape, with the length change being dependent on the extent of transformation. If the length of the specimen before the beginning of transformation is l_1, and that at the termination of transformation at a time $t = t_2$ is l_2, then at time t,

$$\frac{V_t}{V_2} = f\left\{\frac{l_t - l_1}{l_2 - l_1}\right\} \tag{5}$$

where $t = 0$ at the beginning of transformation and l_t is the specimen at any time t. V_t is the volume fraction of transformation corresponding to t, and V_2 is that when reaction has stopped. The latter quantity may either be deduced by using an independent technique, or, if sufficient data are available, it can be calculated from the magnitude of Δl_2, where

$$\Delta l_2 = l_2 - l_1$$

For an austenite (γ) to ferrite (α) transformation in a plain carbon steel, in which the formation of ferrite enriches the residual austenite with carbon,

$$\frac{\Delta l}{l} = \frac{2Va_\alpha^3 + (1-V)a_{\gamma 0}^3 - a_\gamma^3}{3a_\gamma^3} \tag{6}$$

where $\Delta l/l$ is the length change per unit length; V is the volume fraction of ferrite; a_α is the lattice parameter of ferrite at the transformation temperature; $a_{\gamma 0}$ is the lattice parameter of austenite at the transformation temperature when the austenite has the mean composition of the steel ($\overline{x}$); a_γ is the corresponding lattice parameter of carbon–enriched austenite. The extent of enrichment can be estimated from mass balance:

$$x_\gamma = \overline{x} + V(\overline{x} - x_\alpha)/(1-V)$$

where x_α is the carbon concentration in the ferrite.

Texture and Anisotropy of Thermal Expansion

Most polycrystalline materials are crystallographically textured. This becomes important when testing materials with low crystalline–symmetry and anisotropic thermal expansion characteristics. The assumption that the measured length change corresponds is about a third of the volume change is no longer valid and it becomes necessary to specify the crystallographic directions along which measurements are made.

It turns out that such effects may be advantageously exploited. Under the influence of neutron irradiation Uranium has a pronounced tendency to swell in the $< 0\ 1\ 0 >$ direction and contact in the $< 1\ 0\ 0 >$ direction. In polycrystalline specimens, the swelling tendency must depend on the texture, which can be determined using tedious X–ray techniques. Alternatively, an indirect measure of preferred orientation can be obtained by measuring thermal expansion and electrical resistivity along a variety of directions of the specimen shape. The expansion coefficient and thermal resistivity characteristics of uranium are both anisotropic. High resistivity in a particular direction indicates an excess of $< 1\ 0\ 0 >$ directions over random, while a low expansion coefficient indicates an excess of $< 0\ 1\ 0 >$ directions. Hence these two measurements made in the same direction on the specimen give an estimate of the tendency to irradiation growth. (Journal of Nuclear Materials, 4, 109, 1969).

Miscellaneous

It is known that cycling a specimen through a phase transformation can lead to permanent length change, so that the apparent length change observed may alter with the number of cycles, even though there may be no real changes in transformation behaviour.

When dealing with specimens of low thermal conductivity, care should be taken to ensure that the imposed heat–treatments allow the specimen to attain thermal equilibrium within the time period of the test.