CALCULATION OF ACTIVATION ENERGIES FROM CALORIMETRIC WORK CARRIED OUT AT A CONSTANT RATE OF HEATING

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Summary

Some recovery processes in metals occur at temperatures too high to be readily accessible to isothermal calorimetric studies and such phenomena are more conveniently investigated using a constant rate of heating. It is shown that the activation energies of these processes can be determined from calorimetric work carried out at a constant rate of heating.

I. Introduction

In making calorimetric studies of the annealing of deformed metals, two principal methods have been adopted. The release of energy has been measured either at constant temperature or as the temperature is increased continuously. Both methods have inherent advantages. One feature of the isothermal technique is that the activation energies of the recovery processes can be readily determined (Gordon 1955). It is the purpose of this note to point out that activation energies can also be determined from calorimetric measurements of the type made by Clarebrough *et al.* (1952) and by Clarebrough, Hargreaves, and West (1955) where the rate of heating, i.e. the rate of increase of temperature, is constant. These experimental results comprise a series of curves, each of which shows the rate of release of energy from a deformed specimen as a function of temperature for a particular rate of heating. From the differences between the curves corresponding to different rates of heating, it is possible to deduce activation energies.

II. Method of Calculation

We assume that the state of the deformed metal can be described by one or more of a set of quantities such as the number of vacancies, the density of dislocations, the amount of metal recrystallized, etc. Then, over a limited range of temperature, we assume that the change in state can be ascribed effectively to a change in only one of these, denoted by x, and that the energy is released in proportion to the change in x. This implies that the total energy E which has been released at a given temperature T is a linear function of x.

We now make the usual assumption that the recovery process follows an equation of the form

$$\frac{dx}{dt} = f(x)e^{-Q/RT}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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where $f(x)$ is some function, independent of time and temperature, t is the time, Q is the activation energy of the process, and R is the gas constant. Then, since E is a linear function of x, this can be rewritten to give the rate of release of energy ΔP as

$$\Delta P = \frac{dE}{dt} = g(E)e^{-Q/RT}, \quad \dots\dots\dots\dots (2)$$

where $g(E)$ is independent of time and temperature.

If the rate of heating is α, we can write

$$T = T_0 + \alpha t, \quad \dots\dots\dots\dots\dots (3)$$

where T_0 is some initial temperature, and equation (2) can then be integrated formally to give

$$\int_0^E \frac{d\xi}{g(\xi)} = h(E), \text{ say,}$$

$$= \frac{1}{\alpha}\int_{T_0}^T e^{-Q/R\tau}d\tau$$

$$\sim \frac{1}{\alpha}\left[\frac{R\tau^2}{Q}e^{-Q/R\tau}\left(1 - 2!\frac{R\tau}{Q} + 3!\frac{R^2\tau^2}{Q^2} - \dots\right)\right]_{T_0}^T, \quad \dots (4)$$

the asymptotic expansion being derived by repeated integration by parts. Provided that T is sufficiently greater than T_0 and $RT \ll Q$, equation (4) can be written as

$$h(E) \simeq \frac{RT^2}{\alpha Q}e^{-Q/RT}, \quad \dots\dots\dots\dots (5)$$

that is,

$$\ln(T^2/\alpha) \simeq Q/RT + \ln\{Qh(E)/R\}. \quad \dots\dots\dots (6)$$

If we now choose a particular value of E, say E_1, the last term of equation (6) is fixed and, for each heating rate, the value of T for this E_1 can be determined from the experimental results. Thus, if several heating rates have been used, Q may be estimated by plotting $\ln(T^2/\alpha)$ against $1/T$ and determining the slope of the resulting line. If only two heating rates have been used, Q is given by

$$Q = \frac{RT_1T_2}{T_1 - T_2}\ln\frac{\alpha_1 T_2^2}{\alpha_2 T_1^2}. \quad \dots\dots\dots\dots (7)$$

The error made in neglecting all but the first term of the asymptotic expansion (4) can be corrected by a process of successive approximations.

This procedure is, in principle, capable of high accuracy since the mathematics can be made as accurate as is desired and several estimates for Q may be obtained by measuring values of T for several different values of E_1. However, in practice, a set of temperatures corresponding to a given E_1 is difficult to determine accurately because of uncertainties in the amount of energy released at low temperatures and in the exact position of the base level above which ΔP is measured. Such uncertainties, though small enough to be unimportant in the measurement of total energy evolved, may cause large errors in the estimation

of Q since this depends essentially on the fairly small differences between the temperatures corresponding to a given E_1 for different rates of heating.

However, one set of temperatures which can be determined readily and accurately is the set of temperatures T^* at which the maxima in the curves of ΔP against T occur. Furthermore, it can be shown that these temperatures correspond to the release of approximately equal amounts of energy. For, since a maximum requires that $d(\Delta P)/dT = 0$, we have, by equation (2),

$$\left\{ g'(E)\frac{dE}{dT} + g(E)\frac{Q}{RT^2} \right\} e^{-Q/RT} = 0.$$

By using equations (2) and (3) to substitute for dE/dT we get

$$g'(E) + (\alpha Q/RT^2)e^{Q/RT} = 0,$$

and hence, by use of equation (5),

$$g'(E) + 1/h(E) \simeq 0. \quad \dots\dots\dots\dots\dots (8)$$

Since equation (8) is an equation in E only, its solution, which gives the value of energy for which ΔP is a maximum, is independent of the rate of heating. Thus, to the approximation implicit in equation (5), the temperatures T^* at which the maxima occur correspond to equal values of energy and these temperatures may be substituted into equations (6) or (7) to determine Q.

If the values of T^* are used to determine Q, the result cannot be corrected for the effect of cutting off the asymptotic expansion unless the form of $f(x)$ (and thus of $g(E)$ and $h(E)$) is known, either implicitly or explicitly. However, the effect of such corrections is not likely to be large and, in fact, in one case where equation (6) was used and $f(x)$ was known implicitly (Nicholas 1955), the correction to Q was less than 1 per cent., i.e. insignificant.

The advantages of using the values of T^* are that the temperatures can be taken directly from the experimental curves and will be insensitive to small errors in the position of the base line and to the amount of energy that is released at low temperatures. Furthermore, detailed consideration shows that the procedure will discriminate between two concurrently acting processes which have sufficiently different values of T^*. However, if one particular peak represents a two-stage process or a set of similar processes having almost identical activation energies, then equation (6) will only give some mean value of the energies involved and care must be taken in interpreting the result.

III. APPLICATIONS

Equation (6) can be used to determine activation energies for recrystallization from data given in Clarebrough, Hargreaves, and West (1955). Thus, for electrolytic copper (99·98 per cent. Cu) the activation energy for recrystallization after 45 per cent. elongation in tension is 33 kcal/mole, while for nickel (99·6 per cent. Ni) after heavy deformation in torsion, the corresponding value is 85 kcal/mole.

It is clear that the use of equation (6) need not be restricted to calorimetric studies even though these have the advantages that a quantity proportional

to dx/dt is measured directly and that the amount of energy released by an imperfection is almost independent of the temperature of measurement. In fact, Parkins, Dienes, and Brown (1951) have already derived the equivalent of equation (6) and used it in resistivity studies during the " pulse-annealing " of AuCu. However, their derivation assumes that $f(x)$ is of the form x^{γ} and their integration of $1/f(x)$ is invalid for $\gamma=1$. Furthermore, they do not investigate the integral of $\exp(-Q/RT)$ and assume that the variation, with temperature, of this integral is negligible compared to the variation of the integrand. Actually, their result is valid only because both the integral and the integrand vary with temperature in the same way.

IV. Acknowledgments

V. References

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