Letter

Note on the isothermal decay method for determining trap depth from glow curves

We read with interest "A review of the recent methods for determining trap depth from glow curves" by Shalgaonkar and Narlikar [1] and the subsequent letter "On the methods for determining trap depth from glow curves" by Chen [2]. It is considered that the analysis based on the shape of a glow curve over a range of temperature may be perturbed by interfering effects, such as changes in quantum efficiency, frequency factor, or emission spectra of the luminescence, and that the isothermal decay analysis is the only method unaffected with temperature. According to the former authors [1], the isothermal decay method is limited to the monomolecular kinetics and should not be used unless one is sure its application is justified. However, in our opinion, this is not limited to the first order kinetics. In the following we show that the isothermal decay analysis is also applicable to general order kinetics.

In many cases the kinetics of the luminescence should be expressible as follows,

$$I = -\alpha \frac{\mathrm{d}n}{\mathrm{d}t} = \alpha \beta n^m \tag{1}$$

where $\beta = \gamma \exp(-E/kT)$, *m* is a suitable numerical parameter representing kinetics order and α and γ are constants. The solution of Equation 1 (for $m \neq 1$) is given by,

$(I_0/I)^{1-1/m} = 1$ $+ (m-1)n_0^{m-1}\gamma t \exp(-E/kT)$ (2)

where I_0 is the initial intensity and n_0 is the initial concentration of the reaction centre. For any order other than the first, the plot $(I_0/I)^{1-1/m}$ versus time should then be a straight line as reported by May and Partridge [3], and the activation energy, E, will be directly determined from Boltzmann plots of the slope. For a first order isothermal reaction, the log I plotted against time should, of course, be a straight line and the activation energy may also be determined by Boltzmann plots as shown in [1]. The isothermal decay technique, can, therefore, be recommended as a general technique to determine the trap depth.

References

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- 2. R. CHEN, ibid 9 (1974) 345.
- 3. C. E. MAY and J. A. PARTRIDGE, J. Chem. Phys. 40 (1964) 1401.

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> NOZOMU TAKEUCHI KATSUYUKI INABE HIDEHITO NANTO Faculty of Technology, Kanazawa University, Kodatsuno, Kanazawa, Japan

Striations on the fracture surfaces of glassy polymers

A characteristic feature of the surfaces of fracture of glassy polymers is a pattern of alternating rough and smooth bands which lie in a direction approximately perpendicular to that of the crack propation; they arise during rapid, unstable fracture whether in cleavage, tension or bending tests and especially if the specimens are notched. Preceding the fracture instability the surfaces of fracture are smooth and the transition between this area and the rougher banded area is marked by a conspicuously sharp boundary line. This general pattern of fracture, shown in Figs. 1 and 2, was first noticed by © 1975 Chapman and Hall Ltd.

Rexer [1] and later by others [2-14]; mechanisms for the formation of the bands have also been proposed [15, 16]. In a recent paper, Moskowitz and Turner [17] give an explanation of the banding based on a new phenomenon in which a crack propagating in a craze is diverted towards and then intersects with a microcrack (or advance fracture) formed close-by in another craze propagating roughly parallel with the first. As the direction of the crack propagation changes it leaves a "step" on the surface of fracture, which in their explanation would mark the beginning of the rough band, and it slows down as would be consistent with Hull's explanation of the banding [15]. The mechanism of Moskowitz and Turner, however, occurs entirely