

Velocity and structure of the breakup of a crystal during thermal decomposition

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The problem of the breakup front during thermal decomposition of a solid is solved. The velocity of this front and the size of the resulting particles are calculated. Two regimes are predicted for the process, at different temperatures.

A breakup caused by significant stresses due to a change in specific volume frequently complicates descriptions of structural or chemical conversions of crystals. In many cases of the thermolysis $(AC)_{\text{solid}} \rightarrow C_{\text{gas}} + A_{\text{solid}}$, for example, one observes a clearly defined boundary between the initial solid crystal and the finely divided product.¹ Cracks which arise because of shrinkage promote a rapid escape of a gaseous component, so the limiting parameters should be the diffusion coefficient D of the atoms of species C in the crystal and the rate at which they are desorbed from the surface, ω . We also introduce the young's modulus of the substance, γ , and the critical value of the intensity coefficient, M (Ref. 2), which characterizes the strength of a real crystal with cracks (in the simple case of a purely brittle fracture we would have $M = \sqrt{\pi\alpha Y}$, where α is the surface tension). If the process proceeds in a steady-state fashion, the network of cracks undergoes a translational motion at a velocity v which remains constant, on the average. A very simple characteristic of this network is the typical block size l (the length of a crack). Because of diffusion, the average concentration at the topological edge of the crystal, c_e , is lower than the value (which we adopt as a unit) in the interior of the sample (Fig. 1). In the discussion below we show how to calculate c_e , l , and v if we know elementary kinetic and mechanical properties of the substance mentioned above.

We focus on one of the cracks, ignoring the mutual effects of the cracks. We write the equilibrium condition for this crack in the concentration-stress field $\sigma(x)$, following Barenblatt²:

$$M = \int_0^l \frac{\sigma(x) dx}{\sqrt{l-x}}. \quad (1)$$

Ignoring the variations in the concentration in the plane of the edge, we can write the following local relation for a plane-stress state of this sort³:

$$\sigma(x) = Y\beta[1 - c(x)], \quad \beta \equiv \frac{\beta'}{3(1-\nu)}, \quad (2)$$

where ν is the Poisson ratio, and β' is the volume shrinkage coefficient. A limit is

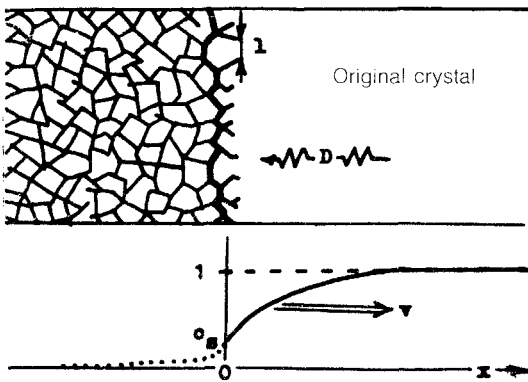


FIG. 1. Structure of the decomposition front and profile of the average concentration along the coordinate, $c(x)$.

imposed on the length of a crack by the decrease in the stress in the direction into the crystal, where we have $c = 1$. We find a corresponding estimate by solving the boundary-value problem of diffusion toward a plane which is moving at a velocity v , at which the value $c = c_s$ is given, and at which a condition of the third kind (desorption) is imposed. The concentration profile ahead of the plane is

$$c(x) = 1 - (1 - c_s) \exp(-xv/D), \quad (3)$$

and the velocity itself is related to the boundary value c_s (Ref. 4):

$$v = w \frac{c_s}{1 - c_s}. \quad (4)$$

Substituting (3) into (2) and (1), we easily find

$$\frac{M}{Y\beta(1 - c_s)} \sqrt{v/D} = \sqrt{\pi} e^{-\lambda} \operatorname{erf}(i\sqrt{\lambda}), \quad \lambda \equiv l \frac{v}{D}. \quad (5)$$

The function on the right side is bounded, so there will not always be solutions. The meaning of relation (5) is that if the right side is higher, cracks will grow (from point A to point B in Fig. 2, as shown by the arrows), while if the left side is higher, they will contract. We thus see the mechanism for the size selection.

A significant growth of cracks leads, by virtue of their intersections, to the separation of several fragments and, ultimately, to a shift of the edge of the solid part into a higher concentration region. The corresponding large value of c_s leads to high values of the left side of (5); i.e., the horizontal line in Fig. 2 rises. If it is too high, however, the cracks will not advance, and diffusion will reduce the value of c_s and also the left side of (5). Consequently, the only situation which is stable is that of tangency at point C . The corresponding maximum of the Dawson integral in (5) is $\xi \equiv 1.082$; it is reached at $\lambda_0 = \xi^2 \equiv 0.854$ (Ref. 5). Accordingly, in place of (5), we find

$$\frac{M^2}{Y^2 \beta^2 (1 - c_s)^2} \frac{v}{D} = \xi^2. \quad (6)$$

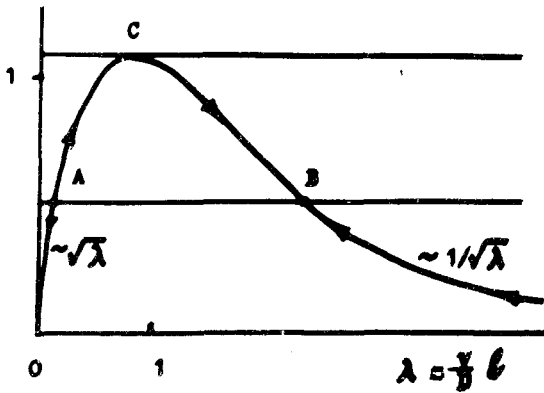


FIG. 2. Plot of the balance of forces corresponding to equality (5). Curve—Tensile stress versus the dimensionless crack length λ ; horizontal straight line—binding forces; arrows—direction of evolution of the crack.

Now substituting (4) into (6), we find an equation for c_s :

$$(1 - c_s)^3 - W c_s = 0, \quad W = \frac{1}{\xi^2} \frac{M^2}{Y^2 \beta^2} \frac{w}{D}. \quad (7)$$

Relations (7) and (4) exhaust the solution of the problem if we supplement them with a direct consequence of the equality $\lambda_0 = \xi l$:

$$l = \xi' D / v. \quad (8)$$

It can be seen from (7) that only the single parameter W plays a governing role here. It contains all of the constants of the process which are assumed to be known. Accordingly, omitting the lengthy solution of the cubic equation, we write the results in two limiting cases.

For $W \ll 1$, the estimate $1 - c_s \approx W^{1/3}$ follows from (7). Substituting it into (4) and (8), we find

$$v = \xi^{2/3} w^{2/3} D^{1/3} (Y\beta/M)^{2/3}, \quad l = \xi' \left(\frac{D}{\xi w} \frac{M}{Y\beta} \right)^{2/3}. \quad (9)$$

In the case $W \gg 1$, the solution of (7) yields $c_s \approx W^{-1}$, so we find the following results for the front velocity and the size of a block of the decomposition product:

$$v = \xi^2 D \left(\frac{Y\beta}{M} \right)^2, \quad l = \xi' \left(\frac{M}{\xi Y\beta} \right)^2. \quad (10)$$

Let us assume that the kinetic constants w and D depend on the temperature in accordance with an Arrhenius law, and for definiteness let us assume that the activation energies are unequal: $E_w > E_D$. As the temperature is raised, we should thus see a transition from mixed regime (9) to diffusion regime (10), when the size of the small product particles reaches a limit, and the decomposition velocity v does not depend on w .

A similar approach could be taken to study the breakup of transparent media

caused by laser light⁶ and to study "low-temperature explosions"⁷ [according to relations like (9) and (10), the latter processes may occur because of a sharp decrease in plasticity with a corresponding decrease in the value of M and an increase in velocity during cooling].

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