Enhanced Reactivity at Dislocations: the Activation Energy for the Thermal Decomposition of Calcite

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In the general study of the role of crystalline imperfections in the chemical reactivity of solids, the particular question of whether the self-energy of a dislocation contributes to the activation energy of a reaction is of importance. Such theoretical assessments as have been made[1] suggest that the free energy of formation of a nucleus at a dislocation ought to be lower than that which characterizes reaction at ideal lattice sites. But it is not certain, on theoretical grounds, whether this lowering arises principally from the core energy or from the elastic strain energy of the dislocation. Relevant experimental data are scarce or completely absent.

Preliminary kinetic measurements[2] between 700—780° on high-purity single crystals of calcite of various dislocation contents tentatively suggest that the activation energy for the initial stages of the thermal decomposition is lower than that which characterizes the reaction in the intermediate stages, 50 ± 4 cal. mole^{-1}. We now report the results of a study, at lower temperatures (520 to 550°) and over a range of α, the fraction decomposed, close to the origin $(0{\cdot}002 < \alpha < 0{\cdot}01)$, the conditions expected[3] to be conducive for the detection of the kinetic influence, if any, of dislocations.

Ideally, the progress of the decomposition should be followed directly by electron microscopy, but for various reasons this is impracticable. However, as dislocations play a vital part in the initial stages of decomposition,[2,4] and since reaction is almost exclusively centred[2] at the sites of emergent dislocations (principally those that glide on $\{100\}$, $\{11\bar{1}\}$, $\{2\bar{1}\bar{1}\}$, and $\{110\}$ planes), sensitive weight-loss measurements, with a vacuum microbalance, serve as a means of determining the time-dependence of α at various temperatures. The Kholmogorow–Avrami–Erofeev equation (see ref. 5 for conditions of applicability):

$$\alpha = 1 - \exp[-(kt)^n]$$

was used to interpret the α–t curves in the range of interest. The value of n was essentially independent of temperature and close to 2·0, and the activation energy based on k, the rate constant for the initial growth of a fixed number of nuclei, centred at dislocations, was 50·7 ± 3·0 kcal. mole^{-1}, indistinguishable from the value for the intermediate range of α, where $d\alpha/dt$ is a constant, and corresponds[6] to the rate of recession of the interface between reactant and product. It, therefore, appears that essentially the same chemical processes are involved in the growth of nuclei at dislocations as in the recession of the $CaCO_3$–CaO interface (compare the related conclusions of Yankwich[7] and Dunning[8]) and, in particular, there is no evidence that, in the decomposition of calcite, a significant contribution to the activation energy is being made by the self-energy of the dislocation.

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