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ABSTRACT

Crystalline aggregates at constant temperature and pressure are unstable toward shape changes for which $\delta G = [\Sigma(\sigma_i A_i + \gamma_i h_i)] < 0$ where δG is a differential change in the Gibbs free energy, $\sigma_i A_i$ is the free energy of surface or interface i, and $\gamma_i h_i$ is the free energy of edge, ledge, or dislocation defect i. The expression reduces to the familiar expression for the driving force for early stage sintering. Line defects play central roles in driving the sintering of crystalline solids.

Sintering theory has been developed to a high degree of sophistication.[1-3] But the theory as usually applied depends upon a fundamental assumption that is known to be invalid for many crystalline solids,[4] the assumption that the driving force for sintering is a function only of different curvatures in surfaces of the same specific surface free energies.

It was evident that at constant temperature and pressure the driving force for sintering of particles with anisotropic surface free energies must be a favorable gradient in Gibbs free energy, but a quantitative expression for the gradient could only be a matter of speculation until the quantitative relationship between the thermodynamics and kinetics of equilibrium among subparts of isolated crystals was known.

When edge effects and defects can be neglected, a particle is stable or metastable relatively to shape changes if for any change

$$\delta w = \delta \Sigma_i \sigma_i A_i > 0 \qquad (1)$$

where δw is a differential change in work of surface formation, σ_i is the work of formation of a unit area of surface i, and A_i is the area of that surface.[5] Herring showed that the relationship also applies when a crystal can be bounded by a combination of planar and rounded surfaces.[6]

Gibbs himself pointed out that, because molecules at crystal edges would be less strongly bonded than molecules near the center of a face, rounding of an equilibrium particle could be expected that is not predicted by eq. 1. Thus, for isolated particles there were two related questions. What is the condition for equilibrium when edge effects are included? How can the net molecular exchange be zero between two parts of a crystal when molecules are more strongly bonded in one part than in the other?

These questions have been answered by explicitly evaluating the roles of vacancies in reducing particle free energies and in equalizing the molecular fluxes between sites of different characteristic bonding environment.[7,8] The condition for equilibrium in a crystal at constant temperature and pressure is

$$\delta G = \delta[\Sigma(\mu_i N_i + \mu_{vi} N_{vi})] > 0 \qquad (2)$$

for every possible differential change in G, the Gibbs free energy, where μ_i is the molecular chemical potential of N_i molecules on i-sites, and μ_{vi} is the molecular chemical potential of each vacancy on N_{vi} vacant i-sites. Particles or aggregates of particles are unstable to any shape changes for which δG as defined by equation (3) is negative:

$$\delta G = \delta[\Sigma(N_i \mu_i + N_{vi} \mu_{vi})] < 0 \qquad (3)$$

For aggregates of particles the summations are over all molecules of the aggregate. The influences of grain boundaries and of line defects such as dislocations, edges, and ledges on surfaces or grain boundaries can be incorporated into equation (3) by introducing additional terms in the summation.

Experimental values of chemical potentials and concentrations of vacancies in or near surfaces and edges are not known. Fortunately, although vacancies play a central role in the kinetics of sintering of crystalline solids, their contribution to the driving force for sintering is probably usually negligible. If, as usually assumed, the vacancy concentration on each kind of site remains near its local equilibrium value during sintering,[4] equation (3) becomes

$$\delta G = \delta[\Sigma(N_i \mu_i + k_i N_i \mu_i)] < 0 \qquad (4)$$

The various terms in μ_i and μ_{vi} are of the same order of magnitude, and $k_i = N_{vi}/N_i$ is expected to be $\ll 1$. Consequently

$$\delta G \simeq \delta \Sigma N_i \mu_i \tag{5}$$

Equation 4 can now be expressed in terms of macroscopic variables:

$$\delta G \simeq \delta[\Sigma(\sigma_i A_i + \gamma_i h_i)] < 0 \tag{6}$$

where σ_i is the unit free energy of the interface or surface of area A_i, γ_i is the unit free energy of the i'th line defect, i.e. an edge, a ledge, or a dislocation, and h_i is the length of that defect. Unlike vacancies, line defects are thermodynamically important; free energies per molecule can be expected to vary in the order edge > ledge > surface > interface > dislocation.

Implications of equation 6 to sintering kinetics will be the subject of another paper. Here several deductions that depend mainly on the thermodynamics of sintering will be presented.

When the special assumptions of early stage sintering theory are adopted the driving force assumed in that theory is recovered. The terms in $\gamma_i h_i$ and interfacial free energies are neglected and surfaces are assumed to be rounded and of equal specific surface energies. The differential free energy for transfer of molecules from a surface of principal radii of curvature r_{1a} and r_{1b} to a neck of radii of curvature r_{2a} and r_{2b} with T and P held constant is

$$dG = \frac{\partial G}{\partial N_1} \, dN_1 + \frac{\partial G}{\partial N_2} \, dN_2 \tag{7}$$

But $(\partial G/\partial N_1)$, for example, is $\mu^\circ + (\sigma v/r_{1a} + \sigma v/r_{1b})$ where μ° is the potential of the particle when surface effects are negligible, and v is the molar volume. But $dN_2 = dN_1$. Therefore

$$\frac{dG}{dN_1} = \sigma v \left(\frac{1}{r_{1a}} + \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}}\right) \tag{8}$$

Equation 8 is a form of the familiar expression.[1]

Equation (6) provides a quantitative basis for the assertion[9] that particles or cavities with anisotropic surface energies will often persist in metastable shapes. To illustrate the point, suppose the most stable shape of a particular solid is a cube. Suppose a particle of that solid is formed as a rectangular box with exactly the number of sites required to accommodate the molecules and their equilibrium concentration of vacancies without surface ledges. Transformation to a shape with more nearly equal edge lengths would require, assuming no screw dislocation are present, passage through intermediate shapes in which a ledge is present both on the surface from which molecules are removed and on the surface to which molecules are transferred. The energy of formation of such a ledge is positive, so that the intermediate shapes have positive free energies of formation. These shapes can form by statistical fluctuation, but the length of ledges increases directly with particle or cavity cross section. Consequently, the probability of transformation through the unfavorable intermediate shapes decreases with increasing particle or cavity size. Small particles or cavities can be expected to have on the average more nearly ideal shapes than do larger particles or cavities subjected to the same isothermal annealing treatment, unless, as discussed below, screw dislocations interupt the surfaces. Observed shapes of cavities in annealed LiF appear qualitatively consistent with this prediction.[10]

A major driving force for filling pores and for sintering is the free energy of reduction of crystal edge lengths. Figure 1 illustrates the reason with a two dimensional analogue in which the incomplete rows A and B on an outer crystal surface and pore surface respectively play the roles of incomplete sheets on outer surfaces and pore surfaces of a three dimensional crystal. In the nearest neighbor bonding approximation, one or two molecules of the two dimensional crystal can be transferred from B to A with no net change in free energy. One molecule can also be transferred from A to B with no net change in free energy, but transfer of two molecules completes the row and produces a net free energy decrease because a net increase of one nearest neighbor bond has been produced. In a dislocation-free three dimensional crystal, much larger statistical fluctuations produce negligible free energy changes. But when fluctuations produce shapes of increased total number of bonds, return to the initial shape becomes improbable.

In the early stages of sintering any lines of particle-particle contact provide sites like those of the pore of Fig. 1 to which additional rows of molecules can be transferred from particle surfaces with eventual decreases in free energy. But the transfer will be similarly impeded if ledges must be periodically nucleated.

When screw dislocations intercept a crystal surface, growth or dimunition in the direction normal to the surface can occur without periodic nucleation of new ledges. Consequently, no matter what is the path by which molecules move from one surface to another, screw dislocations are probably as important in sintering as they are in crystal growth or evaporation.[11-13]

ACKNOWLEDGMENTS

FIGURE

Fig. 1. Two dimensional analogue of a particle with ledges on outer and inner surfaces.

Layer A

Layer B

Pore
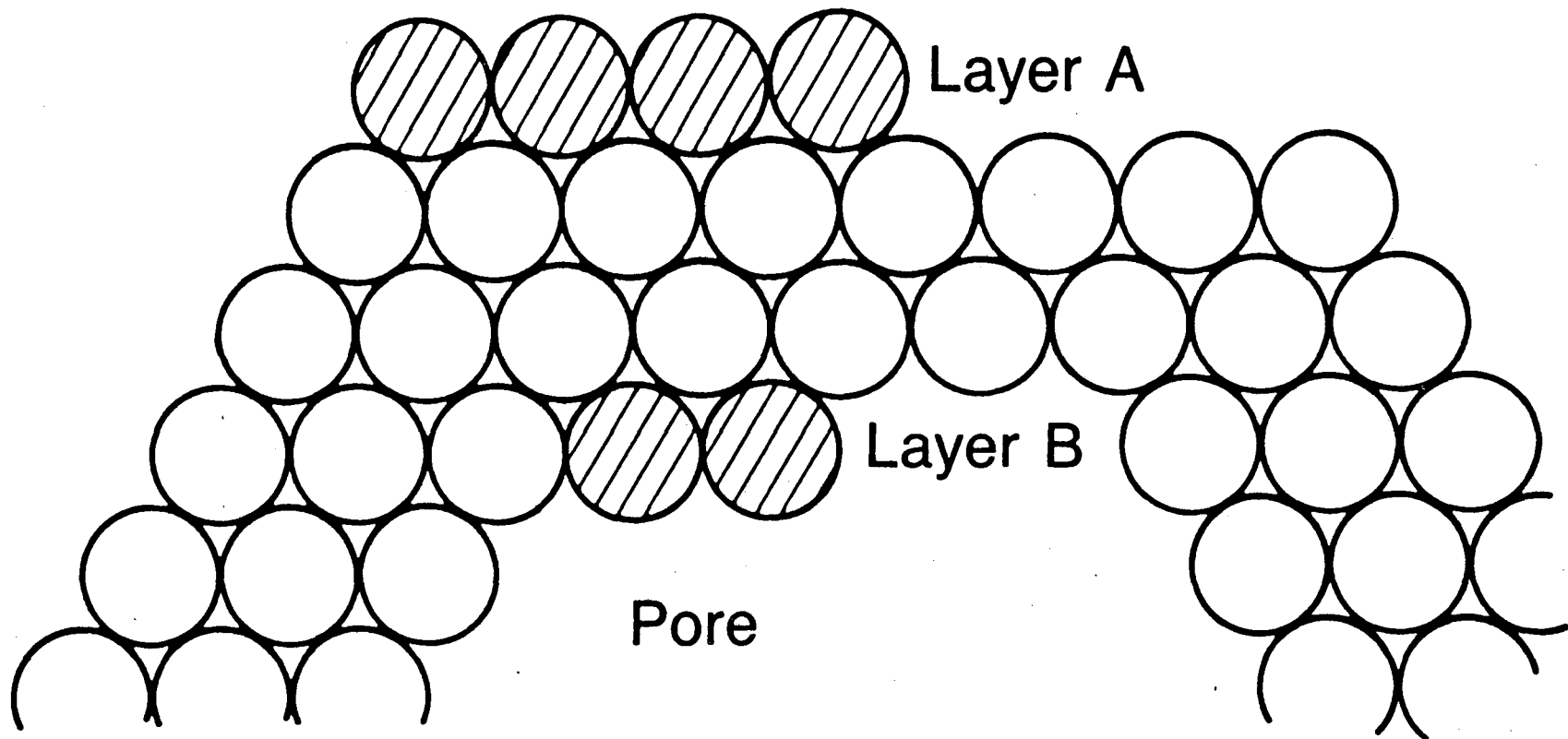
For transfer of one or two atoms from B to A, $\delta G \cong 0$
For transfer of one atom from A to B, $\delta G \cong 0$
But for transfer of two atoms from A to B, $\delta G < 0$

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