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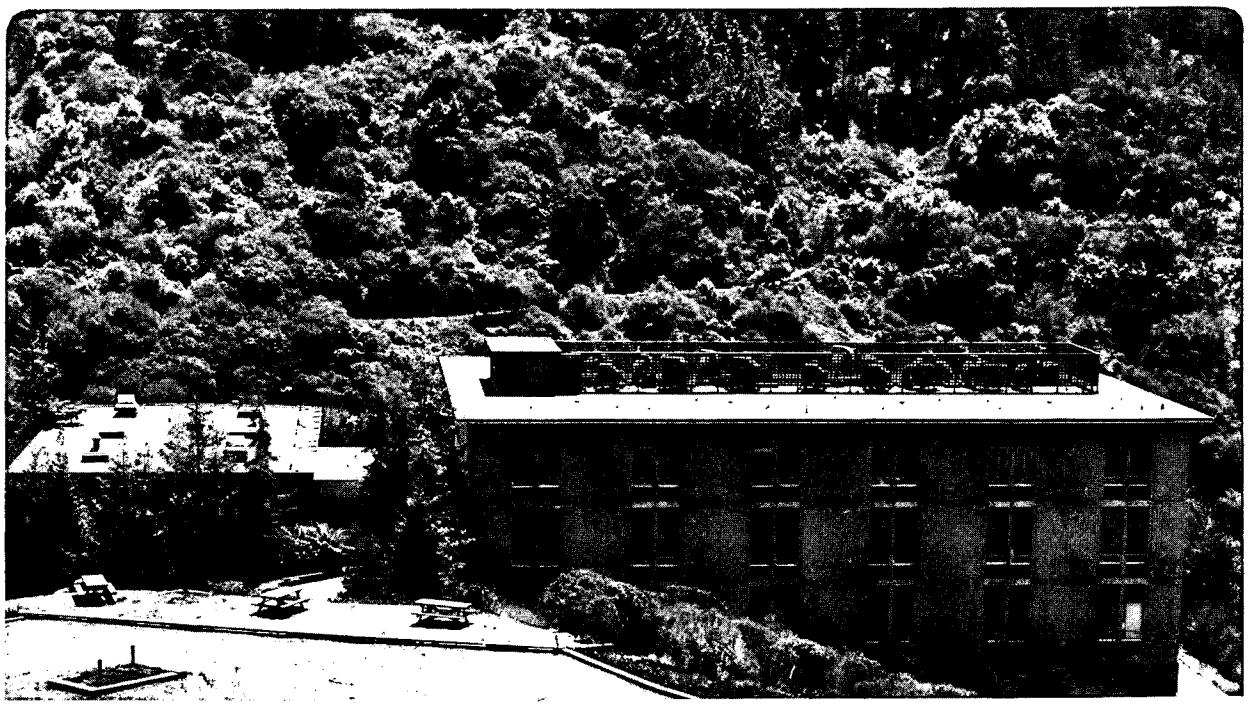

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THE DRIVING FORCE FOR EXAGGERATED GRAIN GROWTH

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ABSTRACT

The driving force for exaggerated grain growth is derived from a new surface thermodynamic theory which reconciles the kinetics of equilibrium to the thermodynamics of equilibrium between subparts of a particle with anisotropic surface energies. Exaggerated growth is driven by the reduction in dislocation and grain boundary free energies produced when a larger grain sweeps out a volume element formerly occupied by small grains. Whether the advancing boundary is planar, concave, or convex depends on the relative rates of ledge nucleation and growth, on the growth direction, and on whether growth occurs at screw dislocations. The model is compared to observations and additional tests are suggested.

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The usual assumption that sintering and related processes are driven by differences in particle curvature is known to be inappropriate for particles which have anisotropic surface energies.[1,2] CoO[3] and MgO[4,5] particles, for example, develop and maintain faceted shapes in the early stages of sintering. An expression for the driving force for sintering[6] that is consistent with such observations has recently been derived from a model for surface thermodynamics that reconciles the kinetics and thermodynamics of intra-particle equilibrium.[7,8]

The purposes of this Communication are to obtain from the new surface thermodynamic model an expression for the driving force for the phenomenon variously called secondary recrystalization or exaggerated, discontinues, or abnormal grain growth and to show that that expression allows growth normal to planar, concave, or convex boundaries, depending on the growth direction and on the rate limiting process. This conclusion can be contrasted with the conclusion from the classical expression for exaggerated grain growth in unworked metals and ceramics,[1,9]

$$\Delta G = \sigma V_m \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad (1)$$

where ΔG is the change in free energy on going across the curved interface, σ is the boundary energy, V_m is the molar volume, and r_1, and r_2 are the principal radii of curvature. This expression predicts that exaggerated growth is always in the direction of the centers of curvature of the segments of the large grain boundary which are defined by the dimensions of adjacent smaller grains, (Fig. 1).

The driving force for sintering in the new theory is[6]

$$\delta G \cong \delta[\Sigma(\sigma_i A_i + \gamma_i h_i)] < 0 \qquad (2)$$

where σ_i is the free energy per unit area of the interface or surface of area A_i, γ_i is the free energy per unit length of the i'th line defect, i.e., an edge, a ledge, or a dislocation, and h_i is the length of the defect. For the conditions now under consideration surfaces are not involved and grain boundary ledge energies can be considered to be components of grain boundary energies.

Figure 2 is a schematic drawing of a large grain which is bounded along one of its facets by randomly oriented smaller grains. The summations of Eq. (2) can be approximated by averages which could be obtained from calorimetric measurements of energies and from microstructural observations of the grain boundaries and dislocations. The excess free energy per unit volume of the large grain is $G_v = \gamma h_v$ where γ is the average free energy per unit length of dislocations in the large grain and h_v is the average length of dislocations per unit volume of that grain. For the collection of small grains $G_v = \sigma_s A_{vs} + \gamma_s h_{vs}$, where σ_s is their average grain boundary free energy per unit area, A_{vs} is their grain boundary area per unit volume (with that volume large enough to contain many small grains), γ_s is the average free energy per unit length of dislocations in the small grains and h_{vs} is the length of dislocations per unit volume of small grains. The free energy change produced by advance of a unit area of the large grain boundary upward by a distance δ_q is then

$$\delta G_v = -[\sigma A_{vs} + (\gamma_s h_{vs} - \gamma h_v)]\delta q \qquad (3)$$

where it can be expected that usually $\gamma_s \cong \gamma$, but $h_{vs} > h_v$.

Equation (3) predicts that exaggerated grain growth can be driven both by reduction in the length of line defects and by reduction in area of small grain boundaries when a differential volume element is swept out by the growing grain. A role of dislocations in the thermodynamics of recrystallization like that described by Eq. (3) is already accepted.[9] Here attention can be concentrated on the difference between the roles assigned to grain boundaries by Eq. (3) and by the classical model.

If Eq. (3) is correct, then rounding of grain boundaries during exaggerated grain growth is not a cause of that phenomenon, but a consequence of the kinetics of the process. Depending upon the relative rates of ledge nucleation and ledge growth and upon the growth direction examined, the boundaries of the growing grain can be planar, can have their centers of curvature outside the grain as predicted by the classical model, or can have their centers of curvature inside the grain. Growth by addition of molecules at screw dislocations that intercept the advancing boundary provides another kinetic path that results in rounded boundaries. Growth in directions normal to low energy facets and then growth parallel to such facets will be discussed in turn.

The most probable sites for nucleation of new ledges on a low energy facet would be at the line of intersection of the facet with small grain-small grain boundaries. When new ledges nucleate at such sites in times shorter than the time required for a ledge to grow the distance between them, the interface will develop the direction of

curvature expected from the classic model (Fig. 1). (But at high resolution the curvature will be seen to be a consequence of a sequence of ledges of successively shorter lengths.) When nucleation of new ledges is slow relative to the rate of growth between nucleation sites, the advancing boundary will be planar with occasional steps. De Jonghe has observed exaggerated grain growth to occur normal to a planar close packed facet of Na β"-alumina by the addition of ledges 1.13 nm in height.[10] No liquid phase is present in the grain boundary.

The principal growth directions of unconstrained anisotropic crystals are parallel to their low energy facets.[11] The boundary formed in a principal growth direction by the edges of low energy crystal layers could, at low magnifications, show a curvature opposite to the curvatures of Figure 1 because layers near the edges of the growing grain are nucleated later than those near the center of a cross section seen normal to the growth direction. Perhaps such a sequence of growth accounts for observations in a film of exaggerated grain growth of BeO of boundaries which are curved in directions opposite to those expected from Eq. (1).[12,13] The same direction of curvature would be produced if grains grow by addition of atoms or ions from the smaller grains at the ends of screw dislocations in the growing grains.

The growth of one grain at the expense of surrounding smaller grains is influenced by the relative orientations of those grain. For example, a low-defect small grain oriented with its low energy facet normal to a principal growth direction could block growth through that small grain. This prediction and those made above should be tested by high resolution transmission electron microscopy. Investigators who

have observed exaggerated grain growth by low resolution techniques and do not wish to undertake a TEM examination are asked to provide specimens for examination by the author and his colleagues in the National Center of Electron Microscopy. For tests of the alternate models, single phase specimens are required.

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13. The author is indebted to H. Palmour, III and J.A. Pask for this information. He has been unable to find a copy of this film.

FIGURES

1. Schematic drawing adapted from Ref. 1 of the curvature that results in exaggerated grain growth for the large crystal according to Eq. (1).

2. Schematic drawing of a large grain growing by a distance δq into adjacent smaller grains.

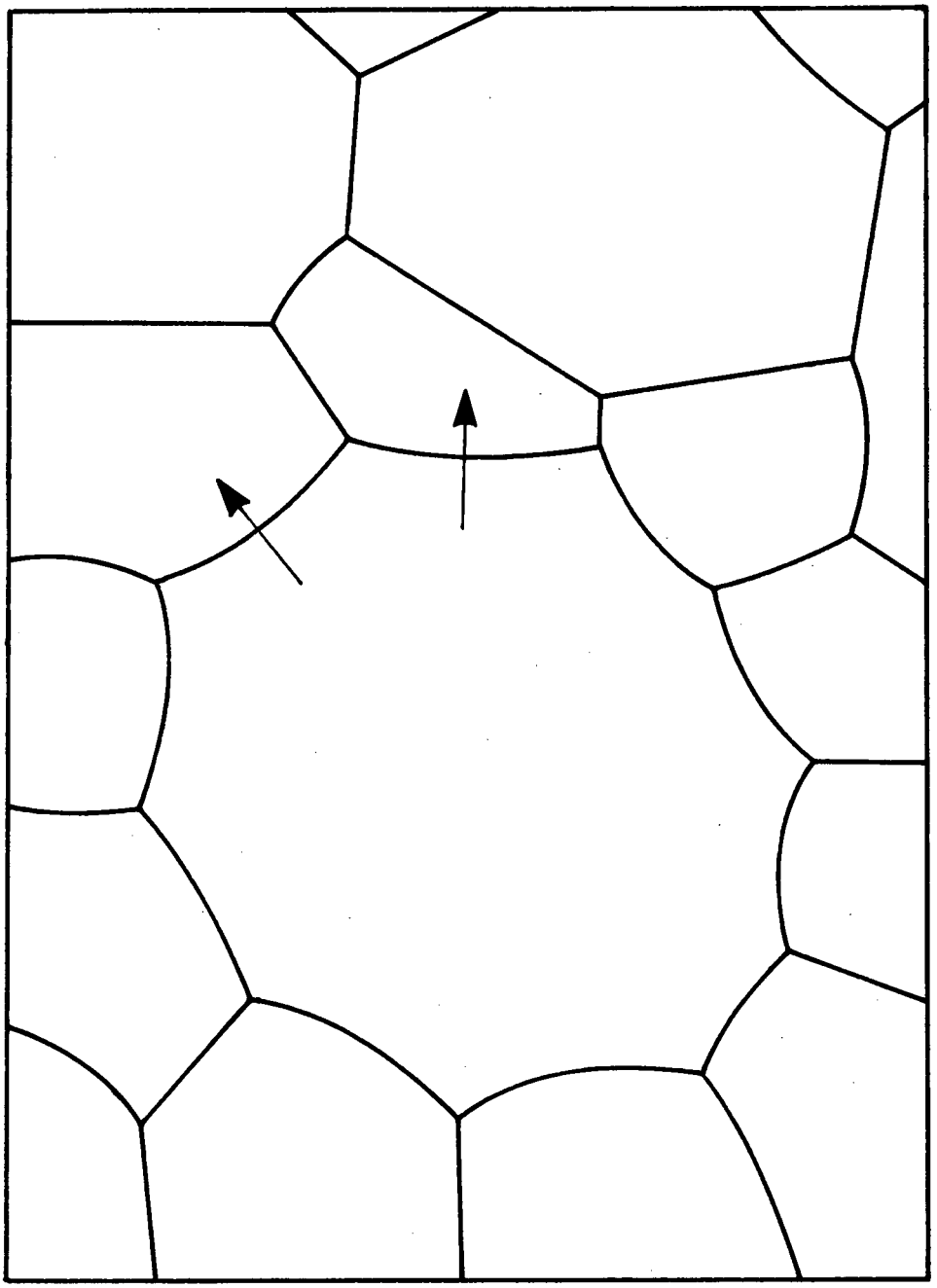

Figure 1. Schematic drawing adapted from Ref. 1 of the curvature that results in exaggerated grain growth for the large crystal according to Eq. (1).

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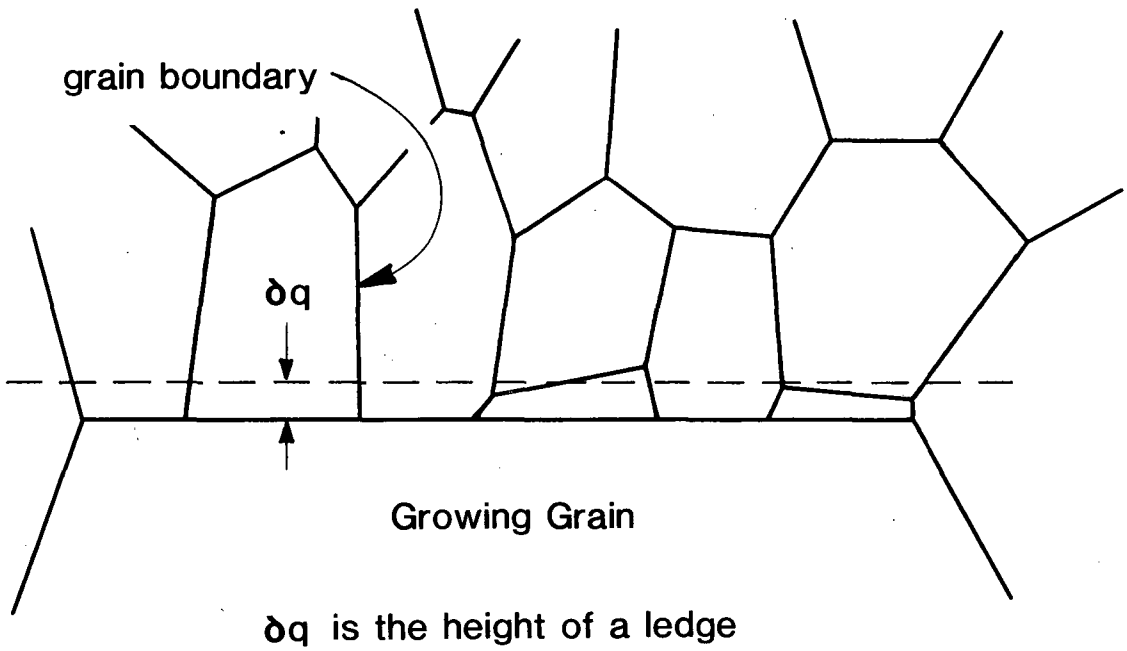

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Figure 2. Schematic drawing of a large grain growing by a distance δq into adjacent smaller grains.

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