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INTRODUCTION

The usual assumption that sintering is driven by differences in surface curvature is known to be a weak component of sintering theory for crystalline solids.[1,2] Another usual assumption of sintering theory—the implicit assumption that temperature gradients need not be considered—may often be mistaken. Experimental observations with which these assumptions are not consistent are cited in the next section of this paper.

A thermodynamic model for vacancy partitioning among sites of different bonding environments,[3,4] yields a more satisfactory expression for the driving forces for sintering[5] and for grain growth[6] at constant temperature. In a section on Theory, this expression is shown to be also a logical consequence of classical thermodynamic theory for faceted particles. Then the driving force for sintering in a temperature gradient is evaluated in terms of gradients in equilibrium vapor pressures.[7,8] The analysis suggests that non-diffusional steps of the overall sintering process are likely often to

limit sintering rates and that in temperature gradients long range vapor phase surface diffusion can be expected to play important roles.

In the Discussion section, tests of the models are suggested. Under Conclusions, implications of the analysis are summarized.

OBSERVATIONS TO BE EXPLAINED

Crystalline ceramic particles often develop and retain faceted surfaces when heated into their sintering range. For example, Kumar and Johnson[9] find that compacted 15 to 20 μm spheres of CoO develop pronounced facets during the first stage of densification. How can sintering of CoO be described when the necks and surfaces both rapidly evolve facets? Kim, Dahmen, and Searcy[10] find that porous aggregates of aligned MgO cubes evolve on heating at 1250°C in vacuum into aligned aggregates of larger cubes (Figs. 1 & 2). Among these cubes are interspersed enlarged pores. What drives this process?

Accepted theory requires exaggerated grain growth in a one-component or pseudo-one-component system to occur by boundary movement toward the centers of curvature of segments of boundary delineated by adjacent small grain-small grain boundaries.[11,12] Burke suggested that planar growth, which is sometimes observed, may be possible because the small grain boundaries are curved as required by the theory and separated by a liquid film from the growing grain.[11] De Jonghe, however, has shown that Na β"-alumina grows by the addition of ledges to a straight boundary when no liquid layer is present (Fig. 3).[13] A

moving picture,[14] of which prints seem no longer to be obtainable, is reported[15] to show exaggerated grain growth of BeO grains along a front that has the "wrong" direction of curvature. How can exaggerated grain growth normal to convex, concave, and planar boundaries be explained?

Long before the first scientific study of sintering was undertaken, it was known that temperature gradients drive mass transport. Partial separation of the components of a solution by distillation, for example, exploits that knowledge. The driving force for crystal growth or evaporation is created by the temperature difference between the vapor and condensed phase.

Small temperature differences cause greater differences in vapor pressure than are calculated from differences in curvature of particles in typical compacts.[7] Clearly, then, the influence of temperature gradients could influence sintering. But a temperature gradient or mass transport is complex either in a two-component phase[16] or in a gas in which molecular streaming can occur.[17] How then can the driving force for mass transport created by a temperature gradient during sintering be formulated and compared with the driving force from particle shape changes? An analysis of the condition for time-independent distribution of vacancies when a one-component solid is held in a temperature gradient provides an answer.[7,8]

THEORY

Driving Force for Sintering of Anisotropic Particles

The equilibrium shapes of particles or of cavities in particles were shown independently by Gibbs[18] and by Curie[19] to be the shapes given by the requirement that

$$\delta(\Sigma \sigma_i A_i) > 0 \tag{1}$$

for any differential change in particle shape, where $_i$ is defined by Gibbs in this context as the work of formation of a unit area of surface i and A_i is the area of surface i.

When the usual assumption—that specific surface free energies are isotropic—is introduced into eq. (1), it becomes

$$\sigma \delta A > 0 \tag{2}$$

where the surface free energy appears as a constant multiplier. Eq. (2) then makes the prediction that a particle is stable toward any change that increases its area.

This approximation is unsatisfactory for solids that, like CoO, evolve faceted particle shapes during sintering.[9] Faceting produces increased surface areas.

Eq. (1) can be made more exact by including terms for edges. The driving force for shape changes of particles of non-equilibrium shapes then can be expressed in terms of deviations in free energy from the modified expression. For isothermal sintering and for related processes like grain growth, energies of grain boundaries and of lines

of intersection of grain boundaries must also be included. The driving force for differential particle shape change and for sintering which results is

$$\delta G = \delta \Sigma (\sigma_i A_i + \gamma_i h_i) < 0 \qquad (3)$$

where the first terms of the summation now includes grain boundary specific free energies and areas, γ_i is the excess free energy per unit length of edge, ledge, or line of intersection of three grains, and h_i is the length of the line defect.

When Eq. (3) is applied to exaggerated grain growth in nonporous solids, surfaces are not involved and grain boundary ledge energies can be considered to be components of grain boundary energies. Fig. 4 is a schematic drawing of a large grain which is bounded along one of its facets by randomly oriented smaller grains. 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 δq is then[6]

5

$$\delta G_v = - [\sigma A_{vs} + (\gamma_s h_{vs} - \gamma h_v)]\delta q \qquad (4)$$

Equation (4) 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. Line defects are important in driving recrystallization in worked metals and alloys, but are usually not important in driving grain growth of ceramics.

Driving Force For Sintering In A Temperature Gradient. The same kind of analyses of the kinetics of equilibrium which yields the equilibrium vacancy distribution among surface, edge, and bulk sites in isothermal crystals has been applied to find the partitioning of vacancies among bulk sites in one-component or pseudo-one-component solids when they are held in a temperature gradient.[7,8] The rate of approach to equilibrium is path-dependent, but the matter-vacancy distribution calculated for every diffusional path is the same as that which is established by vapor transport when only monomer vapor molecules are important. Consequently, the thermodynamic and kinetic parameters are seperable, and the driving force is that which can be calculated for vapor transport as monomers, whether or not vapor transport is actually significant.

Vapor transport between two surfaces of the same area when gas phase collisions are negligible is given by, $J_n = k (P_1 T_1^{-1/2} - P_2 T_2^{-1/2})/P^o$ where J_n is the net flux, k contains the area and kinetic

factors, P_1 and P_2 are the equilibrium vapor pressures at T_2 and T_1, and P^O is the standard pressure. The driving force for diffusional transport is the part of this expression which does not depend on geometry or mechanism. When the difference in the $T^{-1/2}$ terms is neglected, the driving force can be expressed as the activity gradient, a_1-a_2, or

$$\frac{P_1 - P_2}{P^O} = \exp\left(-\frac{\Delta G_1}{RT_1}\right) - \left(\frac{\Delta G_2}{RT_2}\right) \tag{5}$$

where G_1, for example, is the free energy of vaporization at T_1.

The magnitude of this driving force can be illustrated by comparison with the pressure gradient calculated from the Kelvin equation for spherical silver particles at 1175 K (Fig. 5).[7] The Kelvin equation calculations assume the radii of necks between the particles to be one-tenth the particle radii. Pressure differences between particle surfaces and necks were calculated from Eq. (5) on the assumption that the temperature gradient is 1°C/mm. This temperature gradient is calculated to create larger local pressure gradients than do surface energy gradients for spherical particles of radii larger than 30 μm. A 10°C/mm gradient is more important than the surface energies for particles of radii >10 μm.

Kinetic Implications. When Eq. (4) is recognized as the driving force for isothermal exaggerated grain growth, the fact that boundary segments of a growing grain can be concave, convex, or planar can be explained as consequences of the growth kinetics.[6]

7

The most probable sites for nucleation of new ledges on a low
energy facet are at the line of intersection of the facet with small
grain-small grain boundaries (see Fig. 4). 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 classical model.[11] (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 ledge growth, the advancing boundary will
be planar with occasional steps.

The principal growth directions of unconstrained anisotropic
crystals are parallel to their low energy facets. The boundary formed
in a principal growth direction by the edges of low energy crystal
layers could, at low magnifications, show convex curvature (viewed from
without) rather than concave, the classical prediction. Convexity
would result 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. Convex curvature would also be
produced if grains grow by addition of atoms or ions from the smaller
grains at the ends of screw dislocations in the growing grain.

Most analyses of sintering data begin with the assumption that
mass transport is rate limiting. But reasons will be given here for
thinking that, for crystalline particles, a surface step is often

slowest. It is also usually assumed that the critical distances for mass transport during sintering are of the order of the cross sections of particles of the aggregate. But in a temperature gradient, mass transport over distances of half the cross section of the entire aggregate may sometimes be important.

It is informative to first consider a dislocation-free single crystal which is bounded by its lowest energy surfaces, but which could be given a lower total surface energy by rearrangement. The crystal might be, for example, a crystal of MgO with ledge-free {100} facets in the shape of an orthorhombic box. That box is unstable relative to a cube formed with the same facets, but the box is stable relative to any molecular transport processes that move less than half a monolayer from the facet of smallest area to a larger facet. Transformation of the initial shape to one with more equal edge lengths requires nucleation of a new layer on a larger facet and growth of that layer to an area larger than that of the smaller facet. These steps require local free energy increases and are possible only because statistical fluctuations occur in thermal energies and molecular distributions. The rates of occurrence of these fluctuations, not diffusion rates, must determine the rates of change of shape.

If screw dislocations intercept a source or sink surface, mass transfer can occur without periodic nucleation of new layers on the sink surface.[20] Nucleation is also not required in order to initiate

9

a new layer on a surface that has at least one edge bounded by molecules. Thus, for example, nucleation steps are probably not usually required to move molecules in an aggregate from the surfaces of faceted particles to faceted interparticle neck surfaces.

When a non-diffusional step like layer completion or growth at screw sites is rate limiting, the steepness of the temperature gradient across each particle is no longer important. Instead, the absolute difference in temperatures between the source and sink surface determines the activity difference that drives the mass transport. Consequently, until sintering has progressed to the stage in which channels between the particles are closed, vapor phase or surface diffusion can transport matter from the hottest part of an aggregate to the coldest.

Figure 6 illustrates with the same data for silver how the driving force for a surface step-limited process varies with the temperature difference between hot and cold surfaces. A temperature difference of $1^{\circ}C$ would create about the same driving force which is calculated from the Kelvin equation for particles of 1 μm radius, and a $0.1^{\circ}C$ difference would create about the driving force calculated for 10 μm radius particles.

DISCUSSION

Because porous ceramics are poor thermal conductors, the thermal gradients developed during rapid heating must be large. The high densification rates achieved by fast firing[21,22] may be primarily

10

caused by vapor phase or surface diffusion through open channels during heating from the hot surface of a specimen to its cooler center. Braudeau, Morell and Monty[23] have shown that a 6°C/mm temperature gradient at 1600°C increases the rate of decay of periodic grooves in alumina surfaces. Further studies of the influence of temperature gradients should show how they can be used to advantage in ceramic processing. Particular emphasis should be placed on determination of the extent to which densification can be promoted by long range transport in a temperature gradient. Surface diffusion may play on important role in densification. Jacobson, Opila, and Searcy have shown that in 1 μm pores through alumina, surface diffusion is a more important mode of LiF transport than is vapor phase transport.[24]

Careful studies are needed to show that microstructural changes which have been assumed to be driven by surface energy reductions have not in fact been driven, at least in part, by temperature gradients. Definitive proof requires demonstration that a furnace chamber maintains a constant and uniform temperature. The period during which the heating process produces temperature gradients in the sample must be negligible. To this end, small samples of metal powder could be used. Zinc would be of particular interest because it is highly anisotropic. Another approach is to bring a small quantity of ceramic powder to a uniform moderate temperature at which sintering is negligible and then to introduce a gas that catalyzes measurable sintering.[28]

11

The qualitative predictions made here about the relative importance of the nucleation and growth step of a particle shape change could be evaluated using computer simulations by the Monte Carlo technique. The influence of dislocations in promoting sintering of faceted ceramics should be another productive topic for study. The demonstration by Lemaire and Bowen[29] that dislocations are necessary for transport across 10 μm cavities in KCl despite a 1% pressure difference across the cavity implies that dislocations can greatly increase the rate of sintering of some solids.

CONCLUSIONS

For crystalline solids the driving forces for isothermal particle shape changes, sintering and exaggerated grain growth are reductions in total surface, grain boundary, and line defect energies. Shape changes for faceted particles or their aggregates require periodic layer nucleation steps which are thermodynamically unfavorable and also require layer growth that may have negligible driving force. Consequently, statistical fluctuations rather than diffusion rates are likely to be rate limiting. Nucleation is not required for some transfer processes, for example, for transfer from a particle surface to an interparticle neck, and screw dislocations make nucleation unnecessary.

In temperature gradients, the difference in vapor pressures at source and sink surfaces drive transfer processes. Vapor phase and surface diffusion may contribute significantly to densification by

12

transferring matter from the exterior of an aggregate toward its center.

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FIGURES

1. Oriented MgO crystals from $Mg(OH)_2$ decomposition.
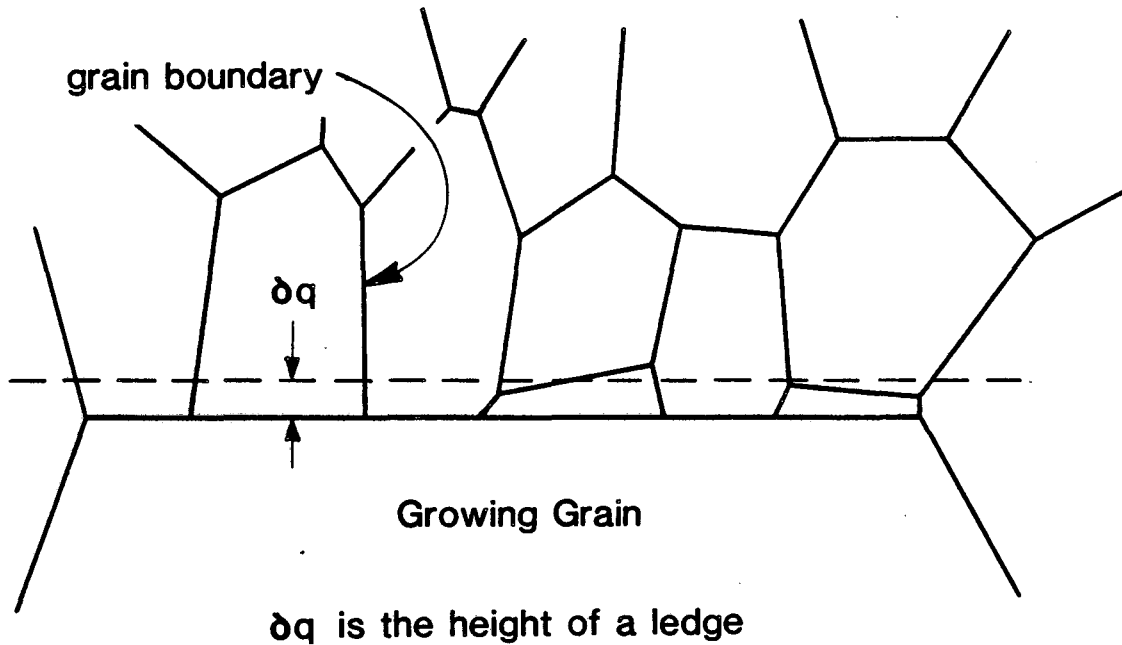
2. MgO from Fig. 1, sintered at 1250^oC in vacuum.

3. Exaggerated grain growth by ledge addition, Na β"-Alumina.[13]

4. Vapor Pressure Gradients across particles of various radii.

5. Exaggerated grain growth (schematic).

6. Vapor pressure differences as function of temperature (top scale) and particle radius (bottom scale).

16

20 nm
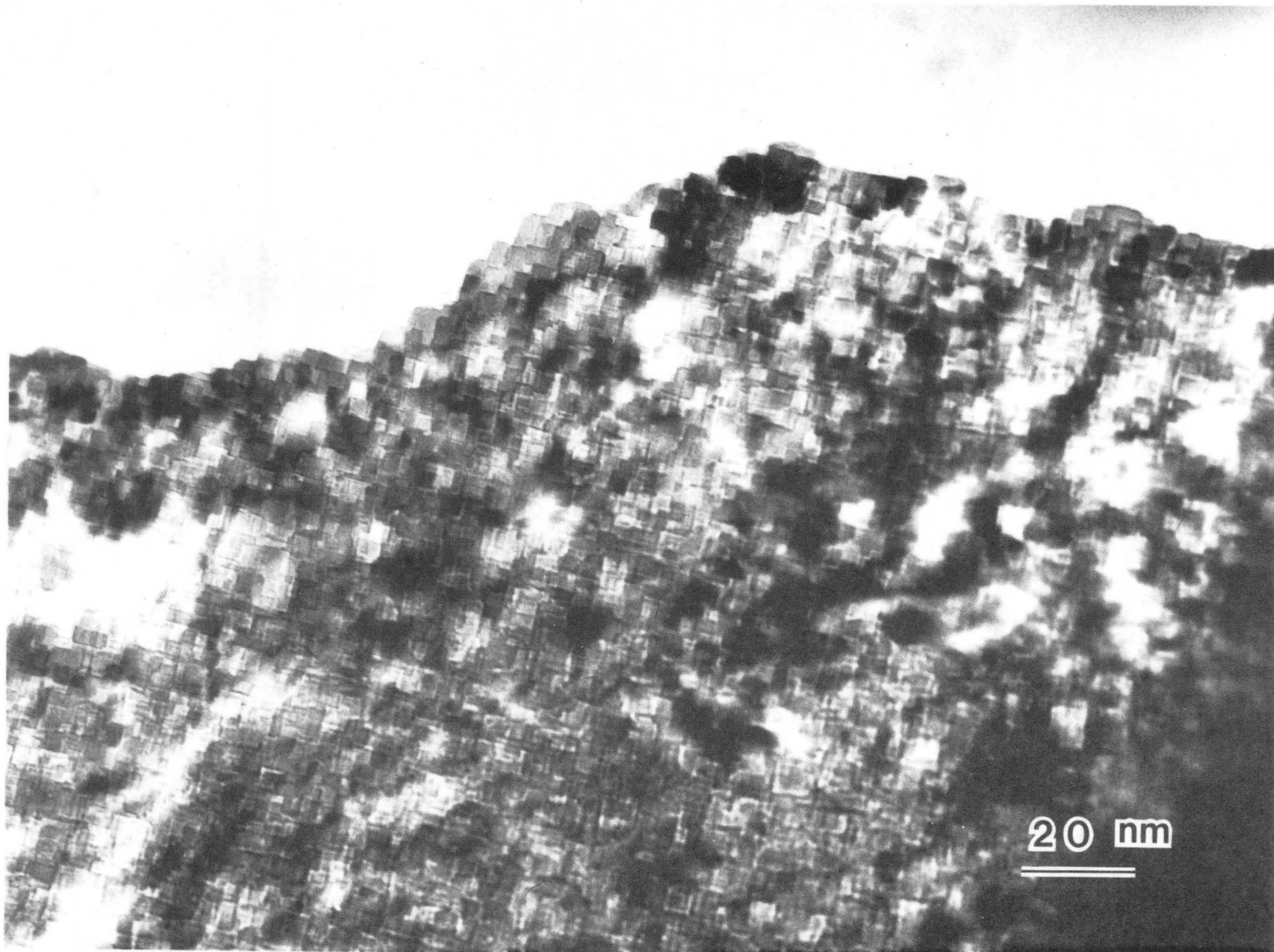
Fig. 1.   Oriented MgO crystals from Mg(OH)$_2$
decomposition.
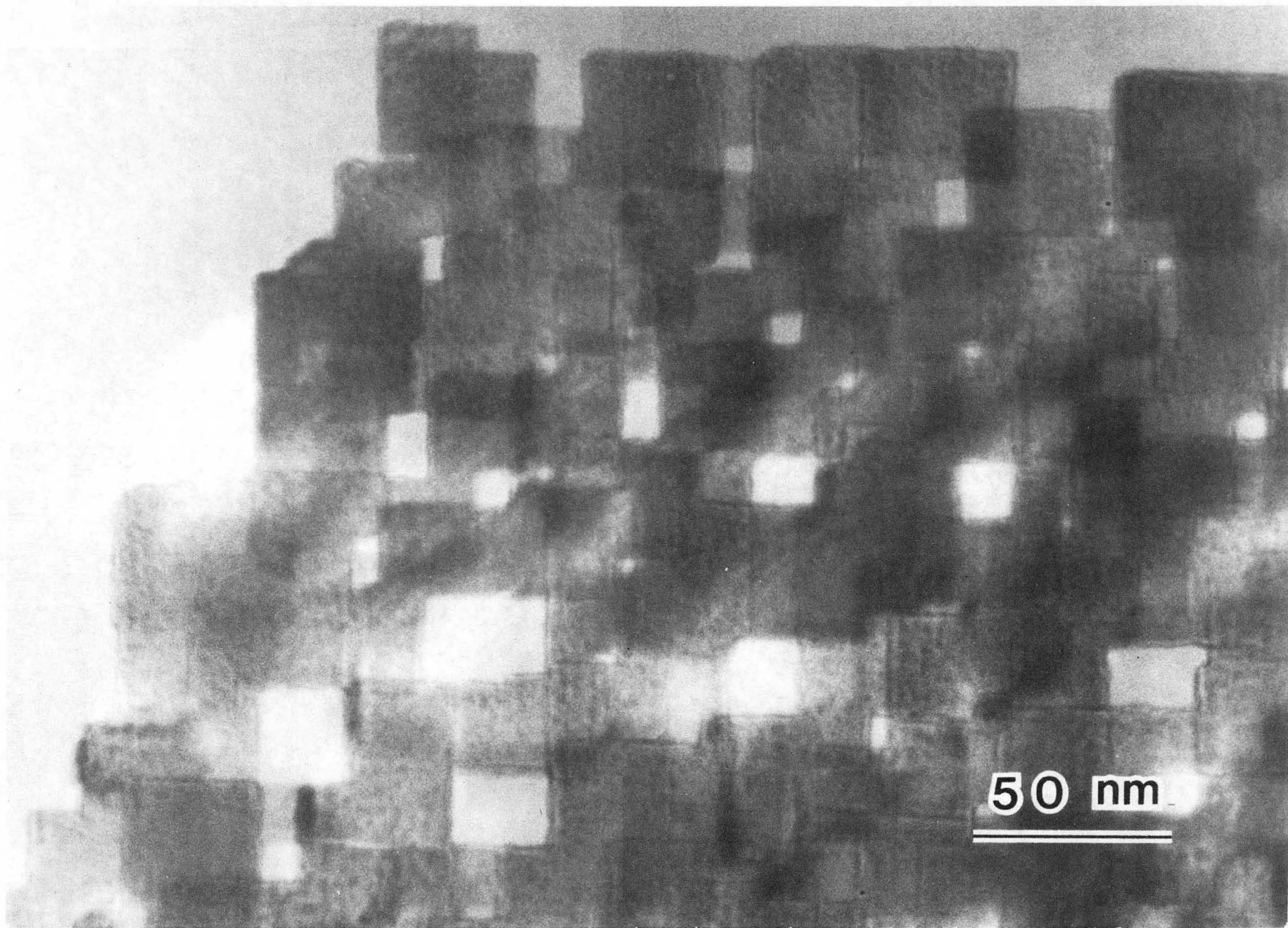
Fig. 2. MgO from Fig. 1, sintered at 1250°C
in vacuum.
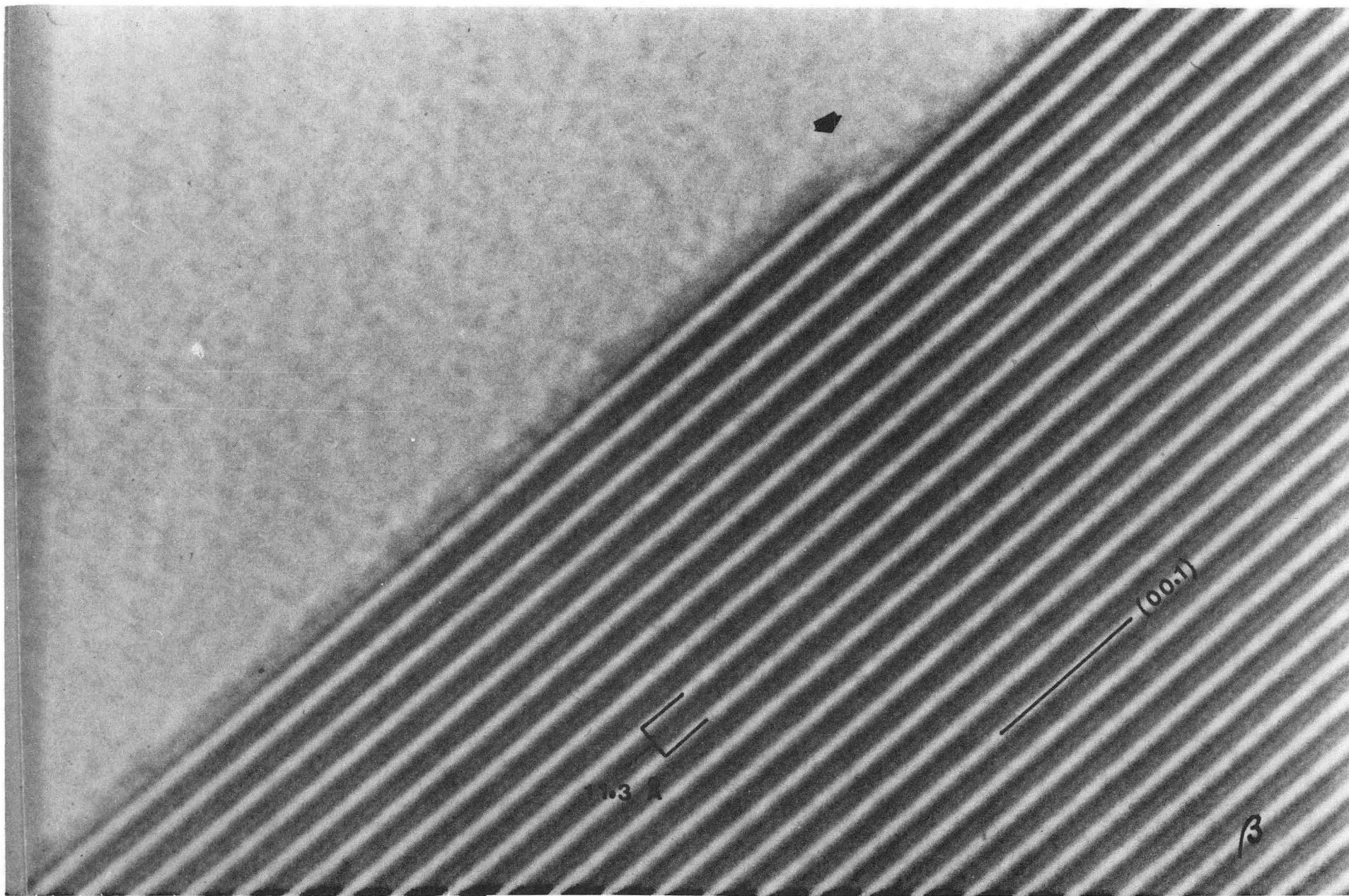
XBB 862-1225

Fig. 3. Exaggerated grain growth by ledge
addition, Na β''-Alumina.

XBB 850-10028

18

grain boundary
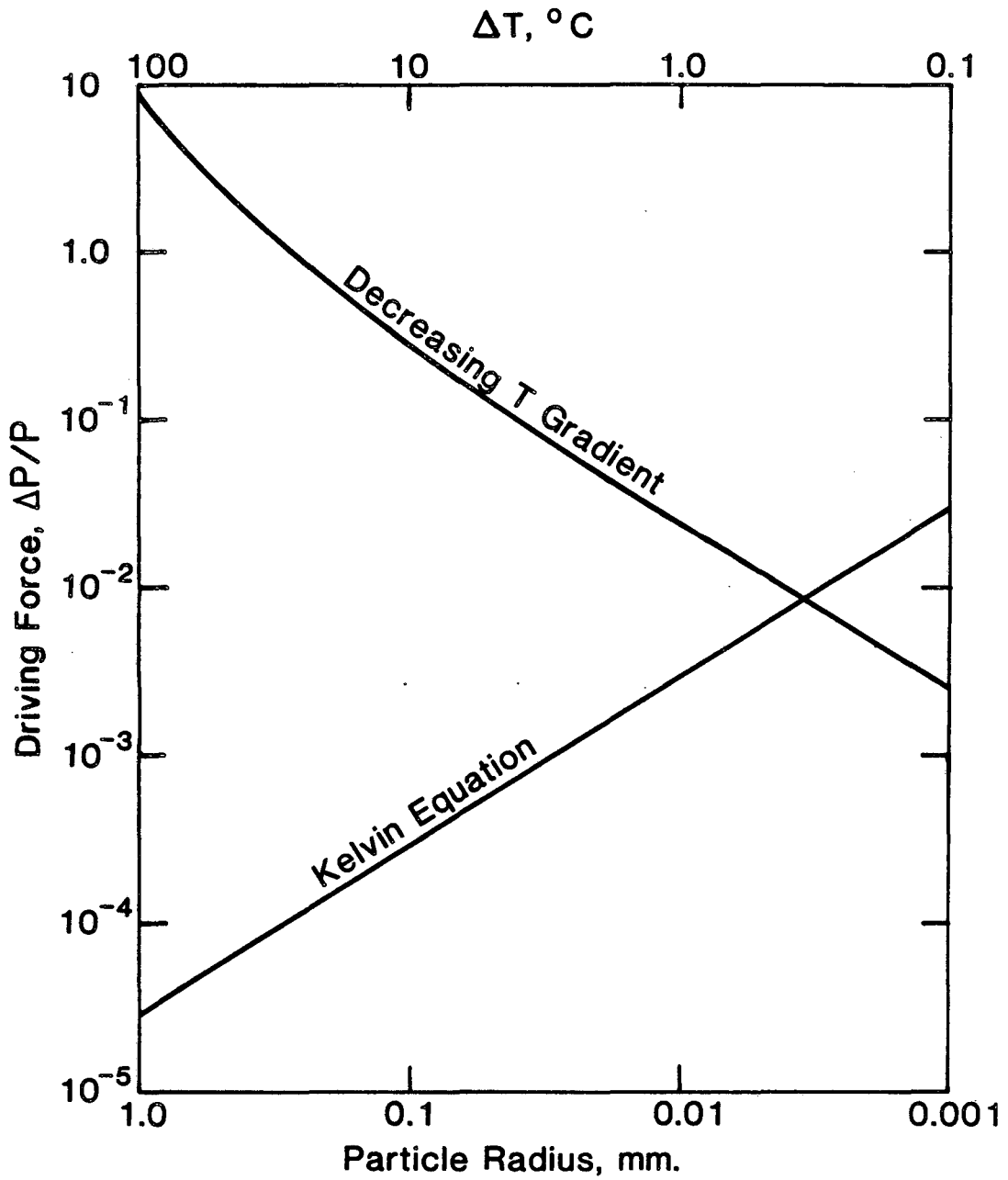
δq

Growing Grain

δq is the height of a ledge

Fig. 4. Vapor Pressure Gradients across
particles of various radii.
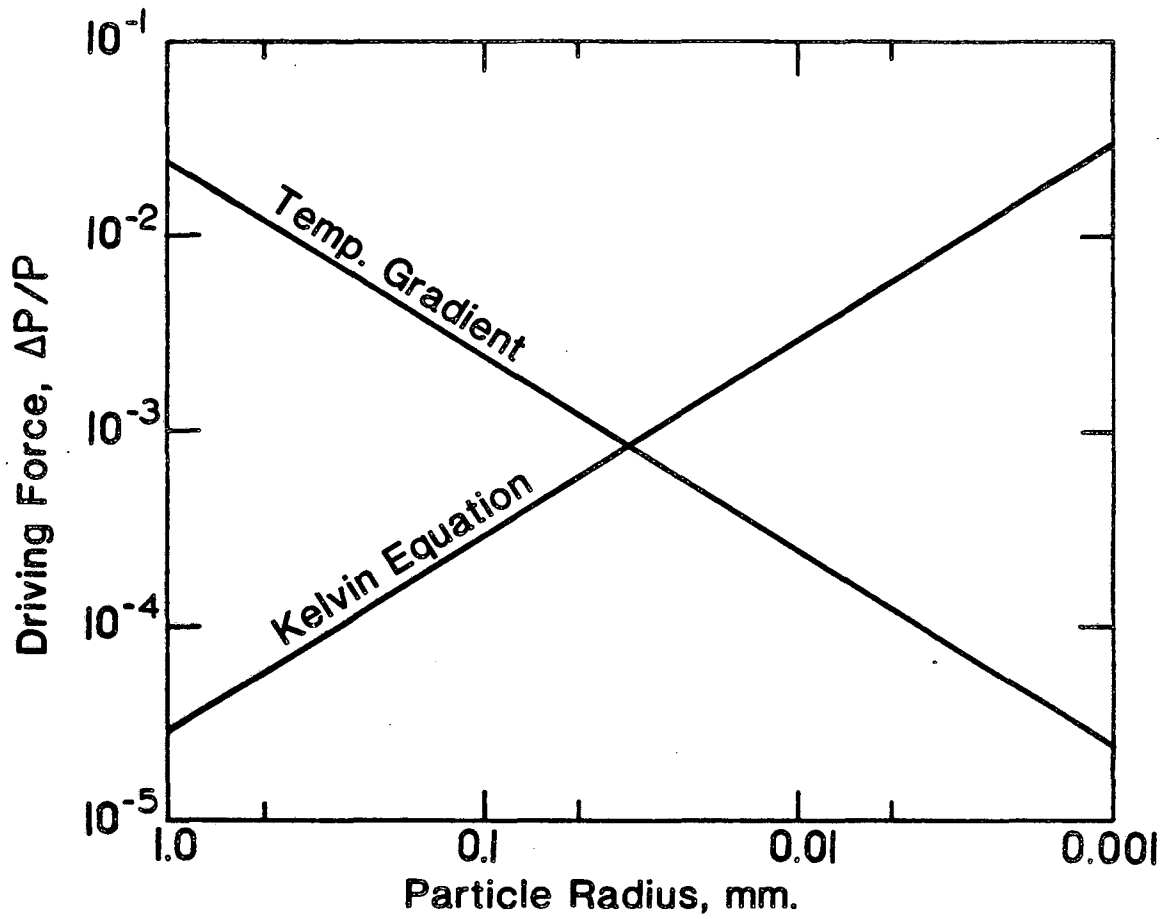
XBL 866-2497

Fig. 5. Exaggerated grain growth (schematic).

XBL 866-2495

Fig. 6. Vapor pressure differences as function
         of temperature (top scale) and particle
         radius (bottom scale).