A

ABNORMAL GRAIN GROWTH (Worner *et al.* 1991; Kang 2005)

Abnormal grain growth involves the excessively rapid growth of a few grains in an otherwise uniform microstructure. It is a particular problem in the later stages of sintering. It is characterized by certain grains or crystallographic planes exhibiting faster growth than average. Figure A1 is a sketch of a microstructure formed as a consequence of abnormal grain growth where one large grain at the top is growing at the expense of the surrounding smaller grains. Abnormal grain growth is favored when segregation changes the grain-boundary mobility or grain-boundary energy. When grain growth occurs, there is an interfacial velocity V_{ij} for the grain boundary between the i–j grain pair given by the product of the mobility M_{ij} and the force per unit area on the grain boundary F_{ij},

$$V_{ij} = M_{ij} F_{ij}$$

where the grain-boundary velocity varies between individual grain boundaries, as indicated by the subscript. The force F_{ij} is given by the product of the interfacial energy and the curvature,

$$F_{ij} = -\gamma_{ij}\left(\frac{1}{G_i} - \frac{1}{G_j}\right)$$

where G_i and G_j are the grain size for contacting grains, and γ_{ij} is the corresponding interfacial energy for the i–j interface. Although not routinely recorded, the interfacial energy depends on the misorientation between grains. Effectively, the energy per unit volume scales with the inverse grain size, so if $G_i > G_j$, then the force is pushing the grain boundary toward the smaller grain center. A critical condition occurs when the mobility of an individual grain boundary, M_{ij}, greatly exceeds the

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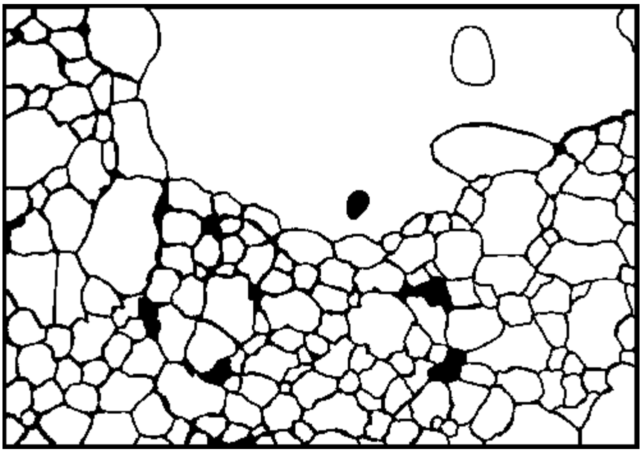

Figure A1. Abnormal grain growth during sintering is evident in sintering by the formation of a very large grain growing into a matrix of much smaller grains. The resulting nonuniform microstructure is evident in this reproduction from a sintered (Sr, Ba)Nb_2O_6 ceramic after heating at 1260°C for 4 h, where the grain at the top of this image is much larger than the surrounding small grains.

average or when the individual grain-boundary energy is excessively low. This critical condition is expressed by the following inequality:

$$\frac{M_{ij}}{M_m} > \frac{16}{9}\left(\frac{\gamma_{ij}}{\gamma_m}\right)$$

where M_m is the mean grain-boundary mobility, γ_{ij} is the individual grain-boundary energy, and γ_m is the mean grain-boundary energy. With respect to abnormal grain growth, the two situations of concern are a twofold higher individual grain-boundary mobility, for example, because of a segregated liquid, or a twofold lower individual grain-boundary energy, for example, due to segregation or near coincidence in grain orientation. In sintering practice, most examples of abnormal grain growth are caused by impurities that segregate on the grain boundaries even at the sintering temperature. For example, in sintering alumina (Al_2O_3), abnormal grain growth is favored by a high combined calcia (CaO) and silica (SiO_2) impurity level.

F_{ij} = grain-boundary force per unit area between the i–j grain pair, N/m^2
G_i, G_j = grain size for corresponding grain, m (convenient units: μm)
M_{ij} = grain-boundary mobility between the i–j grain pair, $m^3/(s \cdot N)$
M_m = mean grain-boundary mobility averaged over the body, $m^3/(s \cdot N)$
V_{ij} = interfacial velocity for the grain boundary between the i–j grain pair, m/s
γ_{ij} = individual grain-boundary energy between the i–j grain pair, J/m^2
γ_m = mean grain-boundary energy averaged over the body, J/m^2.

ABRASIVE WEAR

See *Friction and Wear Testing*.

ACCELERATION OF FREE-SETTLING PARTICLES (Han 2003)

An assumption in Stokes' law, as applied to both particle-size classification and particle-size distribution analysis, is that the particles instantaneously reach terminal velocity. However, this is not the case in practice, and the acceleration of the particle to the free-settling terminal velocity adds an error in a particle-size analysis. The approach to the Stokes' law terminal velocity v_T is described by the following equation for spherical particles initially at rest:

$$v = v_T\left[1 - \exp\left(-\frac{18t\eta}{\rho D^2}\right)\right]$$

where v is the velocity after time t when the particle starts from rest, η is the fluid viscosity, ρ is the theoretical density of the particle, and D is the particle diameter. A plot of this equation is given in Figure A2, where the actual velocity is normalized to the terminal velocity for the case of a 1-mm stainless steel particle settling in water.

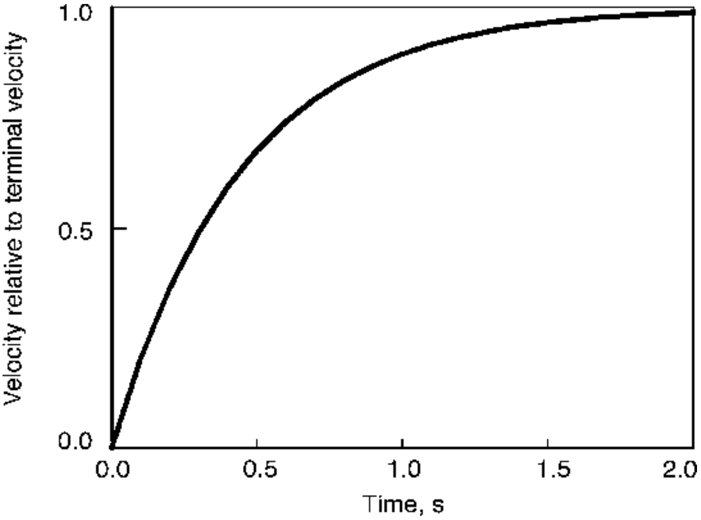

Figure A2. A plot of the relative particle velocity (when starting from rest) versus time to show the acceleration of a particle settling by Stokes' law. The particle velocity is relative to the terminal velocity. This calculation is for a 1-mm stainless steel ball settling in water.

D = particle diameter, m (convenient units: μm)
t = time, s
v = velocity (starting with $v = 0$ at $t = 0$), m/s
v_T = Stokes' law terminal velocity, m/s
η = fluid viscosity, Pa · s
ρ = theoretical density of the particle, kg/m^3 (convenient units: g/cm^3).

ACTIVATED SINTERING, EARLY-STAGE SHRINKAGE (German and Munir 1977)

Activated sintering is associated with a treatment, usually by an additive, that greatly increases sintering densification at lower temperatures than typically required. In activated sintering the initial sintering shrinkage depends on the rate of diffusion in the activator, which is segregated to the interparticle grain boundary. Figure A3 provides a schematic of the sintering geometry used to model first-stage activated sintering. The growth of the interparticle bond results in attraction of the particle centers, which gives compact shrinkage $\Delta L/L_0$ as follows:

$$\frac{\Delta L}{L_0} = \frac{L - L_0}{L_0} = \frac{g\Omega\delta C\gamma_{SV}D_A t}{D^4 RT}$$

where ΔL is the change in length, L_0 is the initial length, L is the instantaneous length during sintering, g is a collection of geometric terms, Ω is the atomic volume, δ is the width of the second-phase activator layer coating the grain boundary, C is the solubility of the materials being sintered in the second-phase activator, γ_{SV} is the solid–vapor surface energy, D_A is the diffusivity of the material being sintered in the activator (note this changes dramatically with temperature), t is the sintering time, D is the particle size, R is the gas constant, and T is the absolute temperature.

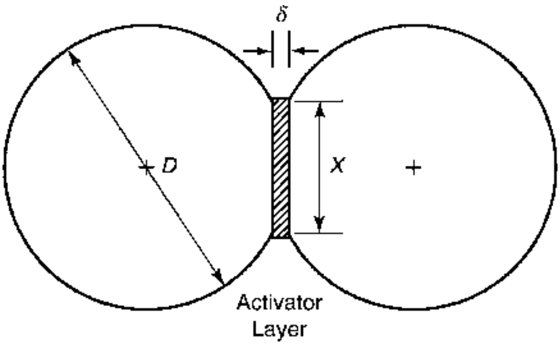

Figure A3. Simple two-particle geometry for activated sintering, where the activator is segregated to the interparticle grain boundary to form a layer of width δ for a neck of diameter X and a grain or particle of diameter D.

Faster diffusion in the activator induces early sintering gains, but this mandates that the solid be soluble in the activator. The controlling step is the diffusivity in the activator layer. The difference in effectiveness between various activators is explained by their differing diffusivities and solubilities.

C = volumetric solubility in the activator, m^3/m^3 (dimensionless)
D = median particle size, m (convenient units: μm)
D_A = diffusivity of the base material in the activator layer, m^2/s
L = instantaneous length, m (convenient units: mm)
L_0 = initial length, m (convenient units: mm)
R = universal gas constant, 8.31 J/(mol · K)
T = absolute temperature, K
g = collection of geometric terms, dimensionless
t = isothermal sintering time, s
ΔL = change in length, m (convenient units: mm)
$\Delta L/L_0$ = sintering shrinkage, dimensionless (convenient units: %)
Ω = atomic volume, m^3/mol
δ = activator phase width on the grain boundary, m (convenient units: nm or μm)
γ_{SV} = solid–vapor surface energy, J/m^2.

ACTIVATION ENERGY

See *Arrhenius Relation*.

ADSORPTION

See *BET Specific Surface Area*.

AGGLOMERATE STRENGTH (Pietsch 1984)

Powder that is wetted by a relatively small quantity of liquid or polymer will agglomerate. If the fluid phase is not solidified or hardened, then the crush strength σ for an agglomerated mass of powder depends on the fractional porosity ε and the degree of pore saturation S,

$$\sigma = 7S\gamma_{LV}\frac{1-\varepsilon}{D\varepsilon}$$

where the saturation S is the fraction of pore volume that is filled with liquid (often as small as 0.01), γ_{LV} is the liquid–vapor surface energy, and D is the particle size.

Unless the agglomerate is wetted by a high-strength polymer, the strength of a typical agglomerated powder is dominated by capillarity effects.

D = particle diameter, m (convenient units: μm)
S = degree of pore saturation, dimensionless fraction [0, 1]
ε = fractional porosity, dimensionless [0, 1]
γ_{LV} = liquid–vapor surface energy, J/m^2
σ = strength of the agglomerate, Pa.

[Also see ***Capillarity***.]

AGGLOMERATION FORCE

When a small powder is exposed to water or other condensable vapor, a liquid bridge can form at the contact points between particles. Initially the liquid bridges are small and do not merge, giving a structure termed the *pendular state*. As long as the liquid is wetting, then at low concentrations the resulting capillary bonds provide an attractive force. As an approximation, the attractive force F between contacting particles varies with the liquid–vapor surface energy γ_{LV}, and particle size D, as follows:

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$$F = 3D\gamma_{LV}$$

D = particle diameter, m (convenient units: μm)
F = attractive force between contacting particles, N
γ_{LV} = liquid–vapor surface energy, J/m^2.

AGGLOMERATION OF NANOSCALE PARTICLES

See *Nanoparticle Agglomeration*.

ANDREASEN SIZE DISTRIBUTION (Andreasen 1930)

Originally isolated in colloidal particle-packing studies, the Andreasen particle size distribution is applicable to all powders where a high packing density is desired. The cumulative particle-size distribution is expressed in terms of the weight fraction of particles $F(D)$ given as the fractional weight of powders with a size less than particle size D. The Andreasen size distribution is described as follows:

$$F(D) = A\left(\frac{D}{D_L}\right)^q$$

where A is a fitting parameter, D_L is the largest particle size in the distribution, and q is the distribution exponent. For the highest packing densities, it is observed that the exponent q tends to range near 0.6. As an alternative, the cumulative particle-size distribution can be expressed with respect to a limiting size by defining a distribution constant $B = A/D_L^q$, giving

$$F(D) = BD^q$$

A = fitting parameter, dimensionless
B = distribution constant, $1/\mathrm{m}^q$
D = particle size, m (convenient units: μm)
D_L = size of the largest particle, m (convenient units: μm)
$F(D)$ = cumulative weight-based particle-size distribution, dimensionless [0, 1]
q = distribution exponent, dimensionless.

APPARENT DIFFUSIVITY (Porter and Easterling 1981)

In cases where both volume diffusion D_V and grain-boundary diffusion D_B are acting to induce sintering shrinkage, the data from shrinkage experiments only provide a means to extract an apparent diffusivity, not an absolute diffusivity. For a constant temperature, the combined or apparent diffusivity D_A depends on the two contributions as follows:

$$D_A = D_V + \frac{\beta\delta}{G} D_B$$

where G is the grain size of the microstructure, δ is the grain-boundary width (usually assumed to be 5 to 10 times the atomic size), and β is an adjustable parameter near unity (typically ranges from 0.5 to 1.5). Both diffusivities are functions of temperature.

D_A = apparent diffusivity, m^2/s
D_B = grain boundary diffusivity, m^2/s
D_V = volume diffusivity, m^2/s
G = grain size, m (convenient units: μm)
β = adjustable parameter, dimensionless
δ = grain-boundary width, m (convenient units: μm or nm).

ARCHARD EQUATION (Archard 1957)

Sliding wear is commonly treated in terms of the loss of material as a function of the hardness, sliding distance, and normal load. The coefficient of friction between the substrate and sliding component is a factor that can greatly change wear rates. The Archard equation calculates the wear behavior by assuming asperity removal, where a single circular cross section is acted upon by an intense wear event. Fragments form and contribute to the mass loss based on the assumption that the hardness and yield strength of the material are proportional. The resulting wear equation is given as follows:

$$Q = \frac{kWL}{H}$$

where Q is the volume of material removed from the test or wear material, k is a wear constant that provides a measure of the wear resistance, W is the normal (perpendicular to the surface) load causing wear, L is the total sliding length for the wear event, and H is the material hardness (assuming units of Pa or N/m^2, where it is assumed the opposing material is much harder). The first derivative of this equation with respect to time then says the wear rate (volume per unit time) is proportional to the sliding velocity.

H = hardness, Pa (convenient units: MPa)
L = sliding length, m (convenient units: mm)
Q = wear volume, m^3 (convenient units: mm^3)
W = normal load, N (convenient units: kN or MN)
k = wear constant, dimensionless.

[Also see ***Friction and Wear Testing***.]

ARCHIMEDES DENSITY

A standard means to determine the volume of an irregular shape is based on fluid displacement when the component is immersed in a fluid such as water. The measurement must prevent fluid intrusion into surface-connected pores to extract an accurate volume. Combined with the dry mass determined prior to the test, a density calculation follows. First, the sample is weighed dry (W_1), then again after oil impregnation of the evacuated pores (W_2), and finally the oil-impregnated sample is immersed in water for the final weight (W_3). Usually a wire is used to suspend the sample in the water and its weight W_W must be measured in water too. Then the actual or Archimedes density ρ can be calculated from the weight determinations as follows:

$$\rho = \frac{W_1 \phi_W}{W_2 - (W_3 - W_W)}$$

where ϕ_W is the density of water in kg/m^3, which is temperature dependent as given here,

$$\phi_W = 1001.7 - 0.2315T$$

with T being the water temperature in °C. Dividing the measured density by the theoretical density gives the fractional density. One variant uses water impregnation instead of oil to fill the pores, which still involves two immersion events, but there is no oil trapped in the pores.

T = water temperature, °C
W_1 = dry mass of the sample prior to testing, kg (convenient units: g)
W_2 = wet mass of the sample after filling pores with fluid, kg (convenient units: g)
W_3 = mass of the component immersed in water, kg (convenient units: g)
W_W = mass of the suspension wire, kg (convenient units: g)
ϕ_W = temperature-corrected density of water, $\mathrm{kg/m^3}$ (convenient units: $\mathrm{g/cm^3}$)
ρ = component density, $\mathrm{kg/m^3}$ (convenient units: $\mathrm{g/cm^3}$).

[Also see ***Fractional Density***.]

ARRHENIUS RELATION

The change in atomic motion due to a temperature increase or decrease during sintering is described by an Arrhenius relation. It corresponds to an approximation of the integral area under the tail of the Boltzmann energy distribution for the higher energies. Inherently the Arrhenius relation gives the fraction of atoms with an energy of Q or greater at any time. This integral determines the cumulative probability that an atom has more energy than that required to move, as determined by the activation energy Q. For example, the volume-diffusion coefficient D_V is determined from the atomic vibrational frequency D_0, absolute temperature T, universal gas constant R, and the activation energy Q, which corresponds to the energy required to induce atomic diffusion via vacancy exchange, giving,

$$D_V = D_0 \exp\left(-\frac{Q}{RT}\right)$$

Variants on this relation exist for grain-boundary diffusion, surface diffusion, evaporation, creep, and other high-temperature processes.

D_0 = diffusion frequency factor, $\mathrm{m^2/s}$
D_V = volume-diffusion coefficient, $\mathrm{m^2/s}$
Q = activation energy, J/mol (convenient units: kJ/mol)
R = universal gas constant, 8.31 $\mathrm{J/(mol \cdot K)}$
T = absolute temperature, K.

ATMOSPHERE MOISTURE CONTENT

See *Dew Point*.

ATMOSPHERE-STABILIZED POROSITY

See *Gas-generated Final Pores*.

ATOMIC FLUX IN VACUUM SINTERING (Johns *et al.* 2007)

When sintering in a vacuum, a rate of gas impingement exists on any surface, and that rate depends on the pressure and temperature in the sintering furnace. The corresponding atomic flux is the frequency at which gas molecules collide with the surface. Considering an external surface (not inside the pore), the number of gas molecules that strike the surface per unit time and per unit area is the flux J estimated as,

$$J = \frac{P}{\sqrt{2\pi kTm}}$$

where P is the gas pressure, k is Boltzmann's constant, T is the absolute temperature, and m is the molecular weight of the species. In a similar manner, oxide reduction in a partial pressure of hydrogen or vacuum surface carburization both depend on this same flux. If the density of desired reaction sites is known for the exposed surface, then it is possible to estimate from the flux the time required for the desired effect; the characteristic time is the density of surface sites (number per unit area) divided by the flux.

J = flux, atom/(m^2 · s) or molecule/(m^2 · s)
P = gas pressure, Pa
T = absolute temperature, K
k = Boltzmann's constant, $1.38 \cdot 10^{-23}$ J/(atom · K)
m = molecular weight, kg/atom or kg/molecule.

ATOMIC-SIZE RATIO IN AMORPHOUS METALS

The formation of a glassy metal, or bulk amorphous metal, depends on several factors, with the atomic-size ratio of the constituents being one of the important factors. If atoms are very different in size, as well as having differences in valence and crystal structure, then it is difficult to crystallize a solid on cooling a homogeneous liquid so formation of the amorphous state is favored. Accordingly, one factor that helps in the formation of an amorphous metal is a large atomic-size ratio (R_B/R_A). This ratio is linked to the solute concentration C_B needed to form an amorphous phase as follows:

$$\left| \left(\frac{R_B}{R_A} \right)^3 - 1 \right| C_B \geq 0.1$$

where R_B is the solute (minor constituent) atomic radius and R_A is the solvent (major constituent) atomic radius. Less solute additive is needed to access the amorphous structure during cooling, as the atomic sizes are substantially different (such that the size ratio is significantly different from unity).

C_B = solute concentration to form an amorphous phase, m^3/m^3 (dimensionless)
R_A = atomic radius of the solvent phase, m (convenient units: nm or Å)
R_B = atomic radius of the solute phase, m (convenient units: nm or Å).

ATOMIZATION SPHEROIDIZATION TIME

See *Spheroidization Time*.

ATOMIZATION TIME

See *Solidification Time*.

AVERAGE COMPACTION PRESSURE

See *Mean Compaction Pressure*.

AVERAGE PARTICLE SIZE

See *Mean Particle Size*.

AVRAMI EQUATION (Avrami 1939)

The Avrami equation is used to describe the rate of phase transformation in a process that first involves nucleation of the new phase followed by transformation with a

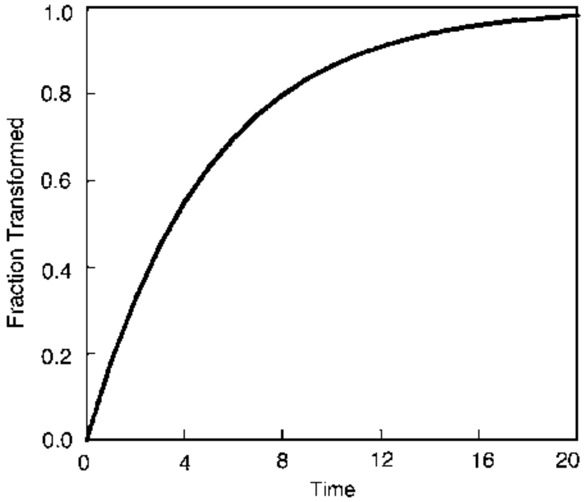

Figure A4. A plot of the Avrami equation showing a typical fit to reaction kinetics using a time exponent of unity.

progressively slower rate as the source species for the reaction are exhausted. As illustrated in Figure A4, the general shape is a lazy-S curve showing the fraction or percent transformed versus time. It is fit by an equation of the form:

$$y = 1 - \exp(-Kt^n)$$

where y is the fraction transformed, t is the time, n and K are constants for a given reaction. Typically the parameter K is temperature dependent (Arrhenius temperature dependence with an activation energy representative of the underlying mechanism) and n ranges from 1 to 4.

K = temperature-dependent reaction rate, $1/\mathrm{s}^n$
n = time exponent, dimensionless
t = reaction time, s
y = fraction of phase transformed, dimensionless [0, 1].