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Authors

Hsueh, C.H.
Evans, A.G.

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September 1982

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MICROSTRUCTURE EVOLUTION DURING SINTERING:
THE ROLE OF EVAPORATION/CONDENSATION

by

C. H. Hsueh and A. G. Evans

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Materials Science and Mineral
Engineering, University of California
Berkeley, CA 94720

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ABSTRACT

The motion of grain boundary located pores by an evaporation/condensation mechanism has been analyzed, and compared with surface diffusion dominated pore motion. It has been demonstrated that evaporation/condensation becomes important at high temperatures and large pore sizes. A lower bound condition for the separation of pores from two grain interfaces, independent of the pore or grain size, has been identified. Subsequent calculations of the motion of pores attached to three grain edges have permitted the prediction of pore/grain size trajectories. The trajectories indicate that the initial pore/grain size ratio must be smaller than a critical value to ensure that pore shrinkage continues and hence, that a fully dense material ensues.

1. INTRODUCTION

The development of microstructure during final stage sintering is frequently dominated by the motion of pores attached to grain boundaries.¹ Specifically, pores attached to three grain edges may impede grain growth (by a pore drag mechanism) and thereby, encourage the formation of fine-grained microstructures²; whereas pores on two grain interfaces are potentially capable of detaching from the associated grain interfaces, resulting in the formation of intergranular pores that substantially retard the approach to final density³⁻⁸ (and may induce exaggerated grain growth). The dual role of pores in final stage microstructure development has been analyzed for sintering conditions that encourage pore motion by surface diffusion and pore shrinkage by grain boundary diffusion.^{2,3} A more dominant mode of pore motion in certain refractory materials (that exhibit a high vapor pressure) involves evaporation from the leading pore surfaces and condensation at the trailing surfaces (fig. 1). The intent of the present paper is to examine the potential influence of evaporation/condensation, vis-a-vis surface diffusion, on the microstructure development process.

2. PORE/GRAIN BOUNDARY SEPARATION

Prior studies of pore motion by evaporation/condensation have been restricted to the motion of spherical pores (a dihedral angle $\Psi=\pi$) limited by gas diffusion.⁹ The analysis conducted herein emphasizes the evaporation/condensation rate controlled motion of pores with arbitrary dihedral angle.

Pore motion by evaporation/condensation is motivated by a curvature difference between the leading and trailing pore surface (fig. 1) that results in a modified pressure, p , at any location over the pore surfaces. The vapor pressure is characterized by the chemical potential;

$$\mu \equiv kT \ln (p/p_0) = \Omega \gamma_s [1/R_1 + 1/R_2] \quad (1)$$

where γ_s is the surface energy, R are the principal radii of curvature of the surface, Ω is the molecular volume and p_0 is the equilibrium vapor pressure over a flat surface. Since, generally, $p \approx p_0$, eqn (1) can be conveniently re-expressed for further analysis as;

$$p/p_0 \approx (1 + \mu/kT) \equiv [1 + (\Omega \gamma_s/kT)(1/R_1 + 1/R_2)] \quad (2)$$

The specific pressure difference Δp , between positions on the leading and trailing pore surfaces and within the pore interior dictate the matter transport between surfaces, in accord with the Langmuir relation;

$$M \approx \Delta p (m/2\pi kT)^{1/2} \quad (3)$$

where M is the mass of material transferred per unit area in unit time (a positive sign refers to net evaporation) and m is the weight of a molecule.

2.1 Steady State Pore Motion

For steady-state pore motion of an axisymmetric pore, conservation of matter within an element dx (fig. 1) requires that the mass transfer rate M be related to the velocity, v_p^e , by,

$$M ds = \rho v_p^e dx \quad (4)$$

where ρ is the density of the material and ds is the length of the pore surface within the element dx (fig. 1), such that

$$ds = dx / \cos \theta \quad (5)$$

where θ is the inclination of the surface to the x-axis. The mass transfer rate within the element dx is also related to the vapor pressure differential (eqn 3) by;

$$M = 2\pi(p-p^*) \sqrt{\frac{m}{2\pi kT}} x ds \quad (6)$$

where p^* is the vapor pressure within the pore. Inserting eqns (2) and (5) into eqn (6) then yields the mass transfer rate;

$$M = 2\pi \sqrt{\frac{m}{2\pi kT}} \left(\frac{x dx}{\cos \theta} \right) [p_0(1+\mu(x)/kT) - p^*] \quad (7)$$

Hence, matter conservation within the pore requires that;

$$\begin{aligned} & \int [p_0(1+\mu_t(x)/kT) - p^*] x dx / \cos \theta_t(x) \\ & + \int [p_0(1+\mu_\ell(x)/kT) - p^*] x dx / \cos \theta_\ell(x) = 0 \end{aligned} \quad (8)$$

where the subscripts ℓ and t refer to the leading and trailing surfaces

respectively. For steady-state pore motion (see section 2.2 for the associated restrictions), eqn (8) becomes

$$\left\{ [p_0(1+\mu_t(x)/kT) - p^*] / \cos\theta_t(x) \right\} + \left\{ [p_0(1+\mu_\ell(x)/kT) - p^*] / \cos\theta_\ell(x) \right\} = 0 \quad (9)$$

which can be rearranged to give;

$$\frac{p^*}{p_0} = 1 + \frac{\mu_t(x)\cos\theta_\ell(x) + \mu_\ell(x)\cos\theta_t(x)}{kT[\cos\theta_t(x) + \cos\theta_\ell(x)]} \quad (10)$$

Combining eqns (4), (5), (7) and (10) enables the steady state pore velocity to be expressed as;

$$\lambda \equiv kT \left(\frac{v_{p^0}^e}{p_0} \right) \sqrt{\frac{2\pi kT}{m}} = \frac{\mu_\ell(x) - \mu_t(x)}{\cos\theta_t(x) + \cos\theta_\ell(x)} \quad (11)$$

Note that, for a finite velocity ($v_p^e > 0$), the chemical potentials along the leading and trailing surfaces, at the pore/boundary intersection, $x=r$ (fig. 1), (i.e. $\mu_t(r)$ and $\mu_\ell(r)$) are unequal. A chemical potential discontinuity thus exists. This discontinuity must be eliminated by a local atom flux either over the cavity surfaces, or through the surrounding lattice. Consequently, pore motion is necessarily accompanied by localized diffusion. The solution of the coupled evaporation/condensation, diffusion process presents formidable problems. It has thus been assumed that local diffusion exerts a negligible influence on pore motion, when the diffusive mass transport rates are relatively low.

Neglect of the diffusive component has still not permitted a general solution of eqn (11). An approximation based on the difference

between the average chemical potential along the leading and trailing pore surfaces is thus invoked. This approximation is most pertinent when deviations from surface sphericity exhibited by the distorted pores are relatively small. Observations¹⁰ obtained (on MgO) within a pore size and temperature range that should yield evaporation/condensation dominated pore motion (section 2.3), indicate that approximate surface sphericity is maintained throughout the pore distortion process (fig. 2). It is presumed, therefore, that the adoption of this simplification yields useful information concerning pore motion.

The analysis can now be completed by noting that, at $x = r$

$$\mu_\ell(r) - \mu_t(r) = \lambda(\cos\psi_\ell + \cos\psi_t) \quad (12a)$$

while at $x=0$

$$\mu_\ell(0) - \mu_t(0) = 2\lambda \quad (12b)$$

where ψ_ℓ and ψ_t are the partial dihedral angles at the leading and trailing surfaces respectively (fig. 1), as related by;

$$\psi_\ell + \psi_t = \psi \quad (13)$$

Obtaining the average chemical potentials from eqn (12), the pore velocity becomes;

$$\lambda \approx \frac{2[\langle\mu_\ell\rangle - \langle\mu_t\rangle]}{2 + \cos\psi_t + \cos\psi_\ell} \quad (14)$$

But, the average chemical potential is related to the average radius of curvature of the pore surface (eqn 1) and to the partial dihedral angle by;

$$\langle \mu_{\ell,t} \rangle \equiv 2\Omega\gamma_s / \langle R_{\ell,t} \rangle = - 2\Omega\gamma_s \sin\psi_{\ell,t} / r \quad (15)$$

The steady-state pore velocity can thus be expressed as;

$$v_p^e \equiv \left(\frac{v_p^e \rho}{p_o} \right) \sqrt{\frac{\pi kT}{2m}} \left(\frac{kTr}{2\Omega\gamma_s} \right) \approx \frac{\sin\psi_t - \sin(\psi - \psi_t)}{2 + \cos\psi_t + \cos(\psi - \psi_t)} \quad (16a)$$

The dimensionless pore velocity, v_p^e , plotted in fig. 3, for several choices of ψ , indicates approximate linearity with ψ_t , as expressed by;

$$v_p^e \approx (\psi_t - \psi/2)(0.47 + 0.09\psi - 0.07\psi^2) \quad (16b)$$

The radius of contact, r , between the boundary and the pore can also be deduced by requiring that the pore volume be independent of pore velocity. The volume, V , of a stationary pore with radius a is given by;

$$V = 2\pi a^3 \left\{ 2/3 - \cos(\psi/2) \left[1 - \frac{\cos^2(\psi/2)}{3} \right] \right\} / \sin^3(\psi/2) \quad (17)$$

and hence, the contact radius for a moving pore becomes;

$$\frac{r}{a} = \left\{ \frac{4 - 2\cos(\psi/2)[3 - \cos^2(\psi/2)]}{\sin^3\psi_t \{2 - \cos\psi_\ell [3 - \cos^2\psi_\ell]\} + \sin^3\psi_\ell \{2 - \cos\psi_t [3 - \cos^2\psi_t]\}} \right\}^{1/3} \frac{\sin\psi_\ell \sin\psi_t}{\sin(\psi/2)} \quad (18)$$

This expression, plotted in fig. 4, indicates that an increase in pore velocity tends to appreciably diminish the pore radius (a behavior that contrasts with the insensitivity of the pore contact radius to pore velocity when the pore moves by surface diffusion³).

2.2 Pore Breakaway

The separation of pores from grain boundaries occurs as a natural consequence of the onset of non-steady-state pore motion. However, the non-steady-state transition does not emerge directly from the preceding simplified analysis of pore motion (in contrast with its natural emergence from the complete surface diffusion analysis).³ However, it is recognized (contingent upon the same approximation) that steady-state cannot exist when the partial dihedral angle at the trailing surface, ψ_t , exceeds $\pi/2$ (fig. 5). This can be appreciated by noting that, when $\psi_t > \pi/2$, evaporation must occur from the leading portion AB of the trailing surface (fig. 5b) in order to maintain steady-state, in violation of the negative pressure difference, $p_t - p^*$, that exists along that surface. Setting $\psi_t = \pi/2$, thus constitutes an approximate criterion for the transition to non-steady-state. At larger ψ_t , the deposition of material on the trailing surface causes the contact points between the grain boundary and the pore to converge onto the pore axis, resulting in eventual pore-grain boundary separation (fig. 5c).

The peak steady-state velocity $\hat{v}$ obtained by equating ψ_t to $\pi/2$ is plotted in fig. 6 and expressed by;

$$\hat{v}_p^e \equiv \left(\frac{v_p^e}{p_0} \right) \sqrt{\frac{\pi k T}{2m}} \left(\frac{k T a}{2 \Omega \gamma_s} \right) = 0.13 \psi^2 - 0.85 \psi + 1.4 \quad (19)$$

The pore shapes that develop at the maximum are constructed for several different dihedral angles in fig. 7.

The separation of pores from grain boundaries is governed by the requirement that the grain boundary velocity v_b exceeds $\hat{v}_p^e$. Noting that

$$v_b = \sqrt{3} \gamma_b M_b \Omega^{2/3} / R_b$$

where M_b is the boundary mobility, γ_b is the boundary energy and R_b is the radius of curvature of the boundary, the separation condition becomes;

$$\frac{a_c}{R_b} > 2 \sqrt{\frac{2}{3\pi}} \left(\frac{p_o \gamma_s \sqrt{m} \Omega^{1/3}}{M_b \gamma_b \rho (kT)^{3/2}} \right) (0.13\psi^2 - 0.85\psi + 1.4) \quad (20)$$

Hence, for a five-sided grain configuration³, with constant R_b (fig. 8), eqn (20) predicts a breakaway condition characterized by a critical pore/grain radius ratio. However, to avert separation from a disappearing three-sided grain³ (fig. 8), the inequality of eqn (20) must be averted when $R_b \sim 2a$. The resultant separation condition becomes grain and pore size independent as given by;

$$M_b > 4 \sqrt{\frac{2}{3\pi}} \left(\frac{p_o \gamma_s \sqrt{m} \Omega^{1/3}}{\gamma_b \rho (kT)^{3/2}} \right) (0.13\psi^2 - 0.85\psi + 1.4) \quad (21)$$

2.3 Relative Rates of Pore Motion By Evaporation/Condensation

A comparison of the present estimate of the maximum steady-state pore velocity induced by evaporation/condensation with that permitted by surface diffusion,³

$$\hat{v}_p^s \approx \frac{6\Omega D_s \delta_s \gamma_s}{kTa^3} (3-\psi) \quad (22)$$

where $D_s \delta_s$ is the surface diffusion parameter, identifies the range of conditions wherein the evaporation/condensation process becomes an important consideration. The resultant transition pore size is given by;

$$a_{s/e}^2 = \left(\frac{3\sqrt{\pi}}{\sqrt{2}} \right) \left(\frac{D_s \delta_s \rho \sqrt{kT}}{p_0 \sqrt{m}} \right) \frac{(3-\psi)}{(0.13\psi^2 - 0.85\psi + 1.4)} \quad (23)$$

such that evaporation/condensation dominates when $a > a_{s/e}$. Explicit pore velocity comparisons are conducted for the important refractory materials MgO and Al_2O_3 (Table I), using the equilibrium vapor pressures plotted in fig. 9. The peak pore velocities, plotted in fig. 10, indicate that evaporation/condensation can be excluded as a significant mechanism in Al_2O_3 at all reasonable pore sizes ($\leq 20 \mu m$). However, evaporation/condensation becomes the dominant transport mechanism in MgO at elevated temperatures ($> 2400^\circ K$ for $1 \mu m$ pores, $> 1900^\circ K$ for $5 \mu m$ pores and $> 1600^\circ K$ for $20 \mu m$ pores). It may also be a major mechanism in non-oxide materials, such as Si_3N_4 and SiC.

3. THE PORE/GRAIN SIZE TRAJECTORY

3.1 Pore Drag

The placement of cylindrical pores at three grain edges (fig. 11) generally modifies the motion of the attached grain boundaries and thereby, influences the grain and pore enlargement processes that occur during final stage sintering. When pore motion occurs by surface diffusion, the pore/grain ensemble exhibits two characteristic velocities;² a 'pore drag' velocity limited by the rate of motion of the pores (which obtains for large pores or at low surface diffusivities), and an 'intrinsic' velocity governed by the grain boundary mobility (which dominates when the pores are small or $D_s \delta_s$ is large). It is of present interest to evaluate the analagous 'pore drag' velocity that obtains when the pores

move by evaporation/condensation and to identify the conditions that dictate the operation of this mechanism.

Surface diffusion dominated pore drag is contingent upon the existence of steady-state pore configurations that modify the grain boundary curvature (fig. 12) and thereby, restrict the available grain boundary driving force. The analagous behavior under evaporation/condensation conditions is qualified by the inability of pores to move in a steady-state configuration when the pore distortion angle at the trailing surfaces, ψ_t , exceeds $\pi/2$ (fig. 12). When $\psi_t > \pi/2$, non-steady state motion results in the separation of the pore from the three grain corner onto the two grain interface. Pore drag is thus experienced over a limited range of conditions.

Pore drag, as expressed through the pore drag angle α (fig. 12), can be addressed using the same procedures described in the preceding section to yield the result (Appendix, eqn (A9));

$$\alpha \approx \pi/6 + \left(\frac{v_p^e \rho}{p_0} \right) \sqrt{\frac{\pi k T}{2m}} \left(\frac{k T a}{\Omega \gamma_s} \right) (0.8 - 0.3\psi + 0.05\psi^2)^{-1}$$

Noting that the grain boundary velocity v_b is dictated by α in accord with the relation;²

$$v_b \approx \frac{\gamma_b \Omega^{2/3} M_b}{\sqrt{3} \ell} (\sqrt{3} \cos \alpha - \sin \alpha) \quad (24)$$

where ℓ is the grain dimension (fig. 12) and that,²

$$v_p^e = v_b \cos \alpha, \quad (25)$$

the grain boundary velocity can be determined (see fig. 15). The two limit solutions of primary interest for determination of the microstructural

trajectory² obtain when $\alpha = \pi/6$ (the 'intrinsic' limit) and $\alpha \rightarrow \pi/3$ (the pore drag limit). The 'intrinsic' boundary velocity is given by;²

$$v_b = \gamma_b \Omega^{2/3} M_b / \sqrt{3} \ell \quad (26)$$

However, the pore drag limit, $\alpha = \pi/3$, is never attained for reasonable choices of the dihedral limit ($2\pi/3 > \psi > \pi/3$). Instead, a maximum pore drag develops when steady state is violated, at $\alpha = (\pi - \psi)/2$. An effective pore drag limit, derived from eqn (A9), by requiring that α exhibits its steady state maximum value, is given by;

$$\left(\frac{v_b^e \rho}{p_o} \right) \sqrt{\frac{\pi kT}{2m}} \left(\frac{kTa}{\Omega \gamma_s} \right) \approx (\pi/3 - \psi/2) \operatorname{cosec}(\psi/2) (0.8 - 0.3\psi + 0.05\psi^2) \quad (27)$$

Comparison with the 'intrinsic' boundary velocity (eqn 26) indicates that evaporation/condensation dominated pore drag obtains when;

$$a/\ell > \sqrt{6} \left(\frac{p_o \gamma_s \sqrt{m} \Omega^{1/3}}{\rho M_b \gamma_b (kT)^{3/2}} \right) (\pi/3 - \psi/2) \operatorname{cosec}(\psi/2) (0.8 - 0.3\psi + 0.05\psi^2) \quad (28)$$

Comparison with the pore drag limit for surface diffusion dominated pore motion;²

$$v_b \approx 8 D_s \delta_s \gamma_s \Omega / (1 + 3\psi) kTa^3 \quad (29)$$

indicates that the evaporation/condensation requirement, specified by eqn (28), is subject to the condition (based on $v_b^e > v_b^s$) that;

$$a^2 > (8\sqrt{\pi/2}) \frac{D_s \delta_s \rho \sqrt{kT} \sin(\psi/2)}{p_o \sqrt{m} (1 + 3\psi) (\pi/3 - \psi/2) (0.8 - 0.3\psi + 0.05\psi^2)} \quad (30)$$

3.2 The Pore/Grain Size Trajectory

The microstructure trajectory during sintering can be related to the grain boundary velocity by;²

$$da/d\ell = a/\ell - \sqrt{3}|\dot{a}|/v_b \quad (31)$$

where $\dot{a}$ is the rate of pore shrinkage, given for grain boundary diffusion by;¹¹

$$\dot{a} = - \frac{8\Omega D_b \delta_b \gamma_s F(\psi)}{3kT\ell a^2 (1-a/\ell)^2} \quad (32)$$

where

$$F(\psi) = \sin(\psi/2 - \pi/6) \left[1 + \sqrt{3} \frac{(\psi - \pi/3 - \sin(\psi - \pi/3))}{2\sin^2(\psi/2 - \pi/6)} \right]^{-1}$$

At the effective pore drag limit for evaporation/condensation controlled pore motion, the differential equation governing microstructural changes can be obtained from eqns (27), (31) and (32) as;

$$\frac{da}{d\ell} = \frac{a}{\ell} - \frac{\omega G(\psi)}{a\ell(1-a/\ell)^2} \quad (33)$$

where, $\omega = \rho D_b \delta_b \sqrt{kT}/p_0 \sqrt{m}$

and $G(\psi) = 8\sqrt{\pi/6} F(\psi) \sin(\psi/2)/(\pi/3 - \psi/2)(0.8 - 0.3\psi + 0.05\psi^2)$.

The coarsening ($da/d\ell > 0$) and shrinkage ($da/d\ell < 0$) regions expressed by eqn (33) are identified on fig. 13. Characteristic microstructural trajectories, obtained by numerical solution of eqn (33), in the range $a_0/\ell_0 = 0.2 - 0.4$, are also plotted on fig. 13 for $\ell_0 = 1 \mu m$. The trajectories reveal that pore shrinkage conditions capable of eventual

approach to full density ($a \rightarrow 0$) only obtain (subject to evaporation/condensation controlled pore motion) whenever the initial conditions satisfy certain prerequisites. These requirements, summarized in fig. 14, are predicated on the existence of both a continuous shrinkage zone (characterized by trajectories 1, 2 and 3 in fig. 13) and an eventual coarsening zone (trajectories 4, 5 and 6 in fig. 13). Evidently, the initial pore and grain size must be located within the continuous shrinkage region to ensure that the final pore size tends to zero. The continuous shrinkage condition may be expressed by the approximate relation;

$$a_0/\ell_0 \lesssim 3.5 \omega G(\Psi)/\ell_0^2 + 0.1 \quad (34)$$

When pore drag is superceded by 'intrinsic' coarsening, dictated by the mobility of the grain boundaries, the differential equation governing the pore/grain size trajectory has been derived as;²

$$\frac{da}{d\ell} = \frac{a}{\ell} - \frac{8F(\Psi)D_b\delta_b\Omega^{1/3}\gamma_s}{\sqrt{3} M_b k T \gamma_b a^2 (1-a/\ell)^2} \quad (35)$$

Some typical trajectories, obtained by numerical solution of eqn (35), are plotted on fig. 15, in conjunction with the regions of pore shrinkage and pore coarsening. In this instance, trajectories that initiate within the pore shrinkage region invariably result in continuous shrinkage (trajectories 1 and 2); while certain initial conditions within the pore coarsening regime are also capable of eventual shrinkage (trajectory 3). The region of eventual pore shrinkage is thus broader than anticipated by the shrinkage region depicted in fig. 15, as demonstrated (fig. 16) by the numerical

evaluation of eventual shrinkage trajectories from eqn (35). The 'intrinsic' region would thus appear to provide greater latitude for the attainment of full density during final stage sintering than the evaporation/condensation dominated pore drag region.

4. DISCUSSION AND CONCLUSIONS

The motion of pores by evaporation/condensation is primarily contingent upon the magnitude of the dimensionless pore size, $A = a^2 p_0 \sqrt{m} / D_s \delta_s \rho \sqrt{kT}$; such that large values of this pore size encourage evaporation/condensation. Specifically, for a typical dihedral angle of $2\pi/3$, pores at two grain interfaces are subject to evaporation/condensation dominated pore motion when $A \geq 18$. Pores on three grain edges exhibit evaporation/condensation control under more restricted conditions. Additionally, such motion requires that the dimensionless pore/grain size ratio, $a \rho M_b \gamma_b (kT)^{3/2} / 2 p_0 \gamma_s \sqrt{m} \Omega^{1/3}$ exceed a specified magnitude.

When the basic conditions for pore motion by evaporation/condensation are satisfied, the separation of pores from two grain interfaces is found to be dictated by the magnitude of the parameter, $Z = \rho M_b \gamma_b (kT)^{3/2} / p_0 \gamma_s \sqrt{m} \Omega^{1/3}$. The more stringent condition for averting separation, pertains to three-sided grains and requires that $Z \leq 1/3$ (for $\psi = 2\pi/3$) independent of the pore or grain size; while separation from five-sided grains (with a radius of curvature R) can be avoided when the size of the attached pores, $a \leq R/6Z$.

The microstructural trajectory exhibited by a system containing pores sufficiently large that evaporation/condensation controlled pore drag dictates microstructural changes is determined by the magnitude of the initial pore grain size ratio, a_0/ℓ_0 , vis-a-vis the dimensionless parameter, $X = \rho D_b \delta_b kT G(\psi)/P_0 \sqrt{m} \ell_0^2$. Specifically, a_0/ℓ_0 must be smaller than a specified value of X (in the range 0.05) to prohibit pore coarsening (resulting in terminal densities less than theoretical). For values of a_0/ℓ_0 small enough to permit pore shrinkage, both the pore size and the pore size ratio diminish and transitions to either surface diffusion controlled pore drag or 'intrinsic' grain growth are likely to occur. Then, the approach to full density is governed by alternate considerations.

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APPENDIX

The Distortion of Pores at Three Grain Channels

Using the approximation (section 2) that the pore surfaces remain nearly circular during pore distortion, the radii of curvature of the leading and trailing pore surfaces are given by;

$$\begin{aligned} R_\ell &= a/\sin\psi_\ell \\ R_t &= a/2 \sin(\psi/4 + \pi/4 - \psi_t/2) \sin(\psi/4 - \pi/4 + \psi_t/2) \end{aligned} \quad (A1)$$

The vapour pressures over both surfaces are;

$$\begin{aligned} p_\ell &= p_0 \exp [-\Omega\gamma_s/kTR_\ell] \\ p_t &= p_0 \exp [-\Omega\gamma_s/kTR_t] \end{aligned} \quad (A2)$$

and the matter deposition rates are;

$$\begin{aligned} M_\ell &= (p_\ell - p^*) (m/2\pi kT)^{1/2} \\ M_t &= (p_t - p^*) (m/2\pi kT)^{1/2} \end{aligned} \quad (A3)$$

Subject to matter conservation;

$$2M_t A_t + M_\ell A_\ell = 0, \quad (A4)$$

where $A_{t,\ell}$ are the pore surface areas per unit length,

$$\begin{aligned} A_t &= (\psi/2 - \pi/2 + \psi_t) R_t \\ A_\ell &= 2\psi_\ell R_\ell \end{aligned} \quad (A5)$$

the pore pressure becomes;

$$p^* = \frac{2p_t A_t + p_\ell A_\ell}{2A_t + A_\ell} \quad (A6)$$

Imposing the requirement;

$$M_\ell A_\ell = 2a_\rho v_p^e \quad (A7)$$

eqns (A2), (A3), (A6) and (A7) yield the pore velocity,

$$\frac{v_p^e}{p_0} \sqrt{\frac{\pi k T}{2m}} \left(\frac{k T a}{\Omega \gamma_s} \right) = \frac{A_t (\Psi - \Psi_t)}{(2A_t + A_\ell) \sin(\Psi - \Psi_t)} [2 \sin(\Psi/4 + \pi/4 - \Psi_t/2) \sin(\Psi/4 - \pi/4 + \Psi_t/2) - \sin(\Psi - \Psi_t)] \quad (A8)$$

Plots of the dimensionless velocity with pore distortion (fig.17), coupled with the geometric relation between Ψ_t , Ψ and the pore drag angle α , provide the following approximate relation;

$$\alpha \approx \pi/6 + \left(\frac{v_p^e}{p_0} \right) \sqrt{\frac{\pi k T}{2m}} \left(\frac{k T a}{\Omega \gamma_s} \right) (0.05 \Psi^2 - 0.3 \Psi + 0.8)^{-1} \quad (A9)$$

Table 1

Mass Transport Parameters for MgO and Al₂O₃

	MgO	Al ₂ O ₃
Density ρ (kg/m ³)	3.57×10^3	3.96×10^3
Molecular Weight m (kg/molecule)	6.7×10^{-26}	1.69×10^{-26}
Molecular Volume Ω (m ³)	1.87×10^{-29}	2.2×10^{-29}
Surface Energy γ_s (J/m ²)	1.0	0.9
D_s (m ² /s)	$3.7 \times 10^{-4} \exp \frac{-239\text{KJ/mole}^*}{RT}$	$10^4 \exp \frac{-544\text{KJ/mole}^{**}}{RT}$
δ_s (m)	4.2×10^{-10}	5×10^{-10}

* S. A. Lytle, M.S. Thesis, Penn. State Univ. (August 1981)

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Figure Captions

- Fig. 1. A schematic illustrating the pore distortion that accompanies pore motion by evaporation/condensation. The parameters used in the analysis are also identified on the figure.
- Fig. 2. Scanning electron micrographs of distorted pores in MgO, in the evaporation/condensation size range, indicating the approximate sphericity of the pore surfaces.¹⁰
- Fig. 3. The effect of dihedral angle on the relation between the normalized pore velocity and the partial dihedral angle at the trailing surface.
- Fig. 4. The change in pore radius with the pore velocity.
- Fig. 5. Schematic illustrating pore distortion effects (a) steady-state (constant shape) pore motion when the partial dihedral angle ψ_t at the trailing surface is $< \pi/2$, (b) Pore motion with constant shape when $\psi_t > \pi/2$; the pore curvature at AB is inconsistent with its projected direction of motion, (c) The non-steady-state pore shape changes that must occur when $\psi_t > \pi/2$.
- Fig. 6. The maximum steady-state velocity as a function of the dihedral angle.
- Fig. 7. Typical pore shapes at the maximum steady-state velocity.
- Fig. 8. Schematic illustrating pores attached to five-sided and three-sided grains.
- Fig. 9. Equilibrium vapor pressures for Al_2O_3 and MgO.¹²
- Fig. 10. The temperature dependence of the maximum pore velocities attained by surface diffusion and evaporation/condensation (a) Al_2O_3 (b) MgO.

- Fig. 11 A schematic illustrating cylindrical pores attached to the corners of a three-sided grain.
- Fig. 12. A schematic illustrating the decrease in the boundary curvature, R_b that accompanies an increase in the drag angle α due to pore distortion.
- Fig. 13. The region of pore coarsening and pore shrinkage identified in the analysis. Also shown are 6 trajectories for different choices of the parameter $\omega G(\psi)$ and different pore sizes. In each case the initial grain size is $1 \mu\text{m}$.
- Fig. 14. Regions of continuous pore shrinkage and eventual pore coarsening identified from the trajectories plotted on fig. 13.
- Fig. 15. The regions of pore shrinkage and coarsening when grain growth is boundary mobility limited. Also shown are some typical trajectories for selected values of both the initial pore size (the initial grain size is $1 \mu\text{m}$) and the mobility parameter: $H(\psi) = (8/\sqrt{3})F(\psi)$.
- Fig. 16. The regions of continuous pore coarsening and eventual pore shrinkage for 'intrinsic' mobility limited, microstructural changes, identified from the trajectories plotted on fig. 15: $H(\psi) = (8/\sqrt{3}) F(\psi)$.
- Fig. 17. The variations in the dimensionless pore and boundary velocities with partial dihedral angle, for pores attached to three-grain edges.

XBL823-5458

Fig. 1

PORE SHAPES IN SEQUENCE DURING BREAKAWAY

Fig. 2

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Fig. 3

XBL 823-5460

Fig. 4

XBL 823-5461

Fig. 5

XBL 823-5462

Fig. 6

(a) $\psi = 80^\circ$

↓ $\hat{\nu}_P^e = 0.46$

(b) $\psi = 100^\circ$

↓ $\hat{\nu}_P^e = 0.31$

(c) $\psi = 120^\circ$

↓ $\hat{\nu}_P^e = 0.19$

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Fig. 7

(a) FIVE-SIDED GRAINS

(b) THREE-SIDED GRAIN

XBL 824- 5488

Fig. 8

XBL 823-5464

Fig. 9

XBL823-5465

Fig. 10a

XBL 823-5466

Fig. 10b

XBL 823-5467

Fig. 11

XBL 823-5468

Fig. 12

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Fig. 13

XBL 823-5470

Fig. 14

XBL 823-5475

Fig. 15

XBL 823-5476

Fig. 16

XBL 823-5471

Fig. 17

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