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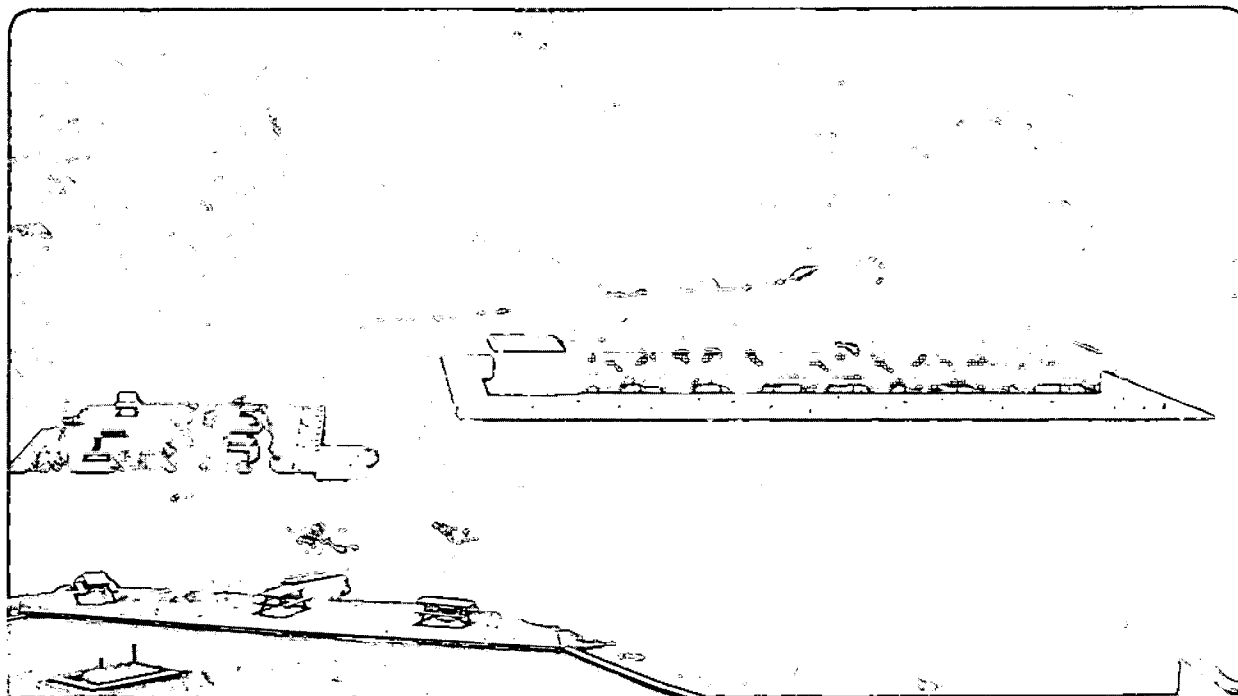
SOME ASPECTS OF THE BEHAVIOR OF VOIDS IN
POLYCRYSTALLINE CERAMICS

M.D. Drory
(M.S. Thesis)

January 1985

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OF VOIDS IN POLYCRYSTALLINE CERAMICS

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M.S. Thesis

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This work was supported by the Director, Office of Energy Research,
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ABSTRACT

An analysis of the growth and shrinkage rates of ellipsoidal voids on three grain junctions is presented. The predicted rates are compared with those for cylindrical pores on the same interfaces. It is demonstrated that the sintering of ellipsoidal pores occurs more rapidly, by virtue of the increased surface curvature. The formation of such pores by the Rayleigh instability mechanism thus appears to constitute an important step in final stage sintering. Conversely, under creep loading, cylindrical voids grow at a faster rate, suggesting that creep damage develops more slowly when discrete ellipsoidal voids are maintained on three grain junctions.

In a second part of this work a preliminary study was conducted of the removal of surface porosity in a typical ceramic polycrystal. Surface voids were observed to be eliminated in hot-pressed MgO packed in a fine powder and heat treated at an elevated temperature. Surface diffusion along the specimen surface and evaporation/condensation of the surrounding powder are considered as filling mechanisms. Mechanism maps are plotted to identify the relevant parameters for the dominant filling mechanism.

Acknowledgements

The author wishes to express his gratitude for the guidance and strong encouragement from Professor A.G. Evans.

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PART I.

GENERAL INTRODUCTION

1. General Introduction

Void behavior in polycrystalline ceramics, at elevated temperatures, has been extensively studied in recent years to better characterize and predict high temperature mechanical properties. Analogous studies in metals by Greenwood¹ and McClean² have shown experimentally, that under an applied stress, voids form perpendicular to the loading (or straining) direction and grow to eventually link-up causing failure. Similar observations were made in creep studies of Al_2O_3 in early work by Folweiler,³ and more recently by Evans, et al.^{4,5} Typical morphology of the early stages of creep damage in Al_2O_3 is shown in Figs. 1, 2. The figures illustrate that void cavitation and growth produce "equilibrium" shaped voids of constant curvature, and "crack-like" voids at various locations on some grain boundaries.

A comprehensive description of void behavior at elevated temperatures requires examination of several important features*:
 i) void nucleation, ii) inhomogeneous damage accumulation and
 iii) void growth. Void nucleation has been studied by Raj and Ashby.⁶ Damage accumulation has been more recently examined by Hsueh and Evans.⁷ Part of this thesis will focus on aspects of void growth.

The first model of void growth, in polycrystalline materials at elevated temperatures, was developed by Hull and Rimmer⁸ for a homogeneous square array of spherical voids on a single planar grain

*The effects of an intergranular liquid phase are not subjects of this thesis.

boundary, shown schematically in Figs. 3, 5a. This configuration models the creep growth behavior of intergranular voids on the two-grain interface, and attempts to estimate the void growth rate and creep rupture time. Void growth occurs under an applied stress by a diffusive flux of atoms (or vacancies) along the grain boundary. Matter from the void surface is uniformly removed by rapid surface diffusion and uniformly deposited on the grain boundary which displaces rigidly. An important assumption of this model is the initial spherical shape of the nucleated void, which remains spherical as the void grows. A second key assumption is the grain boundary configuration. Clearly a judicious choice was made for this model by considering axisymmetric voids on the two-grain interface (Fig. 5a). Three-grain junction voids are more typical of ceramic materials (Fig. 1). Consequently, the present study considers this more complex geometric configuration.

Hull and Rimmer's analysis has provided a guide for numerous studies which followed. It is therefore worthwhile to highlight several important features of their work. Foremost is the discussion of driving force which followed work by Herring.⁹ The driving force for diffusive void growth is the difference in chemical potential between sources and sinks, or for example, the void surface and the planar grain boundary. The chemical potential difference between the void surface and an arbitrary reference potential, $\Delta\mu$, is related to the surface energy, γ_s , the atomic volume, Ω , and void radius of curvature by,

$$\Delta\mu = - 2\gamma_s \Omega/R \quad (1)$$

where R is the radius of the spherical void. The chemical potential (difference) for a grain boundary, subject to a normal stress, σ , is given by,

$$\Delta\mu = - \Omega\sigma \quad (2)$$

The preceding equations are boundary conditions for the governing equation which relates the derivative with arc length of the chemical potential, $\partial\mu/\partial s$, to the diffusive flux rate J ,

$$J = - \frac{D_b \delta_b}{kT} \frac{\partial\mu}{\partial s} \quad (3)$$

where $D_b \delta_b$, is the grain boundary diffusivity, k is Boltzmann's constant, and T , is the absolute temperature. From the flux equation and boundary conditions, it can be seen intuitively, that the flux rate, hence the void growth rate, increases with increasing applied stress, but decreases with increasing void curvature. The void growth rate is found from the flux equation by considering conditions of mechanical equilibrium and volume conservation. The void growth rate was found in Hull and Rimmer's study to be linearly related to the stress. Again, the specific void shape and grain boundary configuration are key assumptions in their model.

Another important feature of their analysis identifies the critical size for void growth, R^* ,

$$R^* = 2\gamma_s / \sigma_\infty \quad (4)$$

where σ_∞ is the applied stress.

Void shrinkage occurs for radii smaller than R^* , and void growth with radii greater than R^* . Void shrinkage behavior during final stage sintering can thus be analyzed with the same model by considering void

sizes less than the critical size (for a given applied stress). Hull and Rimmer demonstrated that void models for diffusive growth during creep have the added utility for simultaneously modeling, under appropriate conditions, some aspects of final stage sintering.

Of added interest from Hull and Rimmer's model is the ratio of lattice to grain boundary diffusivities, $D_l/D_b\delta_b$. Since void growth can also occur by diffusion of vacancies from the lattice (which dominates over grain boundary diffusion for large grain sizes and higher temperatures), ratios of diffusivities are employed to identify the dominant mechanism. As an example, implicit in Hull and Rimmer's analysis is a large value of $\Delta \equiv D_s\delta_s/D_b\delta_b$, the ratio of surface to grain boundary diffusivity. A large value of Δ is necessary for maintaining constant void curvature, i.e. a spherical void shape as the void grows. Studies following Hull and Rimmer's examined Δ and other ratios, which are important parameters in specifying void growth behavior (e.g. Refs. 9-14).

Several studies corrected Hull and Rimmer's analysis,^{15,16} however the linear stress relation still follows. Raj and Ashby⁶ reanalyzed the problem for a more general void shape but with the same grain boundary geometry, as shown in Fig. 4. They considered axisymmetric voids with dihedral angles* less $\pi/2$. The solution to the corrected Hull and Rimmer problem follows as a special case with $\psi = \pi/2$.

*The dihedral angle is defined as the ratio of grain boundary to surface energies (see Fig. 4), and is expressed as, $\cos \psi = \gamma_b/2\gamma_s$.

Another important aspect of the void geometry illustrated by these models^{6,8} is the symmetry of the axisymmetric voids. The symmetry simplifies the diffusion analysis to a radial flux problem. Because of symmetry, a one-dimensional analysis also applies to infinitely-long cylindrical voids. Such voids have been emplaced along two and three grain interfaces. The cylindrical and other void geometries are shown schematically in Figs. 5 and 6.

Rice and others^{10,11} considered void growth of crack-like and equilibrium shaped voids with axisymmetric and cylindrical symmetry on the two-grain interface. The crack-like morphology (Fig. 6) dominates for relatively small surface diffusivities, high applied stress, and large void sizes. Void growth rates were also determined for so-called self-similar void shapes which are intermediate shapes between equilibrium and crack-like. Their work also considered the transition between void shapes during growth. Intuitively, a transition from equilibrium to crack-like voids occurs because the corresponding increase in surface area no longer allows constant curvature to be maintained. Similarly at high applied stress, the increased grain boundary flux leads to non-equilibrium shapes.

The first part of this thesis examines the growth and shrinkage behavior of equilibrium-shaped voids at the three grain junction. The void geometry differs from the long-cylindrical void by an out-of-plane radius of curvature equal to the in-plane radius of curvature. That is, a section of the void between adjacent inclined grain boundaries is spherical. A large number of voids are distributed uniformly in a regular array at the three-grain interface, and grow or shrink by

grain boundary diffusion. Surface diffusion is considered rapid enough to maintain constant void curvature. This configuration was previously considered by Raj and Ashby⁶ who correctly developed an expression for volume conservation but neglected contributions to the boundary flux by inclined grain boundaries. The void growth and shrinkage rates will be compared to equivalent configurations of equilibrium cylindrical voids to assess the relative contribution of these configurations in the early development of creep damage and toward void shrinkage during final stage sintering.

The second part of this thesis applies the principles mentioned above to consider the shrinkage of intragranular surface voids by surface diffusion or evaporation/condensation. Eliminating surface voids may improve mechanical strength by decreasing the size of flaws present as surface voids, which interact with machining cracks to form fracture limiting flaws.^{17,18}

It was observed that heat treating nearly fully dense hot pressed MgO eliminated most porosity on or near the surface. The elimination rate, characterized experimentally, was correlated with approximate models of void filling by surface diffusion and evaporation/condensation.

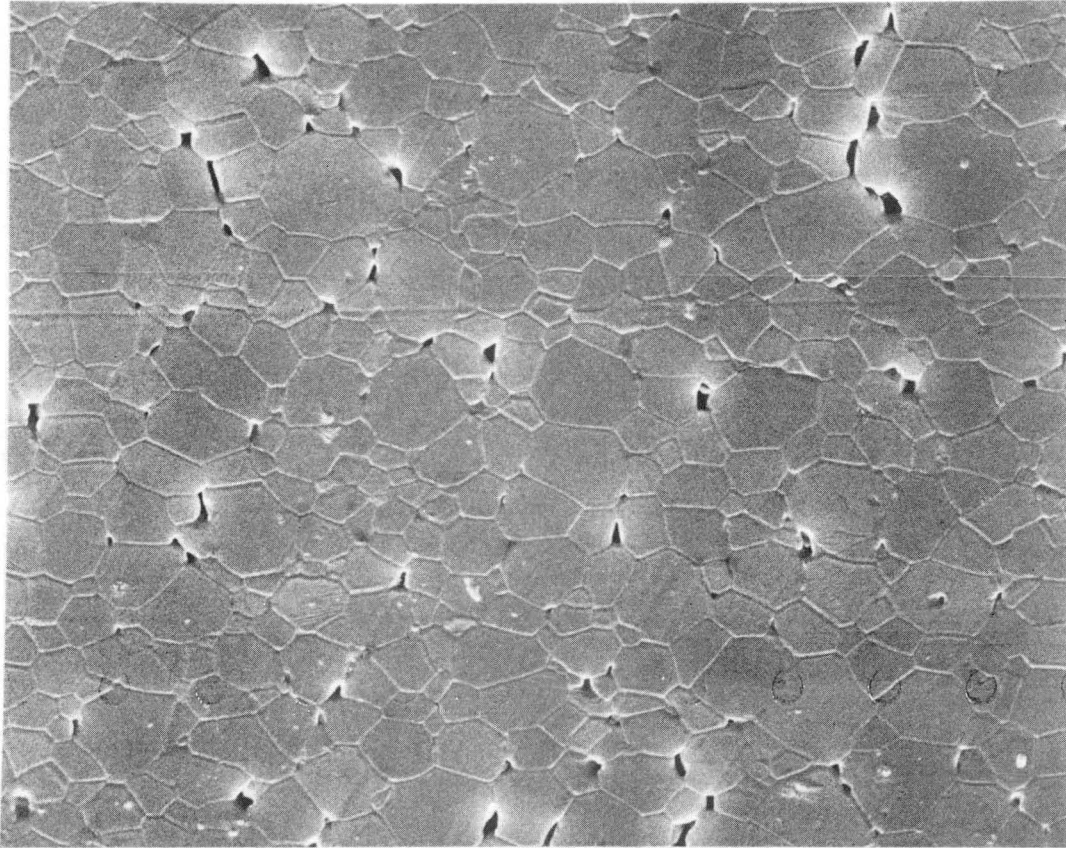
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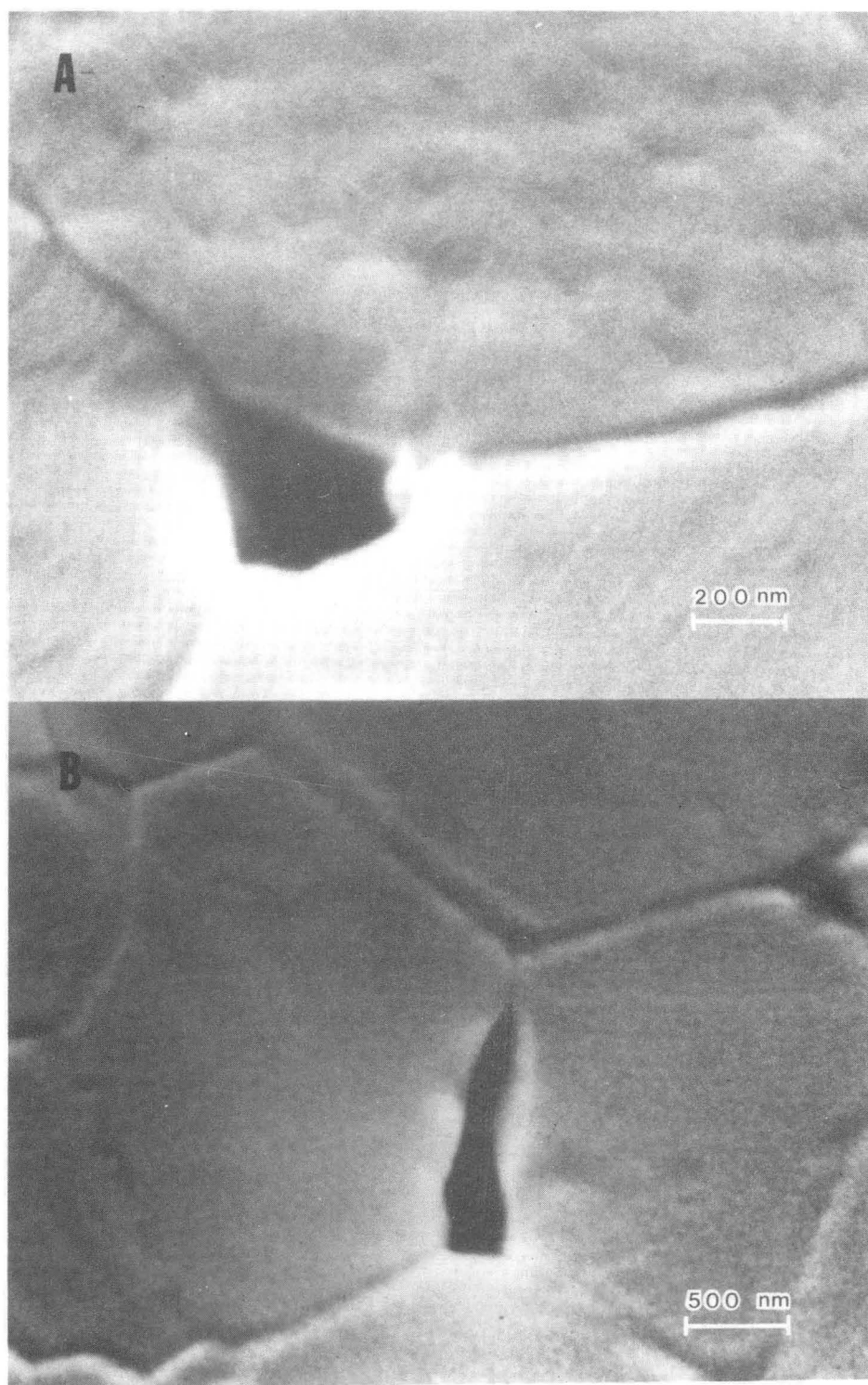
FIGURE CAPTIONS

- Fig. 1. Scanning electron micrograph of creep damage in Al_2O_3 (courtesy W. R. Blumenthal)
- Fig. 2. Scanning electron micrograph of (a) equilibrium and (b) crack-like voids in Al_2O_3 (courtesy W. R. Blumenthal).
- Fig. 3. Void configuration in Hull and Rimmer's⁸ analysis of spherical voids on the two-grain interface.
- Fig. 4. Void configuration in Raj and Ashby's⁶ model of the void behavior on the two-grain interface. The dihedral angle is also defined.
- Fig. 5. Geometry of an equilibrium void on the (a) two-grain interface, and (b) three-grain interface.
- Fig. 6. Geometry of a crack-like void on the three-grain interface.



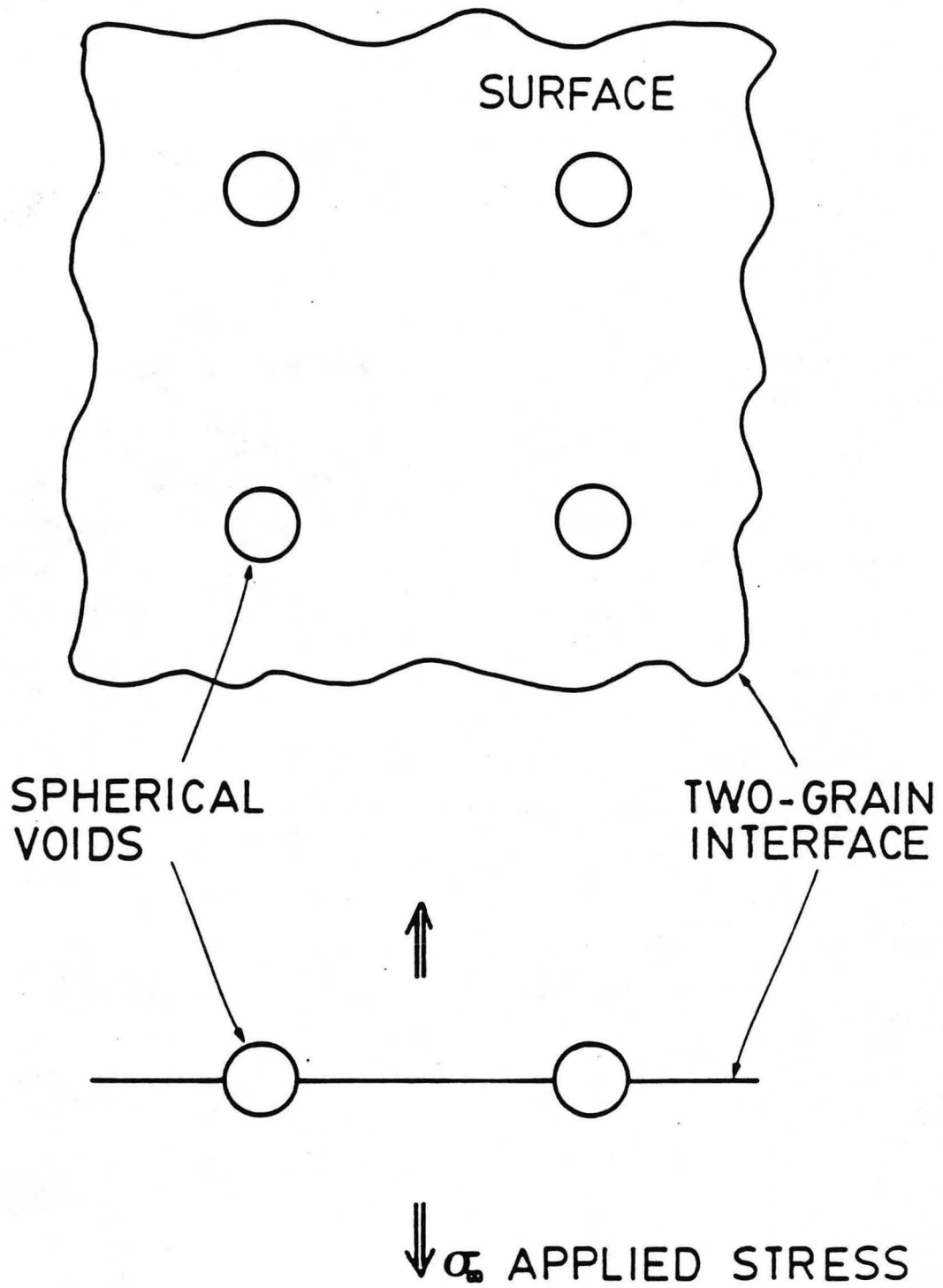
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Fig. I-1



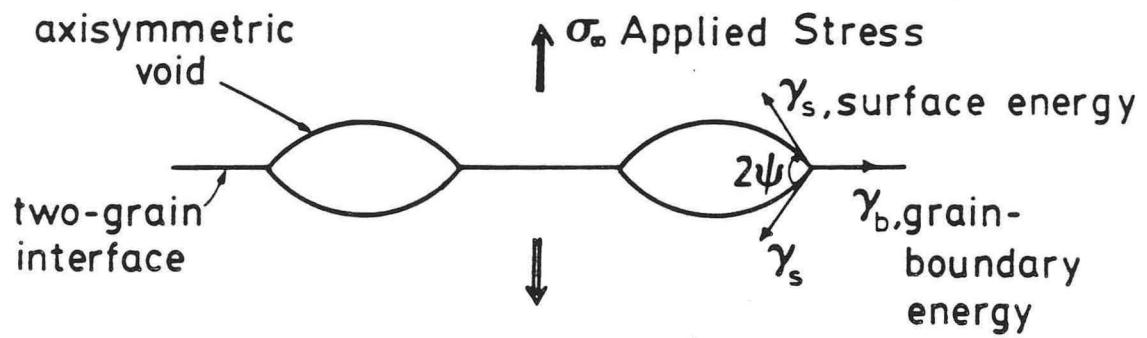
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Fig. I-2



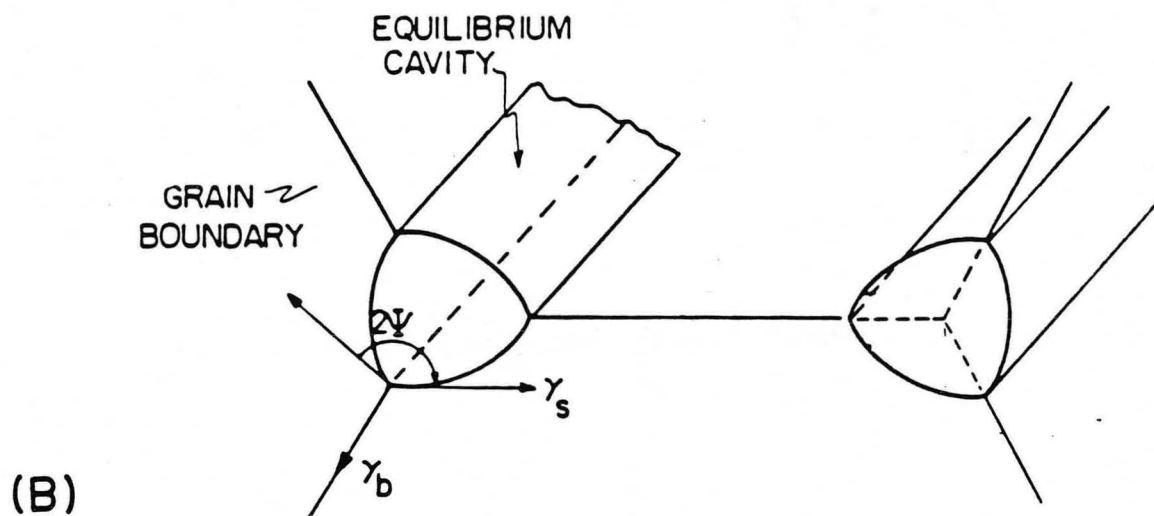
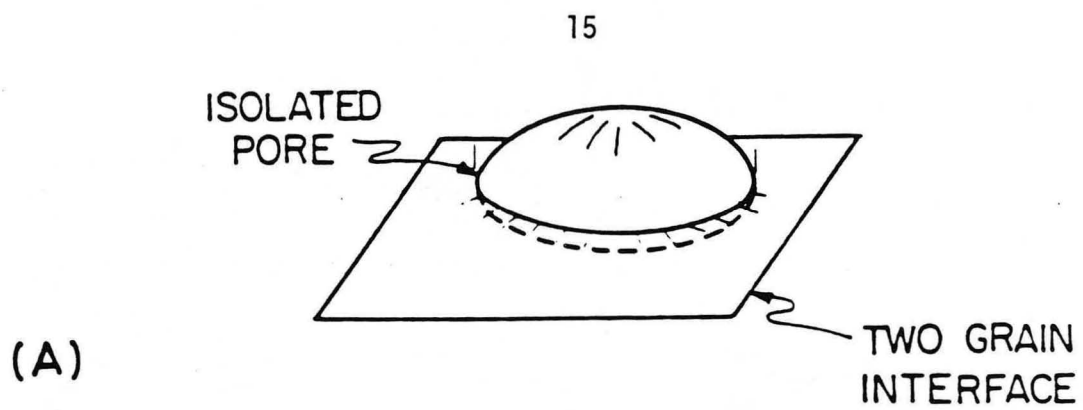
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Fig. I-3



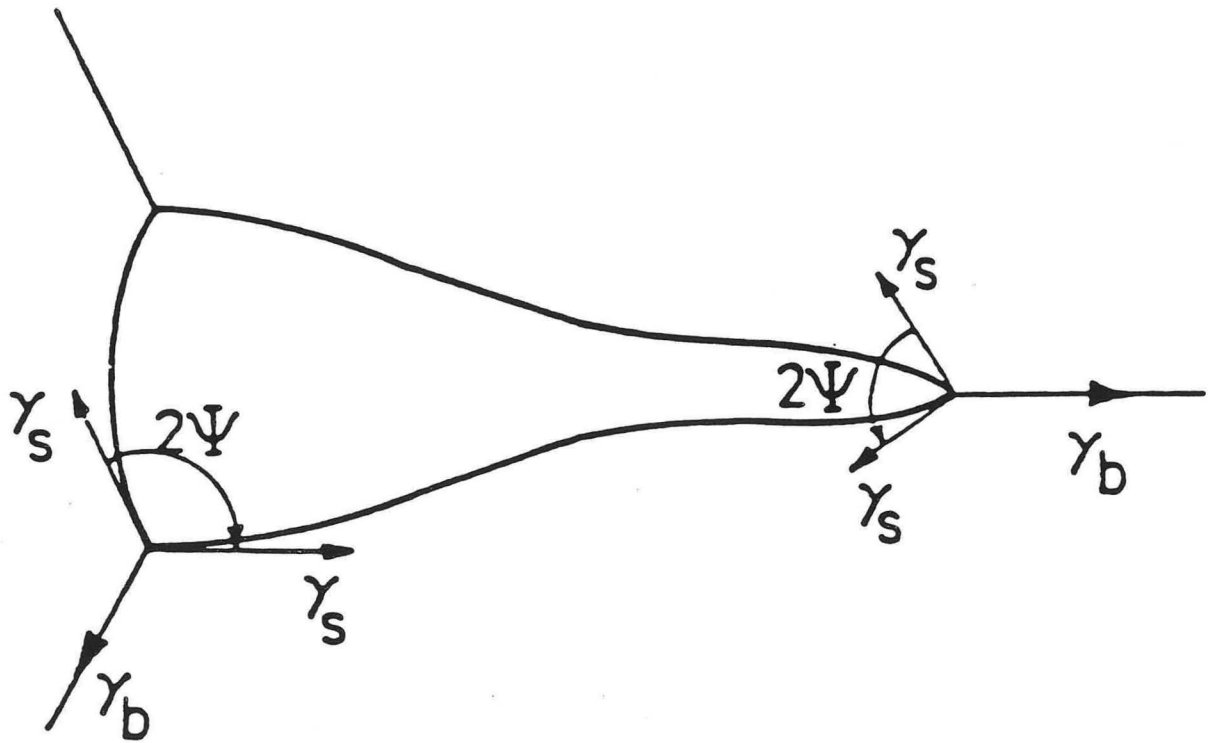
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Fig. I-4



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Fig. I-5



CRACK-LIKE CAVITY

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Fig. I-6

PART II

EFFECTS OF VOIDS AT THREE GRAIN
JUNCTIONS ON SINTERING AND CREEP DAMAGE

1. Introduction

Observations on ceramics sintered into the final stage reveal the ubiquitous presence of pores along three grain junctions (Fig. 1). Such pores must, therefore, exert a significant influence upon the sintering behavior and the eventual microstructure. Similar pores are observed following high temperature creep of fine grained ceramics^{1,2} and contribute significantly to the early stages of failure. The intent of the present paper is to provide an analysis of the growth or shrinkage of such pores during sintering and creep. A prior analysis³ provides a rigorous geometric description of the three grain junction pores, but has the limitation that the pores are arranged in a planar array on a single grain boundary. More realistic pore and grain boundary configurations are used in the present study.

During sintering, it is generally conjectured that three grain junction pores (Fig. 2) form by a (surface diffusion dominated) Rayleigh instability, wherein cylindrical pores located along three grain interfaces develop an unstable perturbation.^{4,5} Various pore arrays may thereby be created along the grain junction, depending upon the wavelength of the perturbation with the maximum growth rate. Total void volume is generally conserved for the duration of the instability, because of the relatively large chemical potential gradients that govern surface diffusion within the perturbed void. The significance of this event for the formulation of final stage sintering theory is thus ascertained by comparing the sintering rate of the "ellipsoidal" voids*

*The term 'ellipsoidal' is chosen to describe the morphology of the voids on the three grain interface.

created by the instability with that of a cylindrical void having equal volume. Furthermore, by varying the number of voids on the three-grain junction, the specific contribution of the Rayleigh instability (or other pore "break-up" mechanisms) to the sintering rate, can be assessed.

In fine grained ceramics, pores are also observed to nucleate on three grain junctions during creep¹ (pores rarely nucleate on two grain interfaces,^{1,2} in contrast to the behavior observed in most metals). The pores nucleated along the three grain junction then grow into cylindrical pores, which thereafter extend into full-facet cavities (Fig. 3) and eventually, induce rupture. The pore growth process along the three grain junction thus constitutes an important early phase in the failure cycle. Specifically, the time taken for ellipsoidal pores to coalesce along the three grain junction is compared with the time for cylindrical voids to enlarge to the same radial dimension.

The present analysis is restricted to equilibrium shaped cavities, viz. cavities which exhibit uniform surface curvatures (Fig. 2b). Such shapes are consistent with the pores generally observed during the final stage of sintering and initial creep of fine grained ceramics.^{1,2} The equilibrium shape assumption implies that the surface flux is relatively rapid,⁶ and that pore growth is either grain boundary or lattice diffusion dominated. For present purposes, grain boundary diffusion is selected as the primary pore growth mechanism, because creep studies in fine grained ceramics have revealed the dominant role of the grain boundary flux on the creep rate.⁸ The results of the analysis should thus be most pertinent to fine grained ceramics.

2. Pore Growth and Shrinkage

The present analysis of the growth or shrinkage of voids follows the general procedures developed in prior void growth studies.^{6,7} However, the complex void morphology requires the introduction of geometric simplifications to achieve analytic tractability. A typical geometry is depicted in Figs. 2,4, consisting of several ellipsoidal pores along the three grain junction and pores at each four grain intersection. The flux from the pores enters the triangular grain boundary area illustrated in Fig. 4, such that the grain facet center is a center of symmetry. An axisymmetric geometric simplification is thus suggested for present purposes (Fig. 4), with the grain facet center as the zero flux location and with the pores emplaced at the circumference. The grain facet area is then approximated by a $\pi/3$ circular section. As a further simplification, four grain junction pores are taken as additional ellipsoidal pores.

2.1 General analysis

For the axisymmetric approximation, the governing equation for the stress along the grain boundary, in the presence of grain boundary diffusion, is⁶

$$\text{or, } (D_b \delta_b \Omega / kT) (1/r) \partial [r \partial \sigma / \partial r] / \partial r + \dot{\delta} = 0$$

$$d^2 \sigma / dr^2 + (1/r) d\sigma / dr + (kT \dot{\delta} / D_b \delta_b) = 0 \quad (1)$$

where $D_b \delta_b$ is the grain boundary diffusion parameter, Ω , the atomic volume, $\dot{\delta}$ the grain center displacement rate and r is the distance from the grain facet center (Fig. 4). For the usual rigid grain assumption,⁶ the grain separation rate, $\dot{\delta}$, is position independent and hence Eqn. (1) has a general solution of the form,

$$\sigma(r) = c_1 + c_2 \ln r - (r^2/4)(kT\dot{\delta}/D_b\delta_b\Omega) \quad (2)$$

where the constants c_1 , and c_2 are to be determined from both the boundary conditions, and geometric considerations. Geometry dictates the relation between the void radius of curvature R , the cavity length, a , and the dihedral angle, 2ψ (Fig. 2). Specifically, since the void surface is a portion of a sphere, and the void intersects each grain boundary at an angle ψ , R is given by

$$R = a/[1-(4/3)\cos^2\psi]^{1/2} \quad (3)$$

Continuity of chemical potential requires that the stress at the surface of the void be a function of the surface energy, γ_s , and the radius of curvature R , such that,

$$\sigma(\ell) = 2\gamma_s/R \quad (4)$$

where the principal radii of curvature, which drive the diffusion, are given by the sphere radius, R . The driving force is considered to be constant at $r = \ell$. Clearly, this approximation is inappropriate when the number of voids, N , spanning the grain junction is small (i.e. $N \leq 5$).

Symmetry requires that the maximum stress occur at the midpoint of the grain facet, i.e.

$$\left. \frac{d\sigma}{dr} \right|_{r=0} = 0 \quad (5)$$

Inserting the preceeding conditions into Eq. (2), the stress distribution along the boundary facet then follows as,

$$\sigma(r) = 2\gamma_s/R + (1/4)(\ell^2 - r^2)(kT\dot{\delta}/D_b\delta_b\Omega) \quad (6)$$

The stress distribution on the facet normal to the applied stress must

satisfy mechanical equilibrium, as expressed for the axisymmetric approximation by,^{†6}

$$\sigma = \frac{2}{\ell^2} \int_0^\ell \sigma(r) r dr \quad (7)$$

Finally in order to determine $a(t)$, the grain center displacement rate, $\dot{\delta}$, must be specified. Rigid grain displacement conditions dictate that the flux along the grain facet normal to the applied stress be twice that along the inclined boundaries. Half of the volume increase of the void is thus deposited along the normal grain boundary. Hence, matter conservation requires that,

$$\dot{\delta} = \dot{NV}/2A \quad (8)$$

where $\dot{V}$ is the rate of increase of the ellipsoidal void volume and A ($= \pi \ell^2/6$) is the triangular grain facet area (Fig. 4). Following the geometric considerations used above in deriving R , the volume can be expressed as a function of $a(t)$, and ψ , and has been reported previously as,³

$$V = 2R^3 [\pi - 2\sin^{-1}(\csc\psi/2) + (1/3)\cos^2\psi (4\sin^2\psi - 1)^{1/2} - \cos^{-1}(\cot\psi/\sqrt{3})\cos(3 - \cos^2\psi)] \quad (9)$$

Combining the stress distribution (Eq. 6), the grain center displacement rate (Eq. 8), and the void volume (Eq. 9), the dimensionless time, $t[D_b\delta_b\gamma_s\Omega/kT\ell^4]$, for the ellipsoidal void to either shrink or grow from an initial size, $\eta_0 [a(t=0)/\ell]$ to a final size, $\eta_1 [a(t=t_1)/\ell]$ can be deduced as:

[†]The force associated with the surface stress at the pore/grain boundary intersection has been neglected, following Rice and Chuang⁹ and several prior analyses^{3,6,10} because of the uncertainties in deriving the surface stresses from the surface energy.

$$t[D_b \delta_b \gamma_s \Omega / kT \ell^4] = [27f(\psi)N/8\pi(\sigma_\infty \ell / \gamma_s)^4] \int_{b_0}^{b_1} (x^2 + 6cx + 12c^2 + 8c^3/x) dx \quad (10)$$

where $b = (\sigma_\infty \ell / \gamma_s) \eta - 2c$, and $c = [1 - (4/3)\cos^2\psi]^{1/2}$.

Integration of Equation (10) gives,

$$t[D_b \delta_b \gamma_s \Omega / kT \ell^4] = [27f(\psi)N/8\pi(\sigma_\infty \ell / \gamma_s)^4] \left\{ (b_1^3 - b_0^3)/3 + 3c(b_1^2 - b_0^2) + 12c^2(b_1 - b_0) + 8c^3 \ln(b_1/b_0) \right\} \quad (11)$$

Cursory inspection of Eqn. (11) might indicate that the sintering time increases as the number of voids, N , increases. However, it will be demonstrated below that the converse behavior prevails, because the integration limits b_1 and b_0 are functions of N .

2.2 The creep growth: sintering transition

A prerequisite for deriving void behavior from Eqn. (11) is the determination of the critical size for the transition between sintering and creep growth. For this purpose, setting b in Eqn. (10) to zero, the critical dimensionless pore size, η_t , at the transition (independent of the number of voids present on the three grain junction) can be found as a function of the stress $(\sigma_\infty \ell / \gamma_s)$, and the dihedral angle ψ , viz.,

$$\eta_t = 2(\gamma_s / \sigma_\infty \ell) [1 - (4/3)\cos^2\psi]^{1/2} \quad (12)$$

For small initial void sizes, $\eta < \eta_t$, sintering conditions prevail, while creep growth occurs when $\eta > \eta_t$. The trends in η_t predicted by Eqn. (12) are illustrated in Fig. 5. Note that, for a given

applied stress η_t increases with dihedral angle, but varies inversely with stress.

2.3 Sintering

Application of Eqn. (11) to the analysis of void removal times by sintering, requires that the initial void size be specified. For present purposes, it is assumed that the initial ellipsoidal void configuration, following the Rayleigh instability, consists of connected voids that span the three grain junction (Fig. 2a). Hence, at zero applied stress, the initial ellipsoidal void size, η_0 , is simply,

$$\eta_0 = \pi/6N \quad (13)$$

The times required for the shrinkage of voids from η_0 to zero are thus obtained from Eqn. (11) as,

$$t[D_b \delta_b \gamma_s \Omega / kT \ell^4] = f(\psi) \pi^3 / \{ 3072 N^3 [1 - (4/3) - \cos^2 \psi]^{1/2} \} \quad (14)$$

The influence of the number of voids on the sintering time, deduced from Eqn. (14) is illustrated in Fig. 6. It is evident that the sintering time decreases as the number of voids increases.

In the presence of an applied stress, the initial void size capable of inducing sintering is limited by the transition size, η_t . Consequently, integration of Eqn. (10), with η_t as the integration limit, yields upper bound shrinkage times, as plotted in Fig. 7. Note that the shrinkage time increases with applied stress, but displays a minimum with varying dihedral angle. The minimum reflects a balance between the larger surface curvature (larger driving force) and the increased void volume, as ψ increases.

2.4 Creep growth

When the initial relative void size, η exceeds the transition size η_t , creep growth conditions prevail. In this regime, stable creep damage is expected whenever the voids nucleate to a size $\geq \eta_t$. When this condition is satisfied, the time required for the voids to coalesce into a cylindrical void along the three grain junction can be found from Eqn. (11), by setting the initial void size equal to the transition size, η_t , and letting the final void size equal the coalescence length, $\eta^*(=\pi/6N)$. Some results are plotted in Fig. 8, showing that the coalescence time increases with increasing dihedral angle but decreases with increasing applied stress.

3. Comparison with Cylindrical Voids

The relative influence of three grain junction pores during sintering or creep can best be appreciated by comparison with the behavior of a cylindrical pore, symmetrically located around the facet center. The stress on the grain boundary at the void surface, for this configuration, is given by

$$\sigma(\ell) = \gamma_s (1/R - 1/\ell) \quad (15)$$

Hence, the stress along the grain boundary, may be derived from Eqns (2) and (5) as;

$$\sigma(r) = \gamma_s (1/R - 1/\ell) + (1/4)(\ell^2 - r^2)[kT\dot{\delta}/D_b\delta_b\Omega] \quad (16)$$

Combining with Equation (8) and inserting expressions for the void radius, R , and volume, V ;⁷

$$R = s[\sin\psi + \cos\psi/\tan(\psi - \pi/6)] \quad (17a)$$

$$V = (\pi\sqrt{3}/4)F(\psi)\zeta^2\ell^3 \quad (17b)$$

where ζ is the distance from the center of the cylinder to the grain boundary intersection⁷, $\zeta = s/\ell$, and $F(\psi) = 1 + (\sqrt{3}/2) [(2\psi - \pi/3 - \sin(2\psi - \pi/3))/\sin^2(\psi - \pi/6)]$, gives the dimensionless time, $t[D_b\delta_b\gamma_s\Omega/kT\ell^4]$, for the cylindrical void to shrink or grow, as

$$t[D_b\delta_b\gamma_s\Omega/kT\ell^4] = (3\sqrt{3}/16)F(\psi)d_1 \int_0^1 \left\{ y^2 / [(\sigma_\infty\ell/\gamma_s + 1)d_1 y - 1] \right\} dy \quad (18)$$

where $d_1 = \sin\psi + \cos\psi/\tan(\psi - \pi/6)$.

As with ellipsoidal voids, distinct sintering and creep regimes are identified by the transition pore size, ζ_t , given by

$$\zeta_t = 1/(\sigma_\infty\ell/\gamma_s + 1)d_1 \quad (19)$$

Below ζ_t , sintering occurs, and the shrinkage time, in the absence of applied stress, follows as

$$t[D_b\delta_b\gamma_s\Omega/kT\ell^4] = - (3\sqrt{3}F(\psi)/16d_1^2) \left\{ d_1^2\zeta_0^2/2 + d_1\zeta_0 + \ln(1 - d_1\zeta_0) \right\} \quad (20)$$

where ζ_0 is the initial void size. Comparison of the shrinkage behavior of cylindrical voids with the previous analysis of ellipsoidal voids, is conducted for initial void configurations of constant volume. Hence, for this comparison the initial volume of a cylindrical void given by Equation (17b) is equated with the volume of N ellipsoidal voids (Equation 9). The equivalent initial cylindrical void dimension, ζ_0 , is thus

$$\zeta_0^2 = f(\psi)\pi^2 / (18\sqrt{3} F(\psi)N^2) \quad (21)$$

The shrinkage times for cylindrical voids computed using this limit are compared with the corresponding lower bound times for ellipsoidal voids in Fig. 6. It is apparent the three grain junction voids shrink faster than cylindrical voids of equal volume. It would thus appear the "breakup" of cylindrical pores by a Rayleigh instability mechanism is an important step in final stage sintering.

In the creep growth regime, the growth time required to achieve a radial dimension equivalent to the ellipsoidal pore radial dimension at coalescence is calculated. This comparison should then determine the relative influence of ellipsoidal pores on the creep damage rate. The equivalent radial dimension, ζ_1 , is given by,

$$\zeta_1 = (\pi/6N)(w - \sqrt{w^2 - 1}) \quad (22)$$

where $w = \sin \psi [1 - (4/3)\cos^2 \psi]^{-1/2}$. The comparative time for the cylindrical void to grow between the transition size, ζ_t , and ζ_1 is thus obtained from eqn (18) as;

$$t[D_b \delta_b \gamma_s \Omega / kT \ell^4] = 3\sqrt{3}F(\psi) / [16(\sigma_\infty \ell / \gamma_s + 1)^3 d_1^2] \times \left\{ (\alpha_1^2 - \alpha_0^2) / 2 + 2(\alpha_1 - \alpha_0) + \ln(\alpha_1 / \alpha_0) \right\} \quad (23)$$

where $\alpha = (\sigma_\infty \ell / \gamma_s + 1) d_1 \zeta - 1$. The comparative growth time is compared with the ellipsoidal void coalescence time in Fig. 8. The cylindrical void grows more rapidly (shorter coalescence time) than the ellipsoidal void for all reasonable values of the dihedral angle. The time required to create the cylindrical void from the initial ellipsoidal voids could thus be an important time consuming phase in the development of creep damage.

The tendencies toward smaller shrinkage times and larger growth times of ellipsoidal voids relative to cylindrical voids are readily rationalized in terms of the stress differences at the void/grain boundary intersections. Specifically, comparison of eqns (4) and (15) reveals that the stress at the ellipsoidal pore is larger, because the net curvature is larger: $2/R$ compared with $(1/R - 1/\ell)$. This larger stress induces a larger chemical potential gradient for grain boundary diffusion, in the absence of stress, and thus provides a reduced shrinkage time. Conversely, in the presence of an applied tensile stress, the net chemical potential gradient for growth is reduced by the larger pore surface stress and the pore growth rate is relatively smaller, leading to longer growth times.

4. Conclusions

The behavior of ellipsoidal voids, which result from break-up phenomena, such as the Rayleigh instability, has been studied. The transition size between the shrinkage and growth of such voids was determined to increase directly with dihedral angle and inversely with applied stress. The shrinkage times for voids smaller than the transition size were found to increase with applied stress, experience a minimum with dihedral angle (except in the absence of applied stress), and vary inversely with the number of voids on the three grain junction. Ellipsoidal voids were invariably found to shrink faster than cylindrical voids of equivalent volume. Consequently, the formation of ellipsoidal pores is deemed an important step in final stage sintering. However, it remains to examine the corresponding behavior when cylindrical pore breakup results in non-contacting ellipsoidal voids, which may shrink at a reduced rate.

Ellipsoidal voids which nucleate to a size greater than the transition size, were predicted to grow and coalesce along the grain junction. The coalescence time was determined to increase directly with dihedral angle and inversely with applied stress. The growth kinetics of these voids have been compared with the behavior of cylindrical voids of equal radial dimension. The cylindrical voids were determined to grow faster than ellipsoidal voids. It may thus be inferred that discrete three grain junction voids reduce the creep damage rate.

5. Future Work

Additional work on the topic should consider a configuration with fewer ellipsoidal voids at the three grain junction. In particular, in the sintering regime, the shrinkage rate should be determined for an ellipsoidal void configuration wherein the voids are not initially in contact, after the break up of the void channel. Additional comparisons could then be made with the shrinkage rate of equivalent cylindrical voids; thus further examining the importance of void spacing (and break up mechanism) on the shrinkage rate.

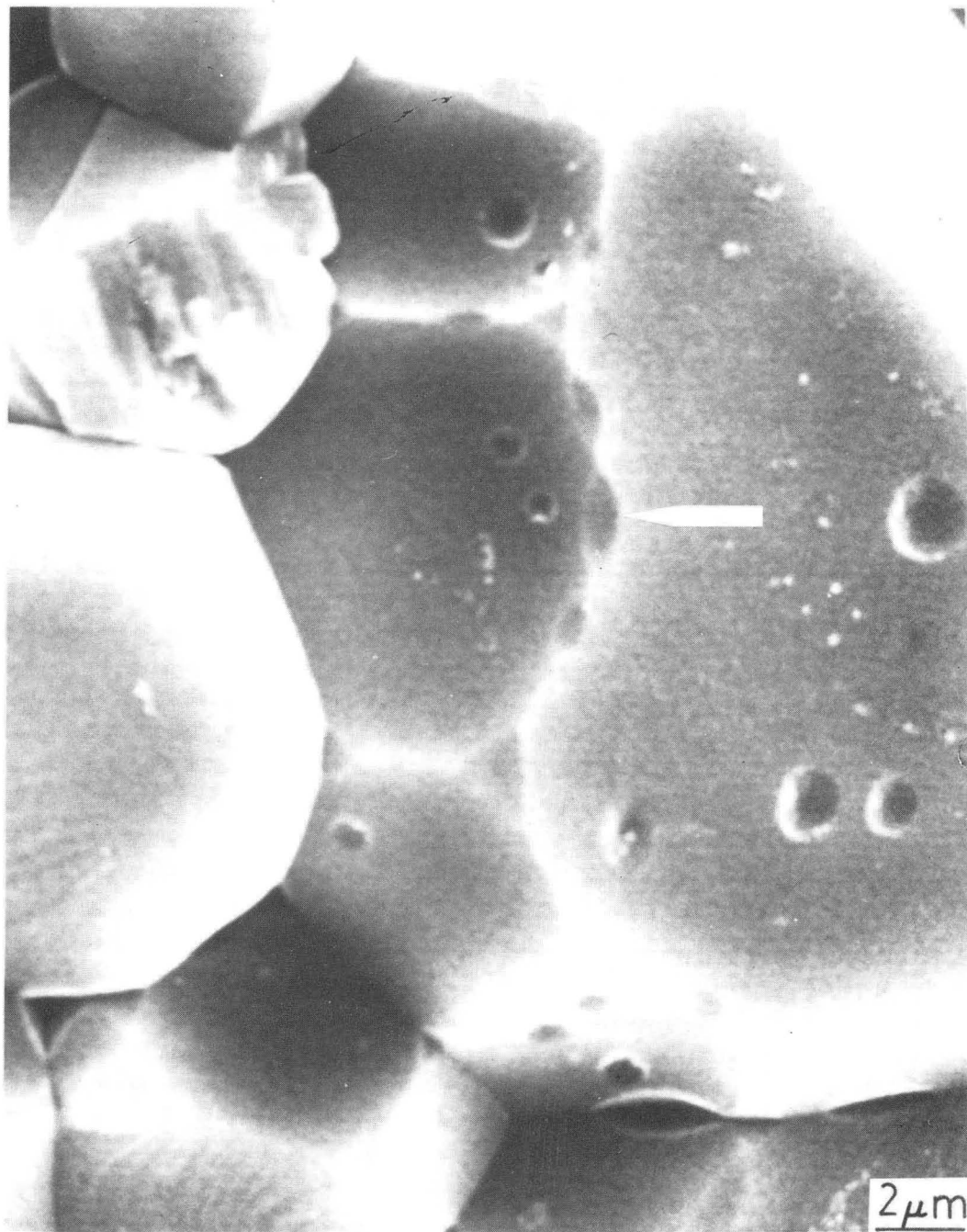
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Figure Captions

- Fig. 1. A Scanning electron micrograph of MgO, illustrating (arrow) "ellipsoidal" pores on a three-grain junction.
- Fig. 2. Schematic of ellipsoidal pores located at a three grain junction. (a) Location of pores along each edge of the grain facet. (b) Views of an ellipsoidal pore indicating uniform curvature and dihedral angle requirements.
- Fig. 3. Schematic of the evolution of pores along the three grain interfaces to full-faceted pores. Nucleated ellipsoidal pores (a) extend along the three grain interface (b) to form continuous pore channels (c), and then along the grain facet (d) to form full-faceted pores (e).
- Fig. 4. Simplifying axisymmetric geometry for analysis of the growth and shrinkage of three grain junction voids.
- Fig. 5. Map specifying the creep and sintering regimes of ellipsoidal voids as a function of dihedral angle and stress.
- Fig. 6. Comparison of the sintering behavior of cylindrical and ellipsoidal voids in the absence of applied stress.
- Fig. 7. Sintering times, for twenty voids along the three grain junction, as a function of dihedral angle and stress.
- Fig. 8. Coalescence times of three-grain-junction voids as a function of dihedral angle and stress. Comparison is made with cylindrical voids.



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Fig. II-1

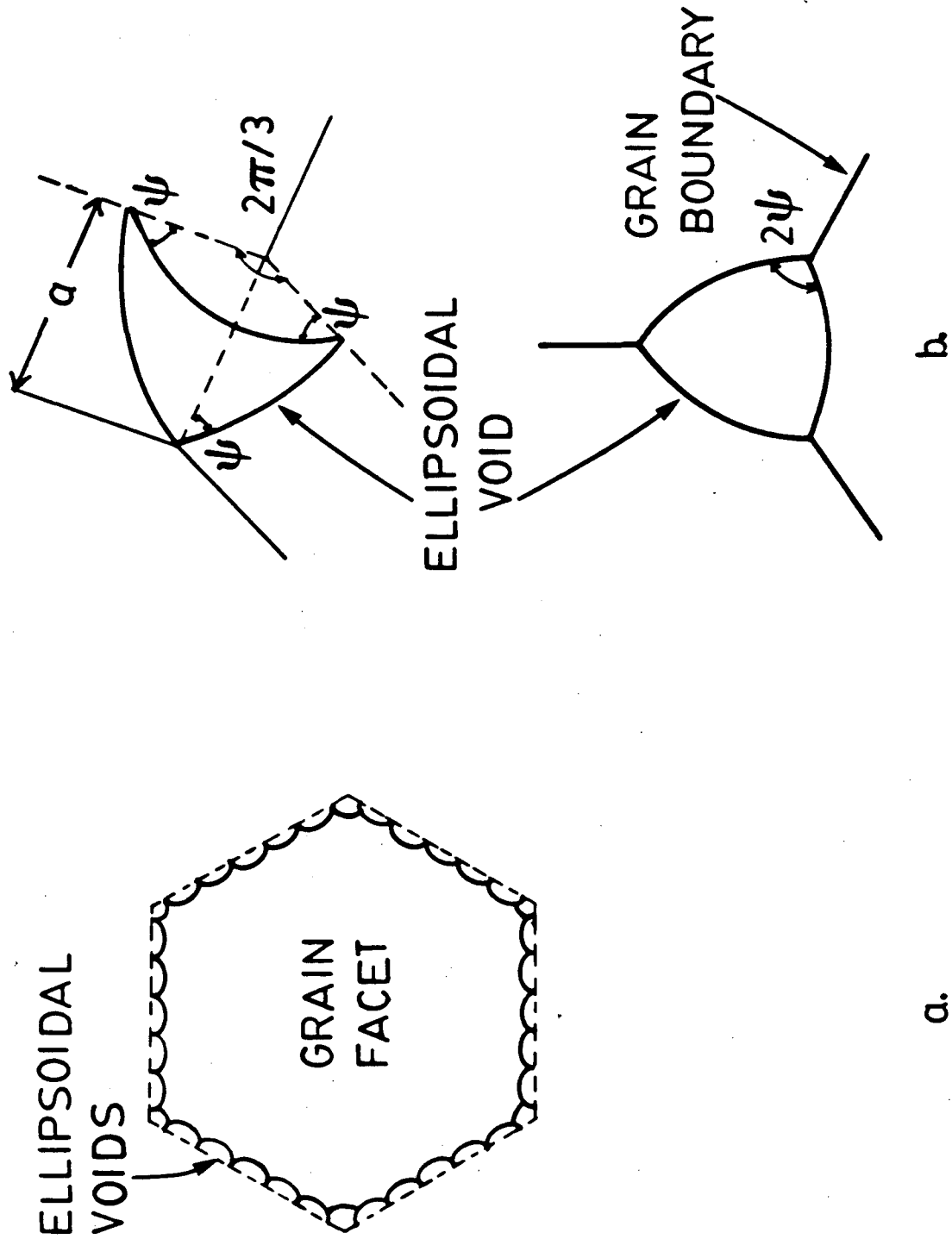
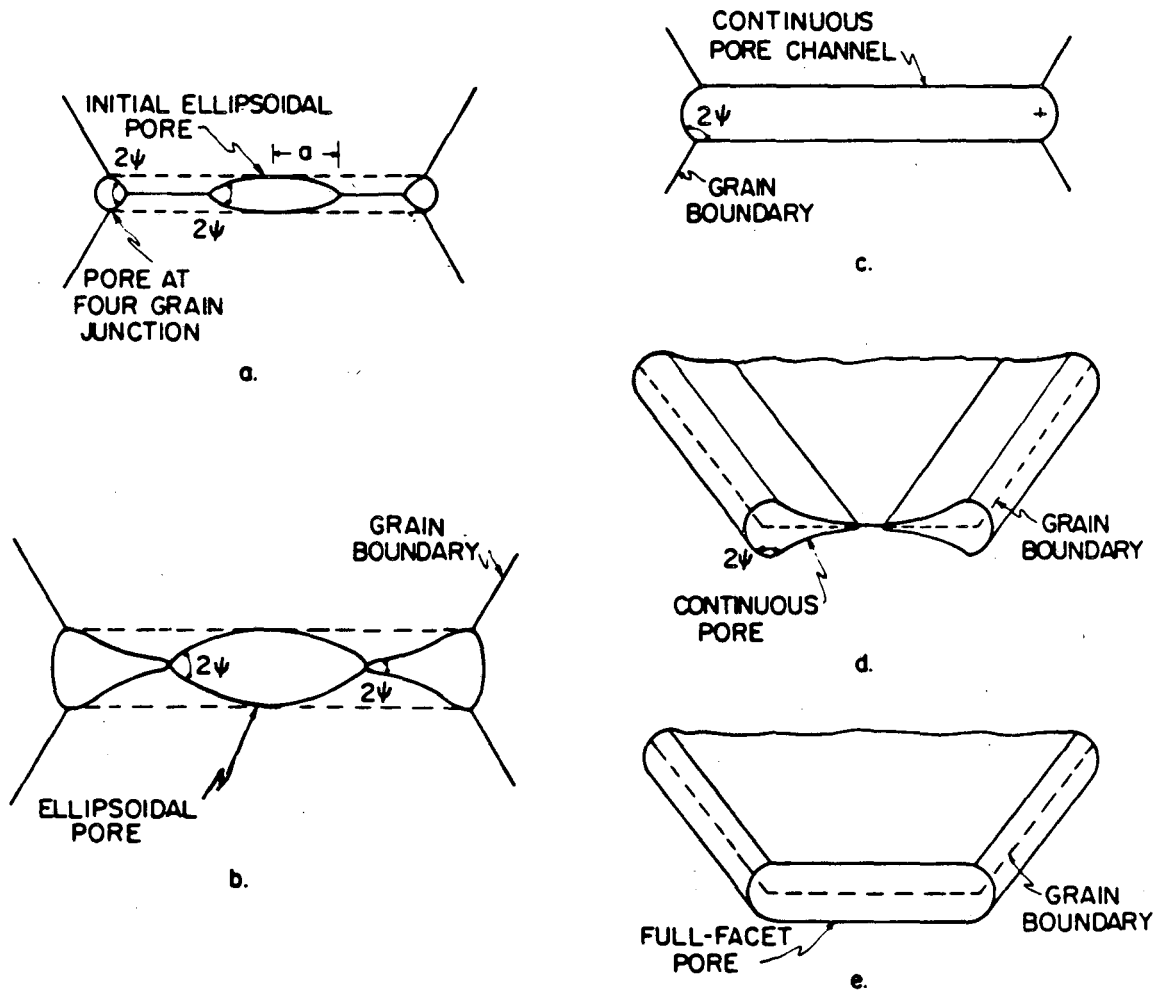


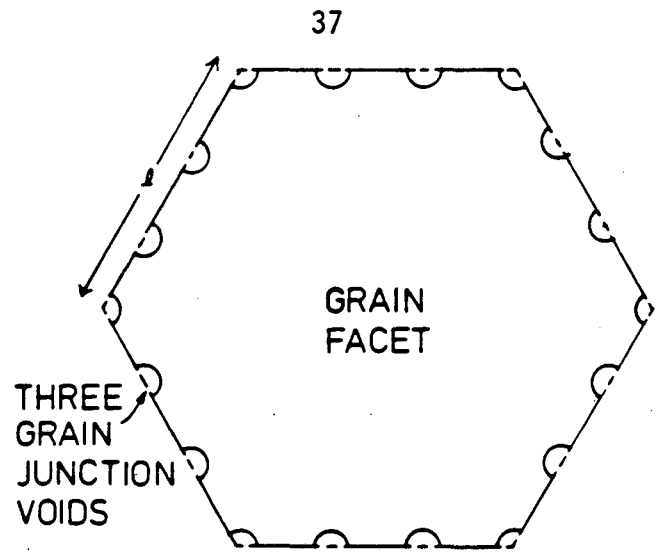
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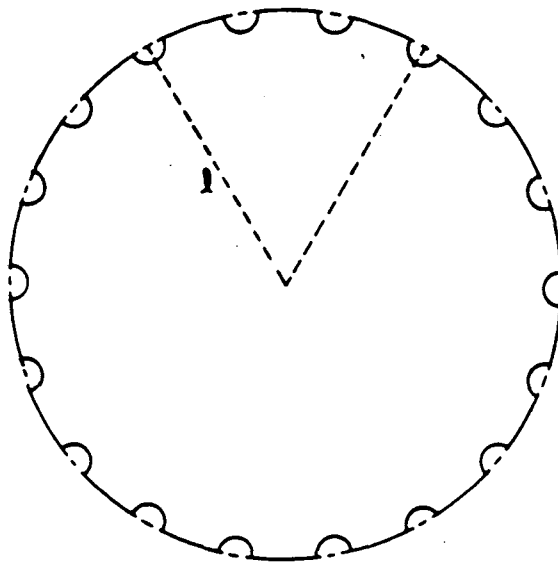


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Fig. II-3

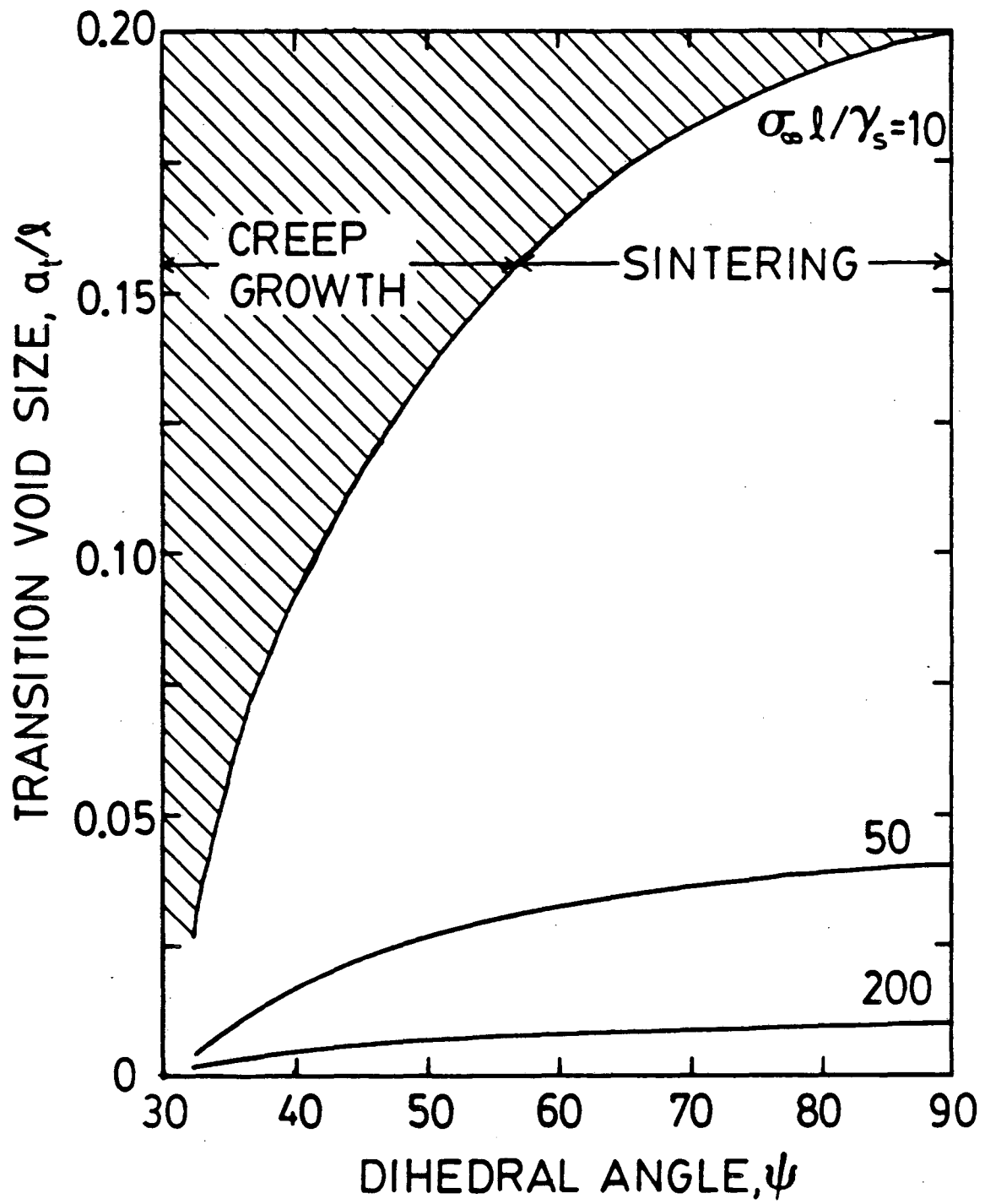


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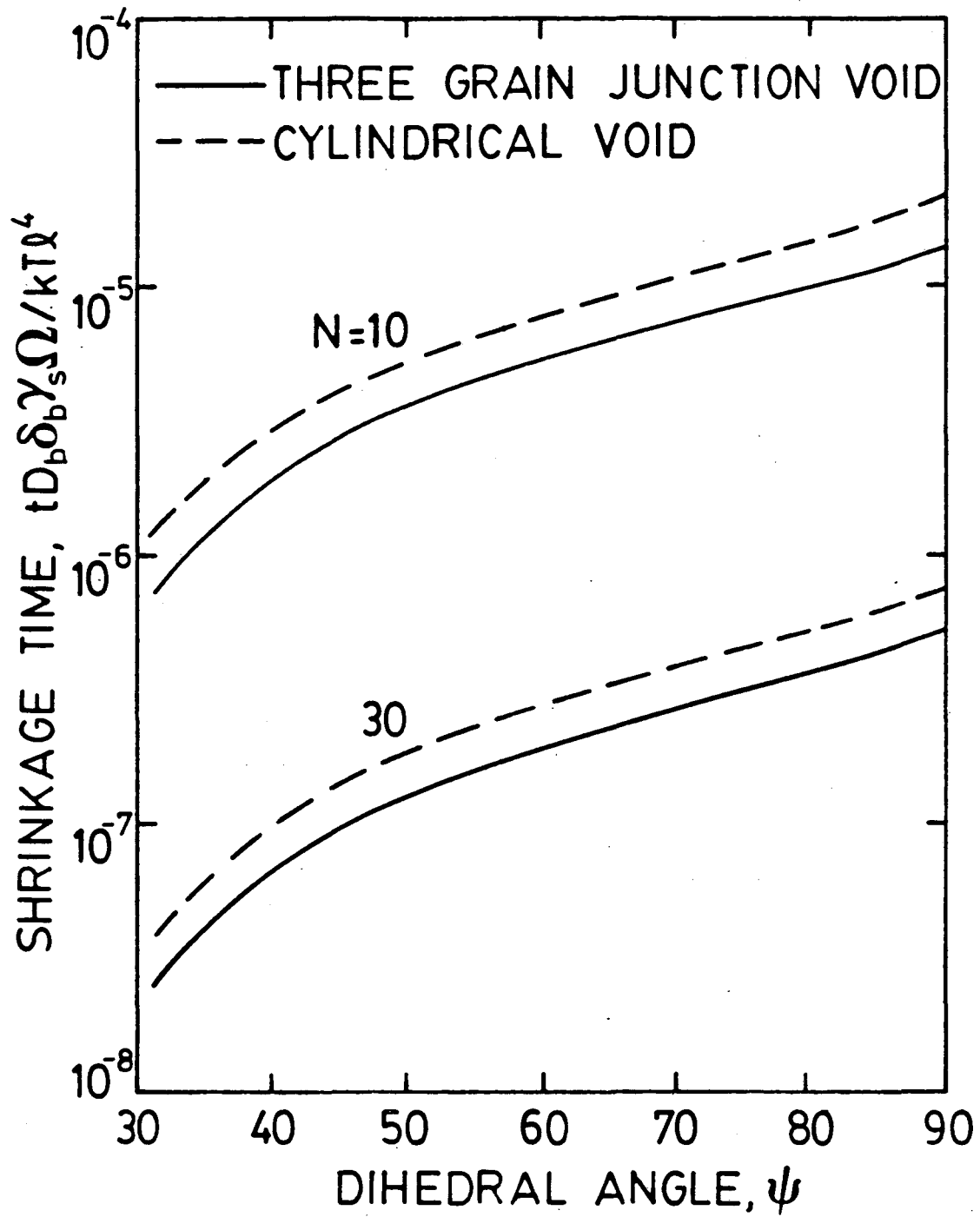
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Fig. II-4



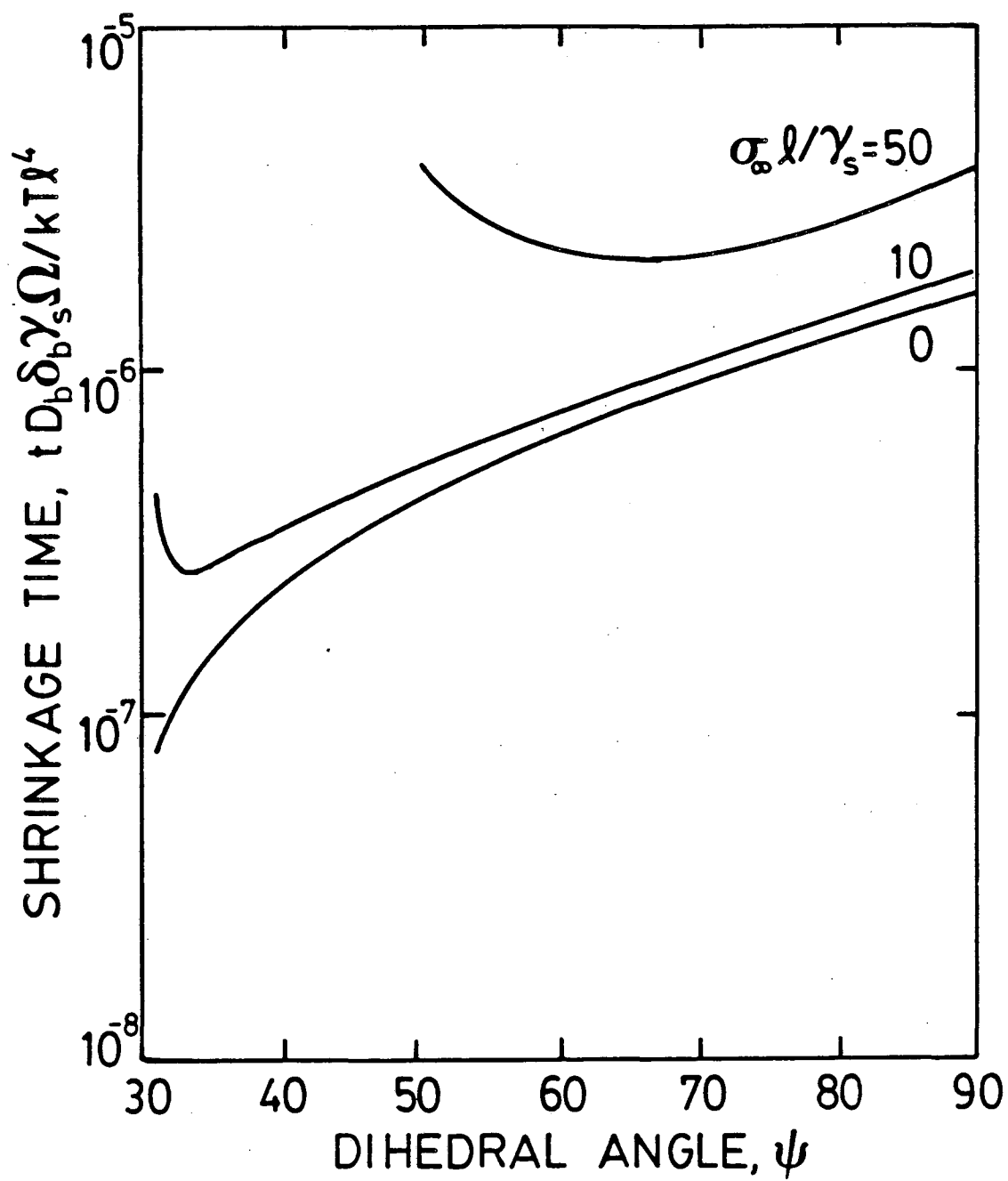
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Fig. II-5



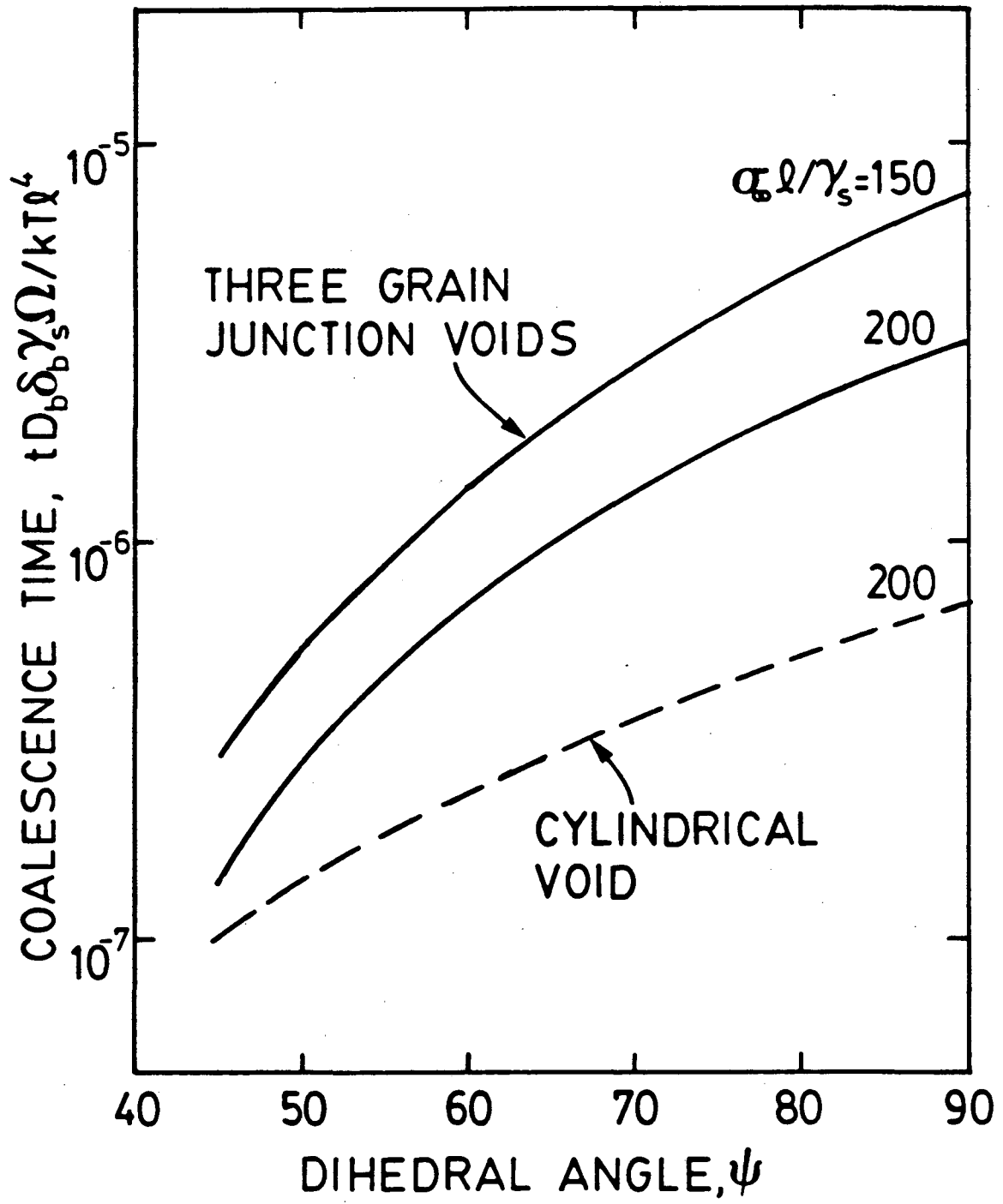
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Fig. II-6



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Fig. II-7



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Fig. II-8

PART III

THE ELIMINATION OF SURFACE VOIDS IN CERAMICS

1. Introduction

Commercial processes for the sintering and forming of structural ceramics generally result in residual porosity, on the order of 2-6 percent. This porosity can have several deleterious effects. In particular, voids located near the surface can interact with surface crack created during machining (or surface finishing) to produce fracture limiting flaws.^{1,2} Such flaws are of special concern in contact fracture problems, wherein cracks occur due to large tensile stresses located near the surface.^{3,4} Elimination of near surface voids should have a beneficial influence on contact fracture. In addition, the elimination of surface voids should prove advantageous in substrate applications, by excluding such voids as preferred paths for metal diffusion into the substrate.

The intent of the present investigation is to provide a preliminary basis for assessing the removal of surface porosity in typical ceramic polycrystals. For this purpose, surface pores are studied in a model system, MgO, for which reasonable information is available regarding the dominant mass transport processes (notably surface diffusion⁵ and evaporation/condensation⁶).

2. Experimental Procedures

The porous specimens were prepared by vacuum hot pressing nominally pure MgO powder (Table 1), with 0.1 μm initial particle size, using a graphite disc at a pressure of 9 MPa applied for 30 minutes at 1100°C. Specimens were cut from the pressed disc and subsequently, heat treated at 1300°C for 1 hr to produce a relatively

uniform final stage microstructure (Fig. 1a). At this stage the remanant porosity was 3 percent and the average grain size $4.3\text{ }\mu\text{m}$. One surface of each specimen was then polished with $1/4\text{ }\mu\text{m}$ diamond paste. Thereafter, heat treatments were conducted at 1400°C for up to 2 hr and finally, the specimens were thermally etched at 1200°C to reveal the grain boundaries. Some of the heat treatments were performed with the specimen surrounded by $0.1\text{ }\mu\text{m}$ MgO powder, having the same composition as the sintering specimen. The remaining heat treatments were conducted with the specimen in contact with a dense MgO body of the same composition.

The gradual elimination of the surface voids during progressive heat treatments were traced by placing Vickers indentations on the polished surface. A grid of indentations placed at $250\text{ }\mu\text{m}$ intervals was found to be convenient for the construction of a microstructural montage from scanning electron micrographs of the surface (Fig. 2a). The void size distributions were then determined from each montage. For this purpose, a specific sample area was initially identified by indentations, as shown in Fig. 2b. This same area was then reexamined for each progressive heat treatment. Void sizes were characterized by measuring both the major and minor axes of the void (Fig. 2b). Additionally, the microstructural locations of each void was noted, viz., either intragranular or at two, three, or four grain interfaces. Finally, surface densities were estimated by determining the total void area on the surface, as described in the Appendix.

3. Results

Heat treatments at 1400° for 2 hr eliminated most surface voids, as demonstrated by the progression in surface morphology (Fig. 1b) and the corresponding change in surface density (Fig. 3). Subsequent sectioning through the specimen revealed that the change in density was confined to a narrow region at the surface (Fig. 4a), and that no significant change occurred in the interior microstructure (Fig. 4b).

Further characterization of the void elimination process was achieved by constructing void size frequency diagrams (Fig. 5) and the related cumulative void size distributions (Fig. 6). The trends suggest that the distributions are essentially lognormal and stationary. Specifically, the mean void size varied little with heat treatment (Fig. 7), but the overall number of voids continuously diminished as the heat treatment proceeded. Furthermore, the behavior of the intra and intergranular voids was indistinguishable (c.f. Figs. 5a and 5b, Fig. 7a and 7b).

Finally, it is noted that the heat treatments conducted with the powdered and solid MgO buffers revealed no significant differences in void removal characteristics.

4. Mechanisms of Void Removal

The absence of interior microstructural changes during the heat treatments excludes sintering as a source of void removal. Mass transport based on lattice or grain-boundary diffusion can thus be eliminated as possible mechanisms. Consequently, surface diffusion or evaporation/condensation emerge as the likely mass transport alternatives. Furthermore, since the vapor pressure should be appreciably

enhanced by the close proximity of fine powder particles to the specimen surface, the insensitivity of the void removal kinetics to the morphology of the buffer (fine powder or large plate) strongly implies that surface diffusion is the dominant mechanism. This conclusion is confirmed by the mass transport analysis presented below.

The major flux paths for surface void filling in a polycrystal are summarized in Fig. 8. The free surface between intragranular voids is presumed to be the major surface source. Matter transport from such sources to the void can occur either by surface diffusion or by evaporation/condensation. However, in the presence of a fine powder, the powder becomes an additional, external source, with matter being transported to the voids by an evaporation/condensation mechanism. In the present experiments, the transport distance from the powder to the voids is relatively small. Consequently, when evaporation/condensation dominates void filling, the external powder source should dictate the void elimination rate.

4.1. Surface Diffusion

The elimination rate of surface voids by surface diffusion is determined for the simplified configuration, wherein matter diffuses over the essentially planar surface to fill the void. The arrangement of voids is approximated by a uniform array, in which the source is the perimeter of a hexagon of dimension, 2λ (Fig. 9). The size of the hexagon is selected to form equidistance regions surrounding each void, such that the void spacing $\sim 2\lambda$. The void surface is assumed to be a portion of a sphere with radius R , such that the radius decreases

as the void fills with material from the surrounding disk. Rounding of the void/surface intersection is thereby neglected and consequently, the calculated void elimination time must be the minimum possible value, as discussed in Section 5. The axisymmetric geometric approximation permits an analytic solution to the void filling problem, adequate for present purposes.

The governing equation for the surface flux,⁷

$$J_s = -(D_s \delta_s / \Omega k T) (d\mu / ds) \quad (1)$$

dictates that the flux, J_s , be proportional to the chemical potential gradient, $d\mu/ds$ and the surface diffusivity, $D_s \delta_s$, the inversely dependent on the atomic volume, Ω , the absolute temperature T , and Boltzmann's constant, k . An approximate solution for the flux can be obtained by replacing the chemical potential gradient, $d\mu/ds$, with a discrete difference, $\Delta\mu/\Delta s$, acting over the diffusion length. For the assumed geometry, $\Delta s = \ell$ and,

$$\Delta\mu = -2\gamma_s \Omega / R \quad (2)$$

where γ_s is the surface energy. Volume conservation requires that the material transported through a length of surface $\sim 2\pi\ell$, be plated over the void surface, such that

$$J_s \ell \Omega \approx -R^2 (dR/dt) \quad (3)$$

Combining equations (1)-(3) and integrating over R , gives the time for void elimination. Specifically, the time, t , for a void of initial radius R_0 , to fill to radius, R , is given by

$$t [D_s \delta_s \gamma_s \Omega / k T R_0^4] = (1/8) [1 - (R/R_0)^4] \quad (4)$$

Representative trends in void size with time are plotted in Fig. 10.

4.2. Evaporation/Condensation

The maximum mass flux between surfaces provided by the evaporation/condensation mechanism is assumed to be determined by the difference in equilibrium vapor pressures between the pore and powder surfaces. The relation governing the mass flux with perfect sticking and emitting characteristics, is,⁵

$$\dot{M} = \Delta p (m/2\pi kT)^{1/2} \quad (5)$$

where $\dot{M}$ is the mass flux rate, m is the molecular weight and Δp is the difference in vapor pressure between either the evaporating or condensing surface, and the gas phase.

The vapor pressure p over the void surface is

$$(p/p_0) = 1 - (2\Omega\gamma_s/kT)/R \quad (6)$$

where p_0 is the equilibrium pressure over a flat surface. The corresponding vapor pressure p^* over the powder surface is

$$(p^*/p_0) = 1 + (2\Omega\gamma_s/kT)/R^* \quad (7)$$

where R^* is the mean radius of the powder. In the presence of a large powder reservoir, the vapor pressure, p^* , is presumed to be pervasive, such that the vapor pressure difference between the pore surface and the gas phase is thus;

$$\Delta p \equiv p - p^* = - (2\Omega\gamma_s/kT)(1/R^* + 1/R)p_0 \quad (8)$$

Hence, in the absence of powder coarsening, eqns. (5) and (8) yield a mass flux rate, to each surface pore, given by;

$$\dot{X} \equiv 2\pi R^2 \dot{M} = 2\pi R^2 (p_0 \gamma_s \Omega/kT) (2m/\pi kT)^{1/2} (1/R^* + 1/R) \quad (9)$$

However the mass flux rate to each pore is also given by,

$$\dot{V} = 2\pi R^2 \rho (dR/dt) \quad (10)$$

where ρ is the theoretical density of the material. Hence, equating eqns. (9) and (10) and integrating over R , gives the time for void disappearance,

$$t[(p_0 \gamma_s \Omega / \rho k T)(m/kT)^{1/2} / (r^*)^2] = \sqrt{\frac{\pi}{2}} [\ln(n/n_0) - n + n_0] \quad (11)$$

where $n = 1 + R/R^*$ and $n_0 = 1 + R_0/R^*$. Trends in void size the time are plotted in Fig. 11. Note that the shrinkage rate is approximately constant for a given initial void radius, (R_0/R^*) .

The void filling times depicted in Fig. 11 are lower bound estimates by virtue of the assumptions regarding perfect sticking, interface control, and the absence of powder coarsening.

4.3. Transition Pore Size

Equating the void filling rates for the two mechanisms, identifies a pore radius, R_c , at which a transition occurs between mechanisms. Consequently, by differentiating equations (4) and (11) to obtain R and equating, we obtain,

$$R_c^3 = (D_s \delta_s \rho R^* / p_0)(2\pi k T / m)^{1/2} \quad (12)$$

such that evaporation/condensation dominated when $R > R_c$. Specific regimes can be identified with equation (12) and plotted as mechanism maps. For example, the effects of powder particle size and temperature on the operative mechanisms in MgO are plotted in Figs. 12a and 12b, using the available material data.^{5,6} However, it is recognized that these material data, especially the surface diffusion coefficient, are appreciably influenced by impurities.

5. Comparison between Theory and Experiment

The experimental parameters pertinent to the present system (powder particle size, $0.1\ \mu\text{m}$, void diameter $0.5\ \mu\text{m}$, and temperature 1400°C) locate the void filling process in the surface diffusion regime, as indicated on Figs. 12a and 12b. The dominance of surface diffusion is consistent with the insensitivity of filling rate to the morphology of the buffer, as noted in Section 3.

A direct comparison between theory and experiment can be made by predicting the change with time of the initial void size distribution using the surface diffusion model. As the voids shrink, their "disappearance" is dictated by a minimum resolvable dimension R_L . For this study, $R_L \approx 0.05\ \mu\text{m}$. Inserting R_L into equation (4) gives the requisite void elimination characteristics. The comparison with experiment is most expediently conducted, in view of the uncertainty in the diffusion parameter (noted above), by ascertaining whether the void elimination data are consistent with a reasonable choice of $D_s \delta_s$. For this purpose, the predicted decrease in the number of voids is adjusted by selecting the diffusivity that yields a best correspondence with the measurements (Fig. 7a). The resultant diffusivity, $9.5 \times 10^{-13}\ \text{m}^2\text{s}^{-1}$, provides an adequate description of the trend in void number with time (Fig. 6) and compares with a literature value of $1.3 \times 10^{-11}\ \text{m}^2\text{s}^{-1}$ (Ref. 6). The difference is typical of variations in diffusivity between materials, due to impurity differences, etc. The same diffusivity is now used to predict the change in the cumulative size distributions of pores with time (Fig. 6). Comparison with the measurements indicates reasonable agreement

at short times, but increasing disparities at longer times. Specifically, at long times, the small pores do not shrink as rapidly as the theory predicts. This discrepancy is considered to derive from the rounding of the pores at the surface (Fig. 1b), which increases the net pore radius and causes the model to overestimate the chemical potential gradients. However, incorporating the rounding into the model would require a major increase in complexity, beyond the scope of the present study.

6. Summary and Conclusions

In the present study, most surface voids in hot-pressed MgO were eliminated by heat treatment at an elevated temperature. The initial distribution of void sizes was approximately lognormal and stationary with heat treatment. Similar behavior was found for intragranular voids.

The mechanisms for filling of intragranular voids were considered to be mass transport either by surface diffusion along a flat free surface, or evaporation/condensation of the surrounding fine powder. An approximate analysis of these mechanisms indicates that surface diffusion dominated filling applies for materials with low vapor pressure, small void sizes, low heat treating temperature, and large surrounding powder sizes. The converse applies for evaporation/condensation dominated void filling. These trends are summarized as mechanisms maps (Fig. 12). The current experiments were located in the surface diffusion dominated regime.

The observations in MgO, and the approximate analysis, demonstrate that a post-sintering heat treatment, under appropriate conditions of temperature and surrounding powder size can readily reduce the number and size of surface flaws, present at voids.

7. Future Work

A variety of experiments should be conducted to further characterize the void filling rate and provide additional correlation with mechanism maps. Specifically, experiments with the present MgO powder can include a range of heat treating temperatures for a series of shorter time intervals. Experiments should also be conducted for evaporation/condensation void filling with higher vapor pressure materials. Mechanical testing in three-point bending, for determining increases in strength, should also accompany further experiments. Additional mechanical testing may also determine enhanced resistance to contact fracture.

Further analysis may consider the effects of powder coarsening on the filling rate by evaporation/condensation. This would be particularly relevant for correlating experimental data from materials with high vapor pressures. The contribution of grain boundary sources should also be examined for surface diffusion dominated void filling.

Appendix: Determining Apparent Surface Area of Voids

The apparent surface density after each heat treatment was found by approximating void area, depending on the void's location in the microstructure. Light thermal etching revealed each void's location and enabled estimates of the major and minor axes, d_1 and d_2 respectively. The intragranular void area is circular and given easily by,

$$A_1 = \pi(d_1 + d_2)^2/16 \quad (A1)$$

Two and three grain void areas are more involved. What appears as two grain voids may in fact be at a three grain junction if the intercepted grain boundary coincides with the polished section; nevertheless, the apparent void area will be the same in both cases. The apparent area for two grain voids is found by fitting the major and minor axes to a portion of a sphere ($d_2 < d_1$),

$$A_2 = (1/8)[(d_2^2 + d_1^2)/d_1]^2 \tan^{-1} [2d_1d_2/(d_2^2 - d_1^2)] + (1/8)(d_2/d_1)(d_1^2 - d_2^2) \quad (A2)$$

The void area on the three grain junction is approximately triangular and given by,

$$A_3 = d_1d_2/2 \quad (A3)$$

Voids on four grain junctions are best estimated by digitizing the grain corner locations (see Fig. 13). The points are taken successively on a continuous circuit, counterclockwise, around the void.

The cartesian coordinates for each void, from an arbitrary but fixed origin, gives the void area by,⁹

$$A_4 = (1/2)(x_1y_2 + x_2y_3 + x_3y_4 + x_4y_1 - y_1x_2 - y_2x_3 - y_3x_4 - y_4x_1) \quad (A4)$$

The apparent surface area of any polygonal void is found by extending the prior equation to N points through piece-wise application of Green's theorem*

$$A_N = (1/2)[x_N y_1 - y_N x_1 + \sum_{j=1}^{N-1} (x_j y_{j+1} - y_j x_{j+1})] \quad (A5)$$

As before, the points must be taken on a continuous circuit in the counterclockwise sense.

*Refer to any standard text in multi-variable calculus, e.g., Ref. 10.

Table 1. MgO impurities (semi-quantitative analysis).

Detected in the form of oxides	Percent
Na	0.1
Si	0.06
Ca	0.06
Ni	0.01
Fe	0.002
Cu	<0.001
B	<0.01
Al	<0.001

References

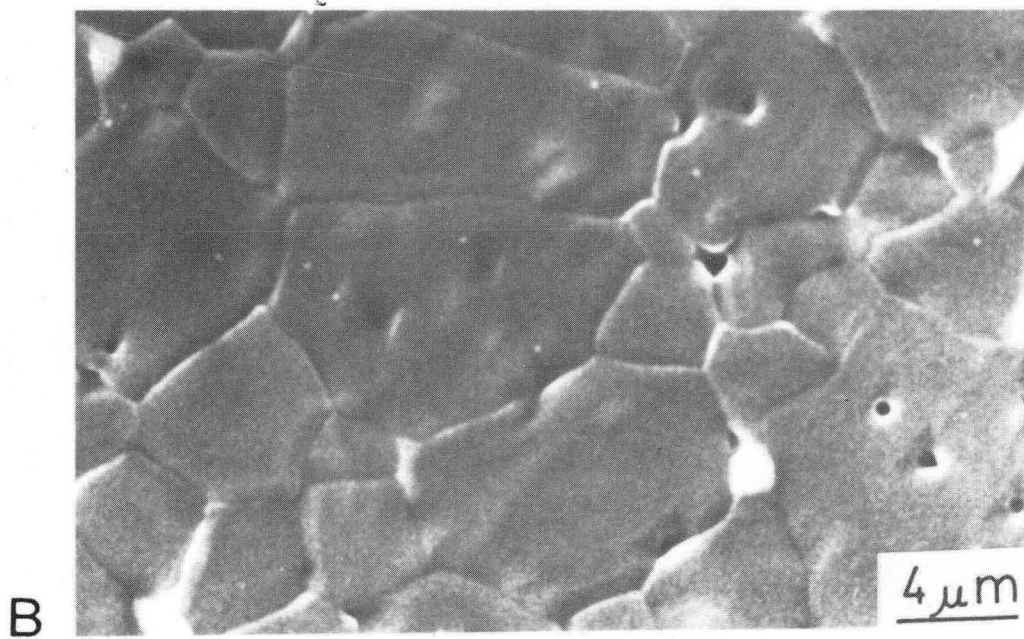
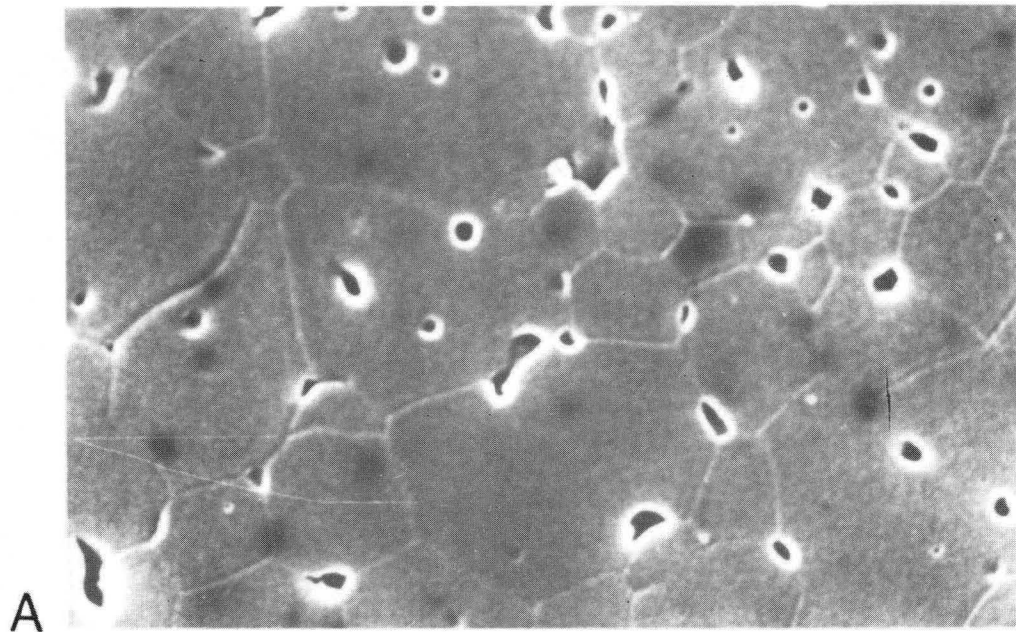
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Figure Captions

- Fig. 1. (a) Initial microstructure containing surface voids,
(b) after 2 hour heat treatment.
- Fig. 2. (a) Microstructural montage to trace surface void elimination, (b) void size measurements for a specific sampling area.
- Fig. 3. The change in apparent surface density with heat treatment.
- Fig. 4. Sectioning below the surface (b) reveals that void elimination is confined to the surface.
- Fig. 5. Frequency distribution of void size for (a) intragranular voids (b) all surface voids including intragranular voids.
- Fig. 6. Cumulative distribution plot of intragranular void sizes. Experimental values are compared with the predicted distribution.
- Fig. 7. Average void radius and the number of voids with heat treatment for (a) intragranular voids and (b) all voids.
- Fig. 8. Major flux paths for void filling by (a) surface sources and (b) external sources, such as the surrounding powder.
- Fig. 9. Geometry used for surface diffusion analysis of void filling.
- Fig. 10. Shrinkage behavior of intragranular voids by surface diffusion as a function of dimensionless radius, R/R_0 .
- Fig. 11. Void filling times as a function of dimensionless void radius, R/R^* , for filling by evaporation/condensation.

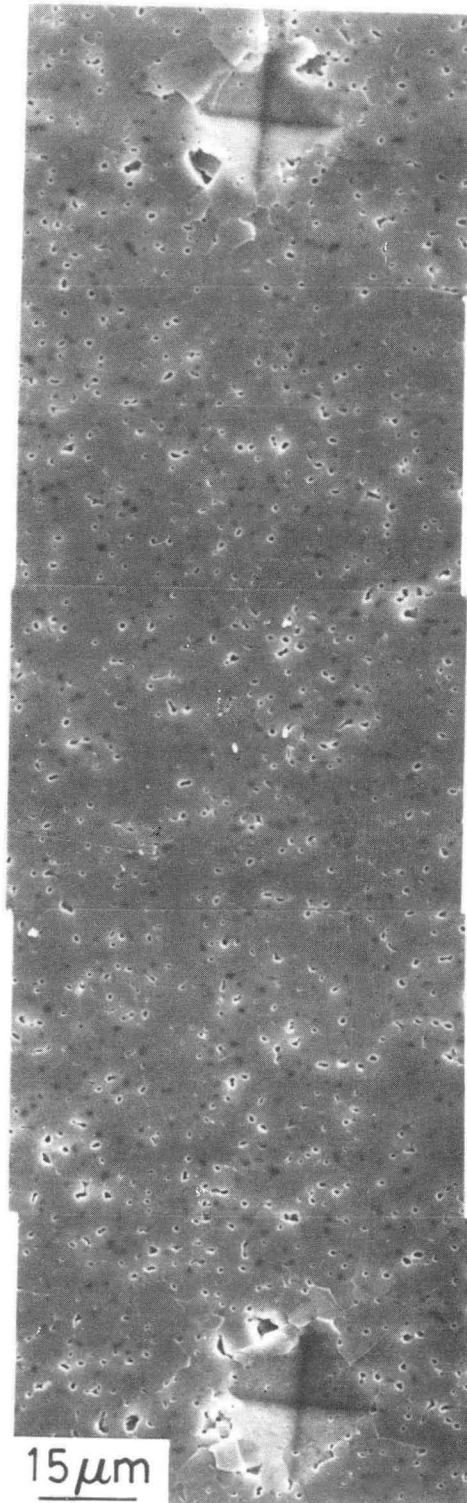
Fig. 12. Mechanism map for void filling specifying the dominant mechanism for void radii as a function of (a) surrounding powder size, and (b) temperature.

Fig. 13. Digitizing scheme for determining the surface area of an n-sided polygonal grain facet.



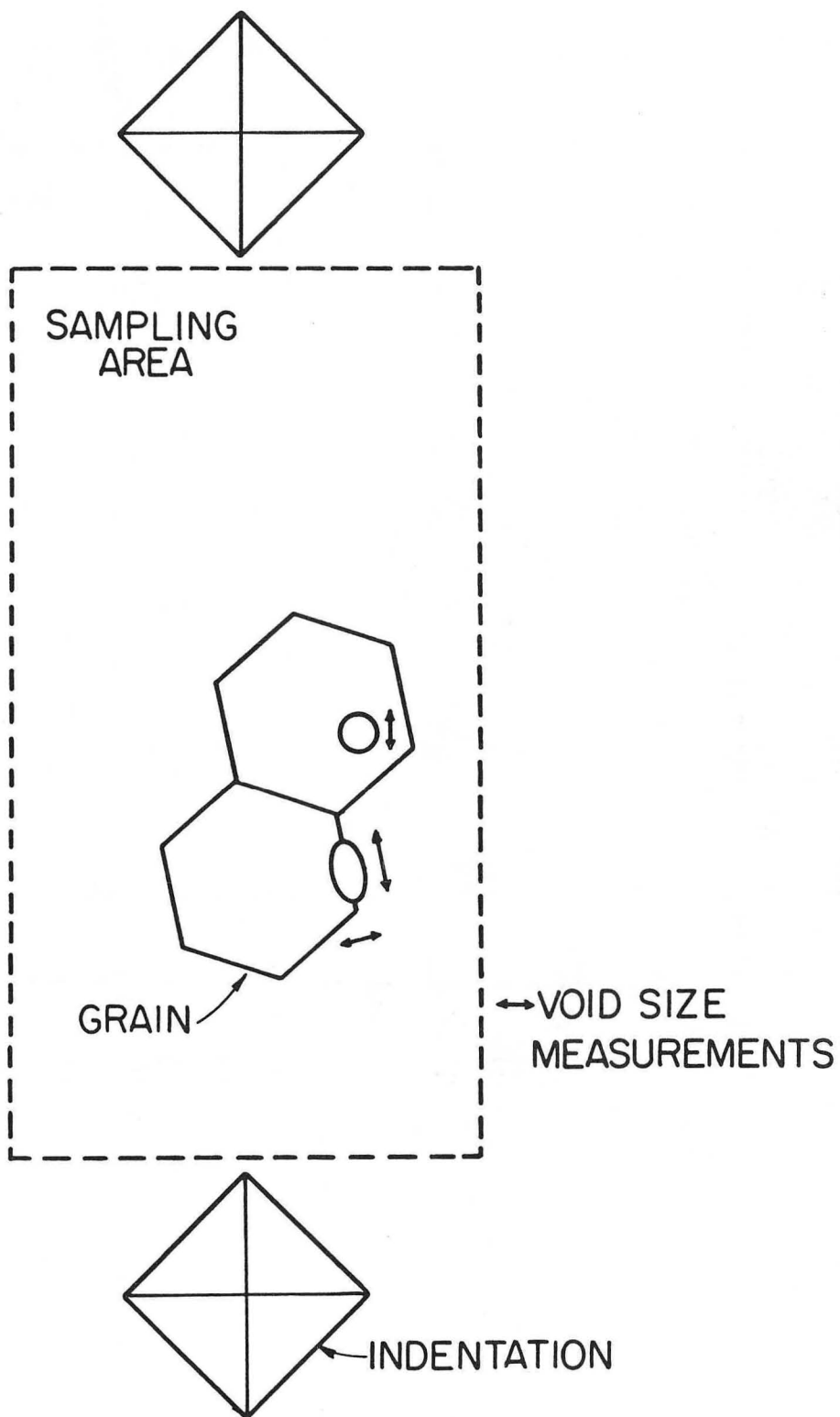
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Fig. III-1



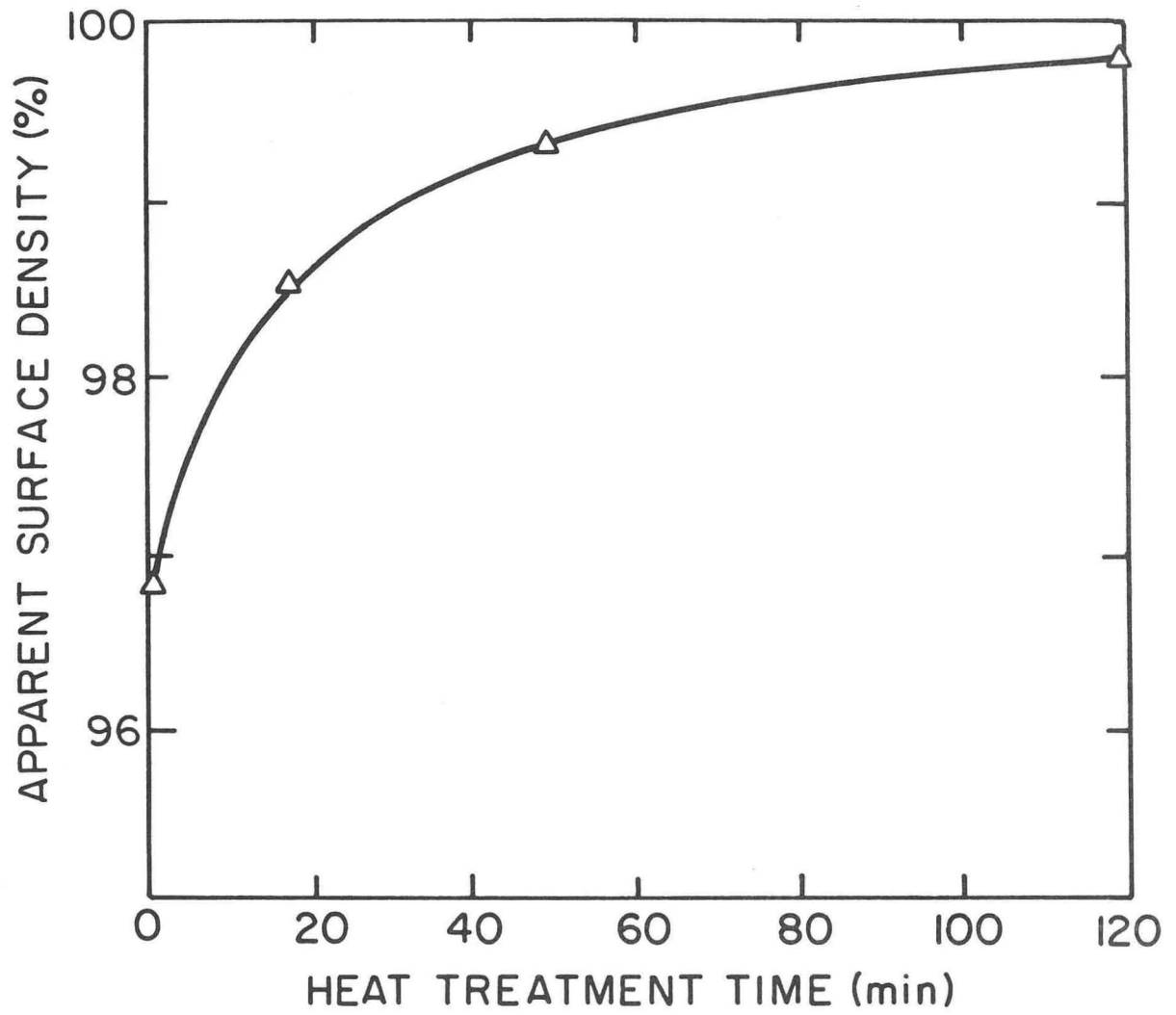
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Fig. III-2a



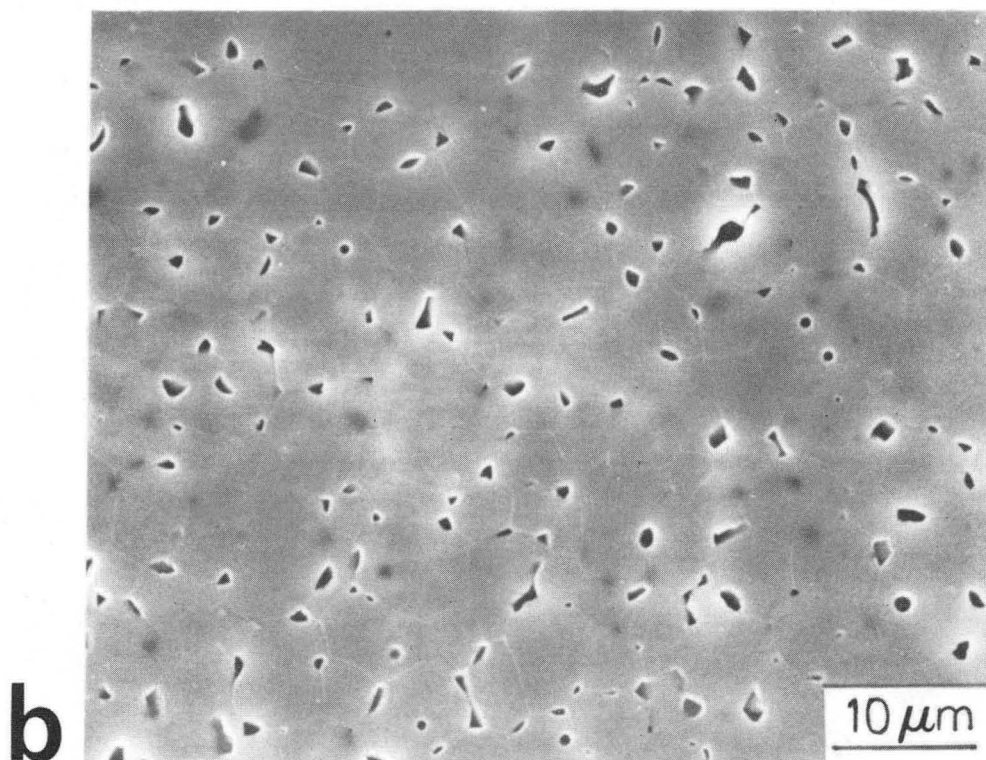
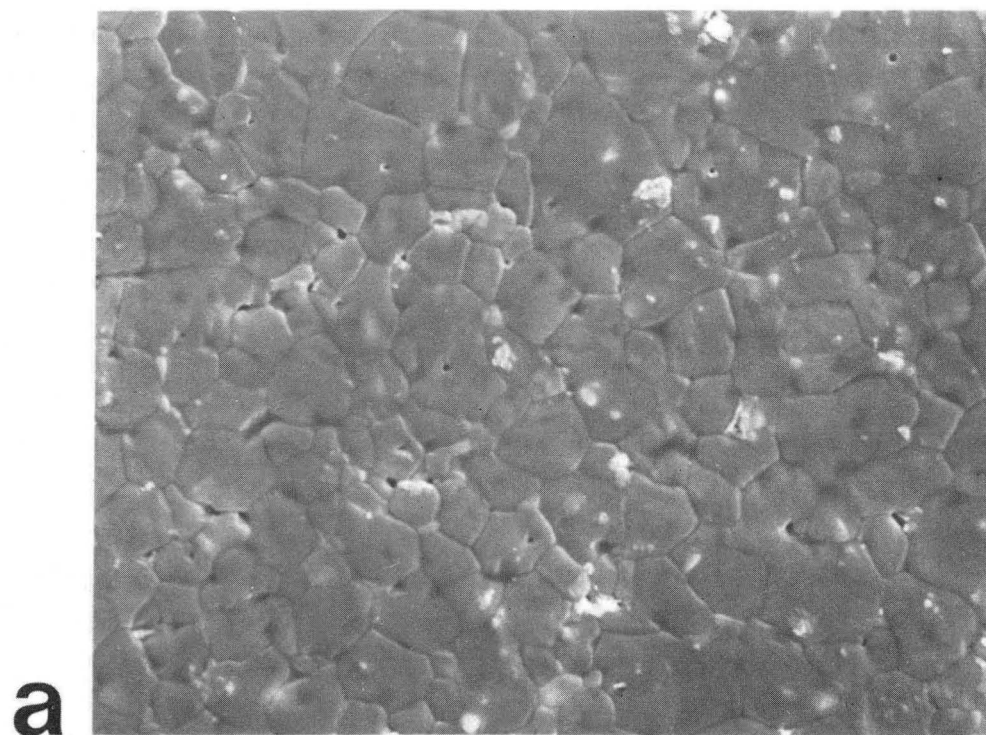
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Fig. III-2b



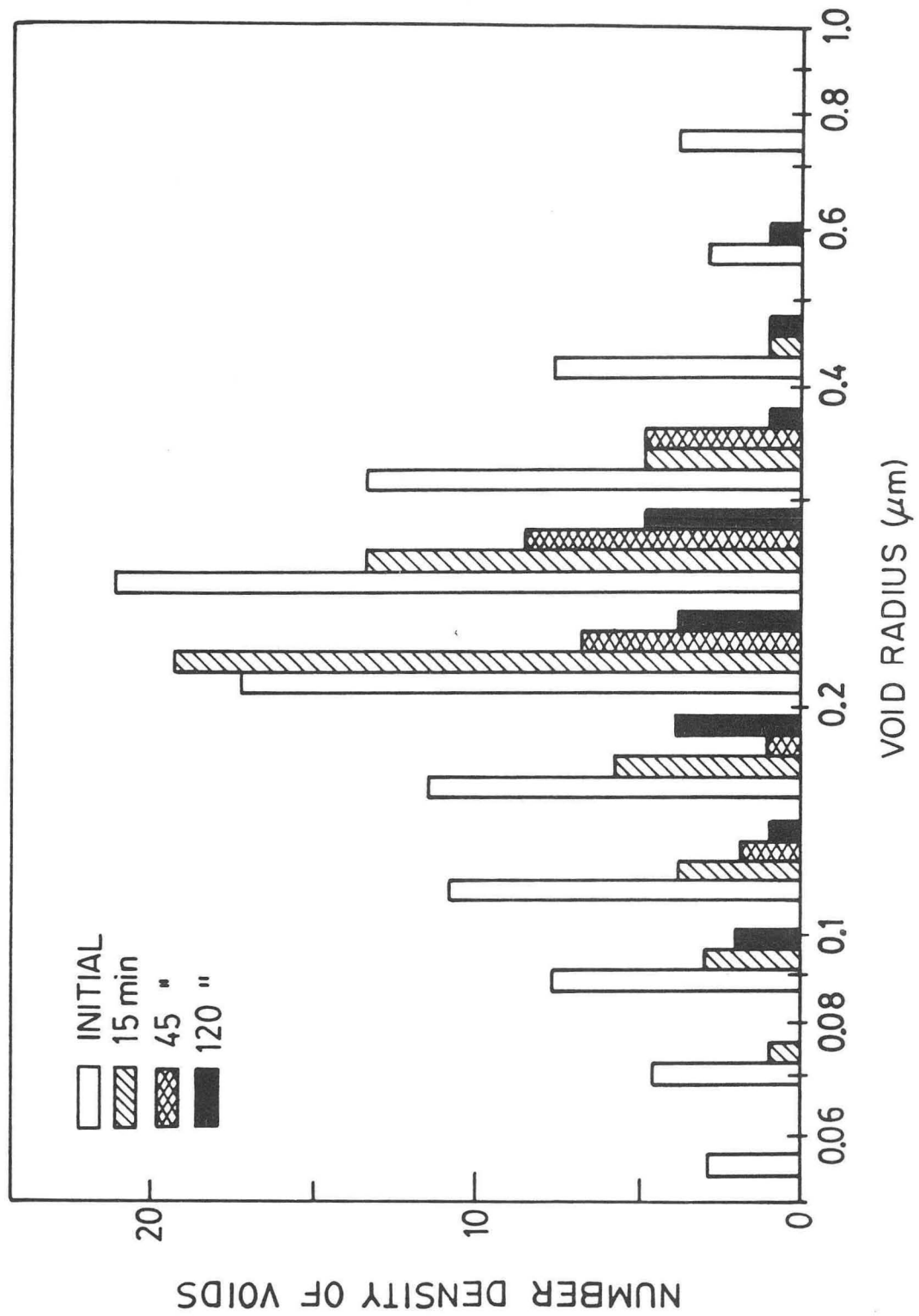
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Fig. III-3



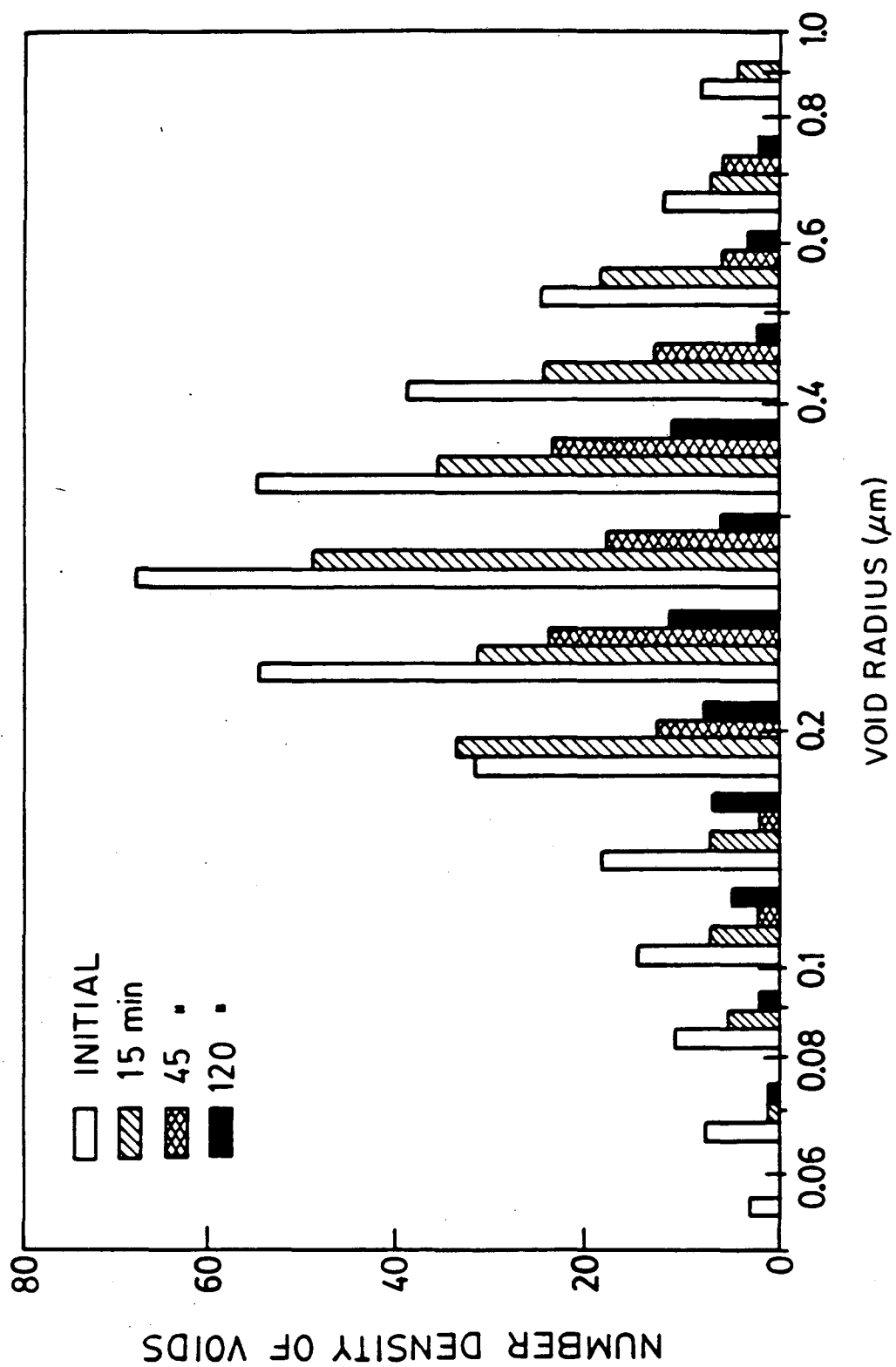
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Fig. III-4



XBL 849-7368

Fig. III-5a



XBL 849-7367

Fig. III-5b

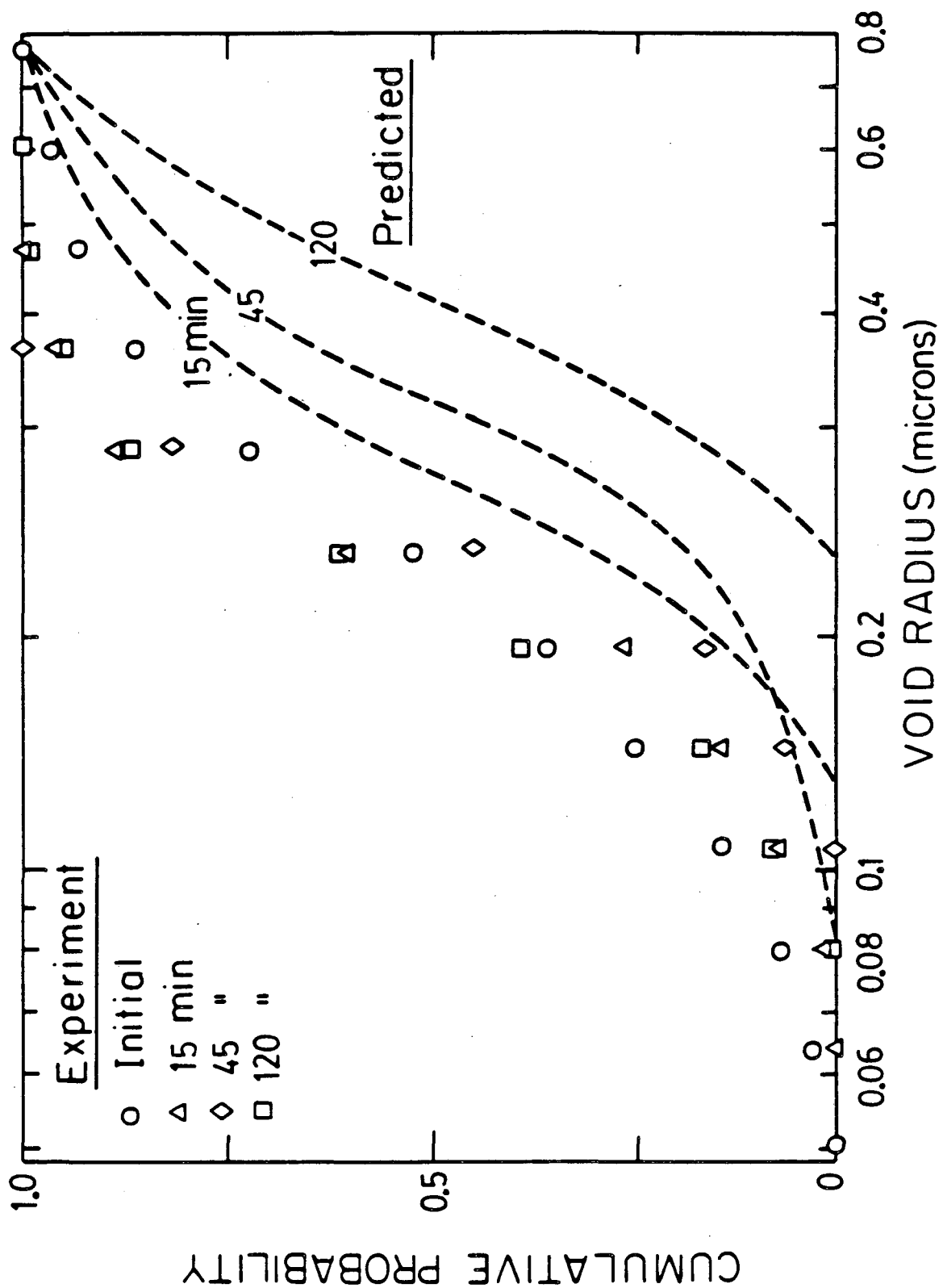


Fig. III-6

XBL 849-7360

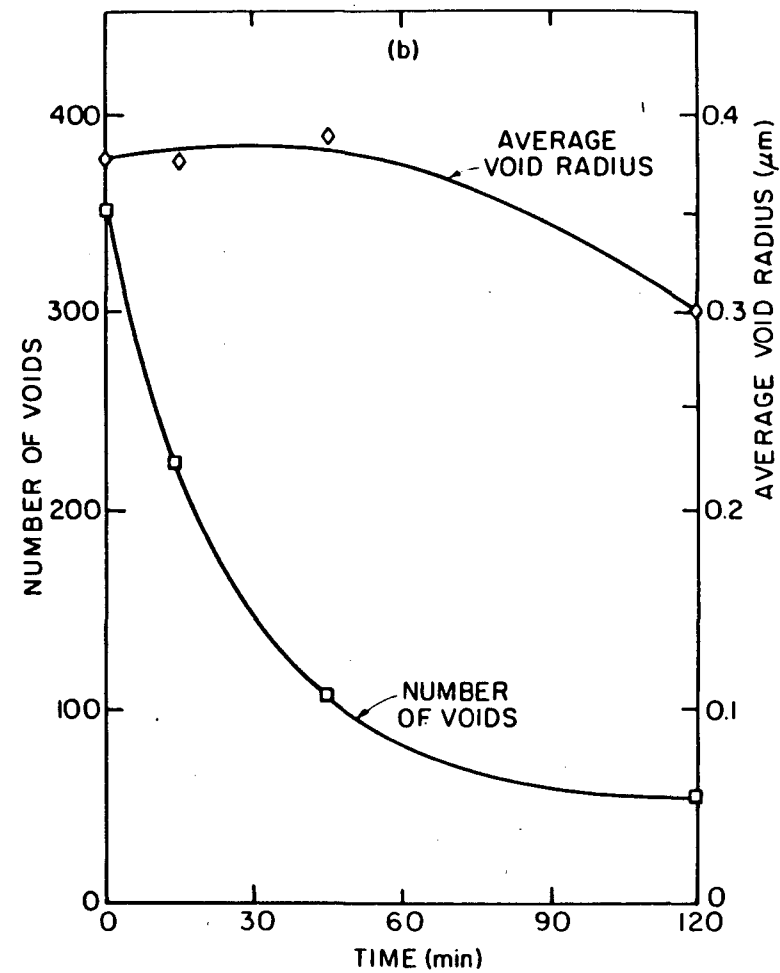
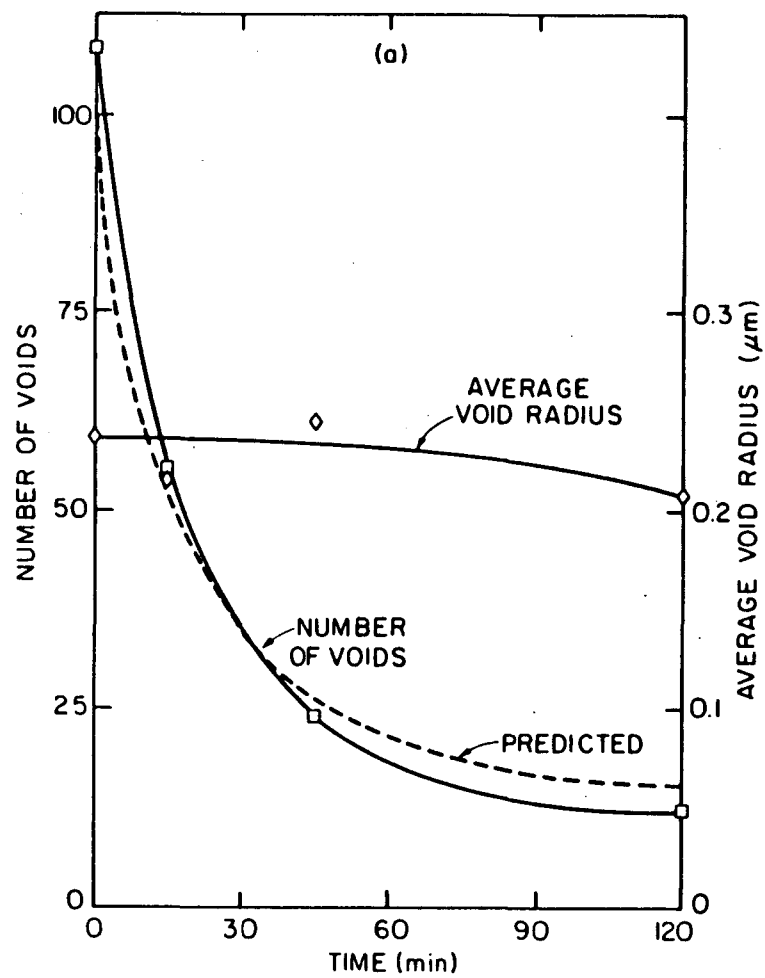
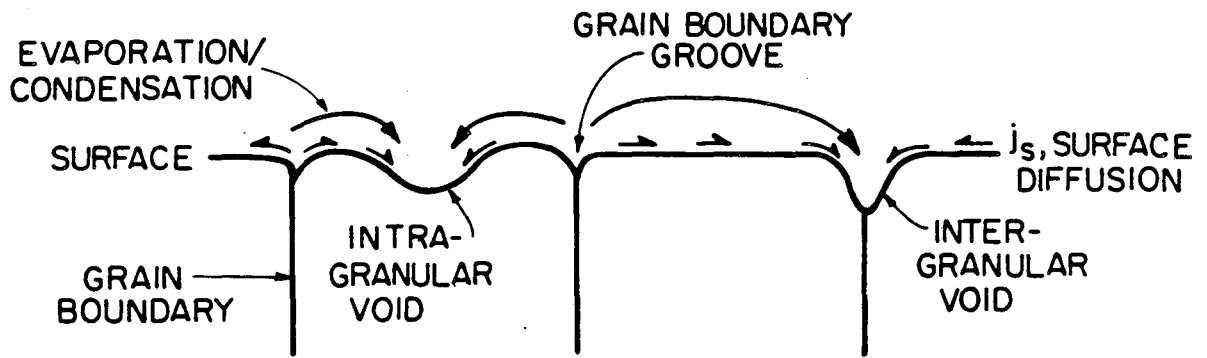
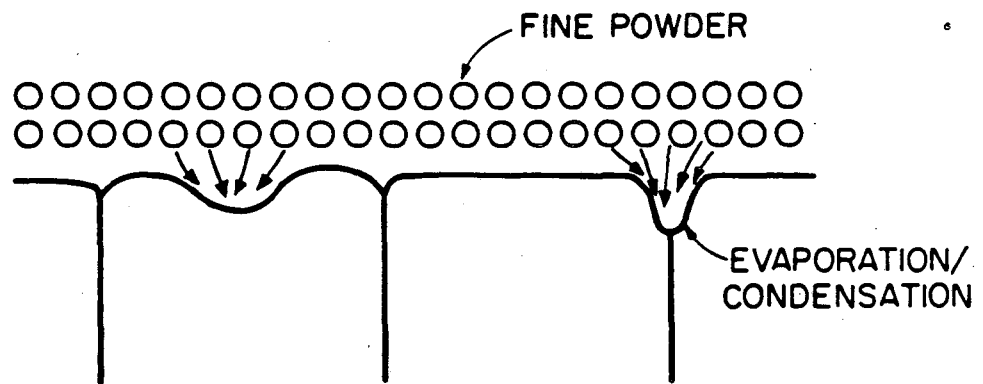


Fig. III-7

XBL849-7361



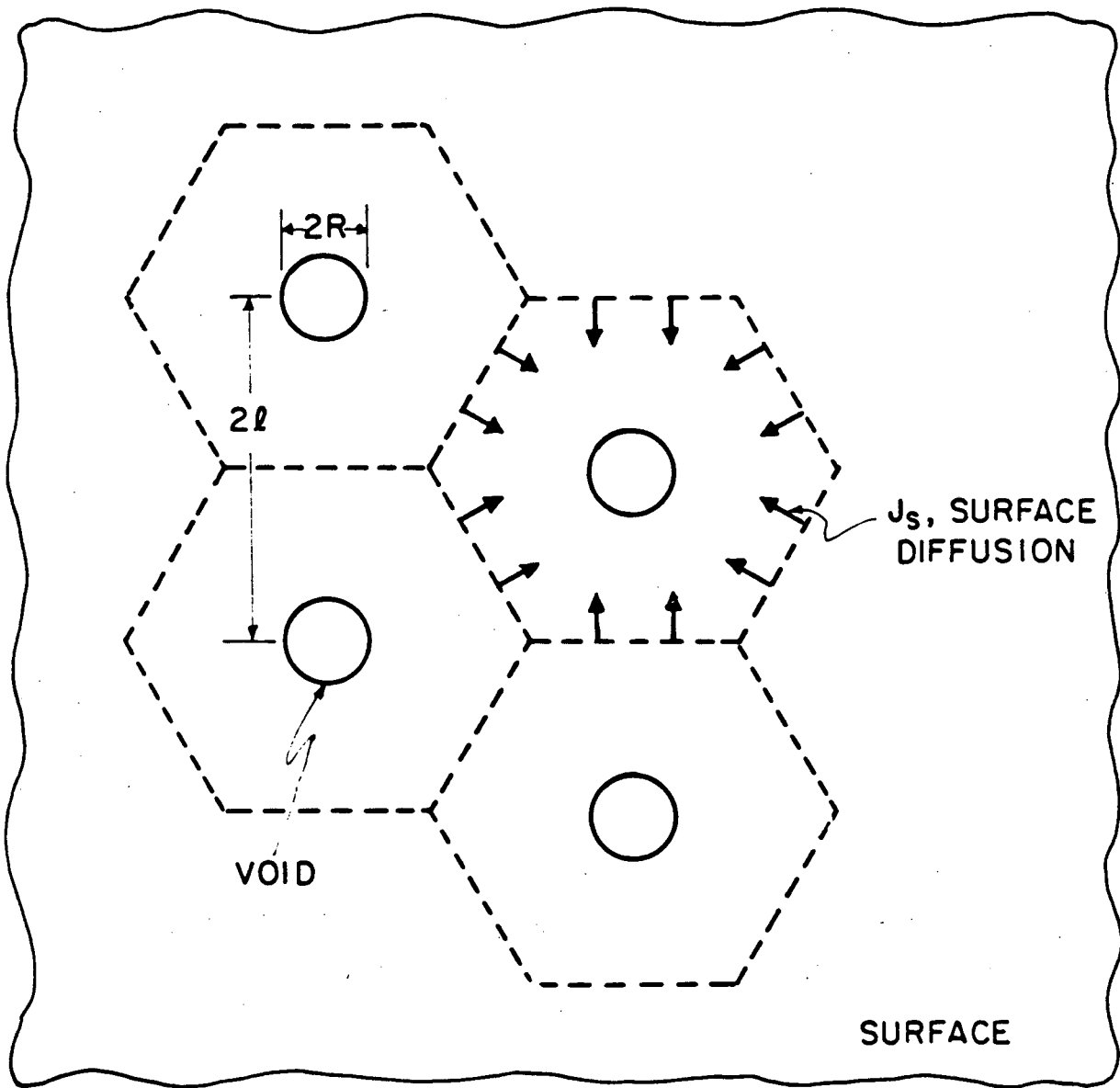
(a) SURFACE SOURCES



(b) EXTERNAL SOURCES

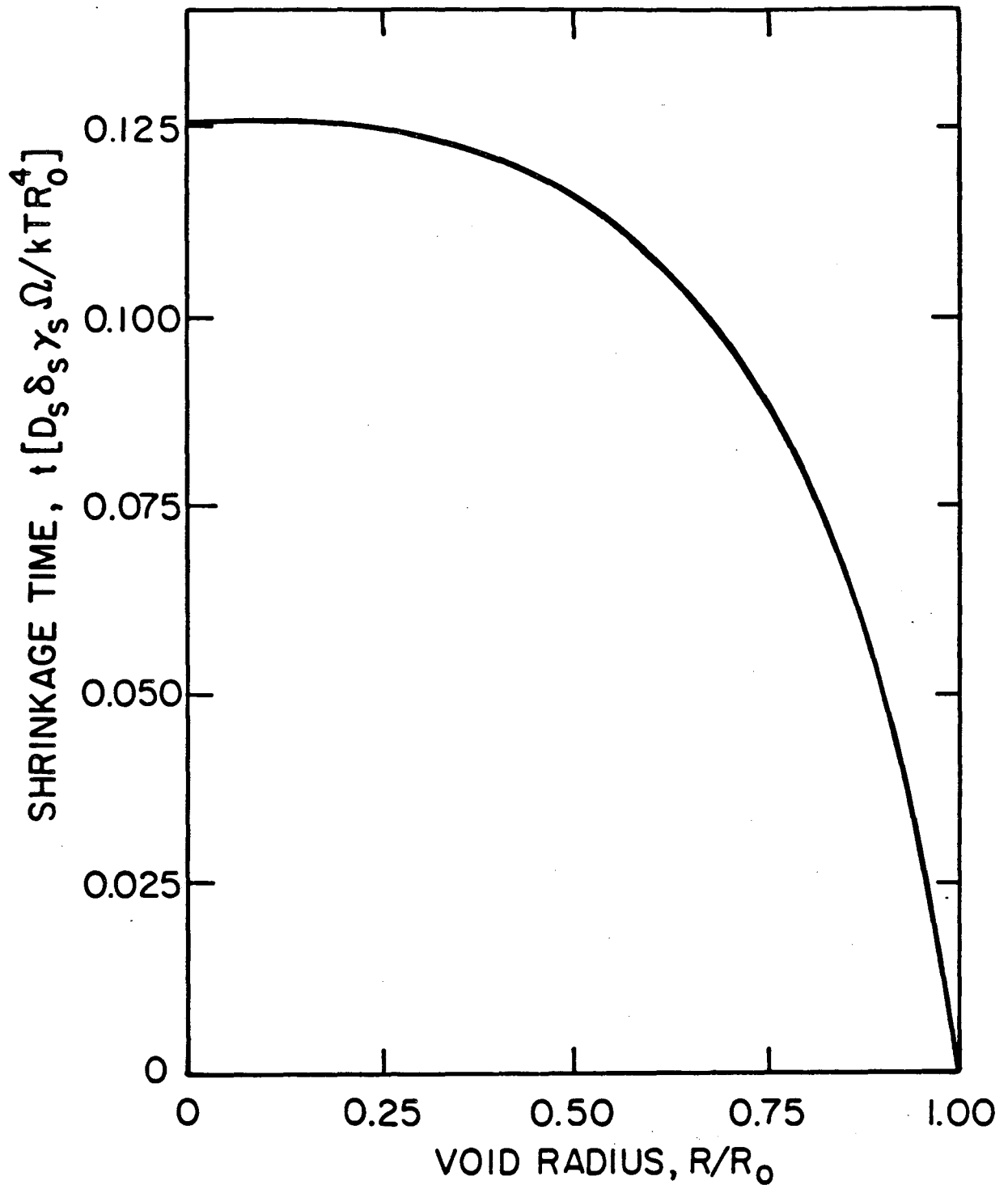
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Fig. III-8



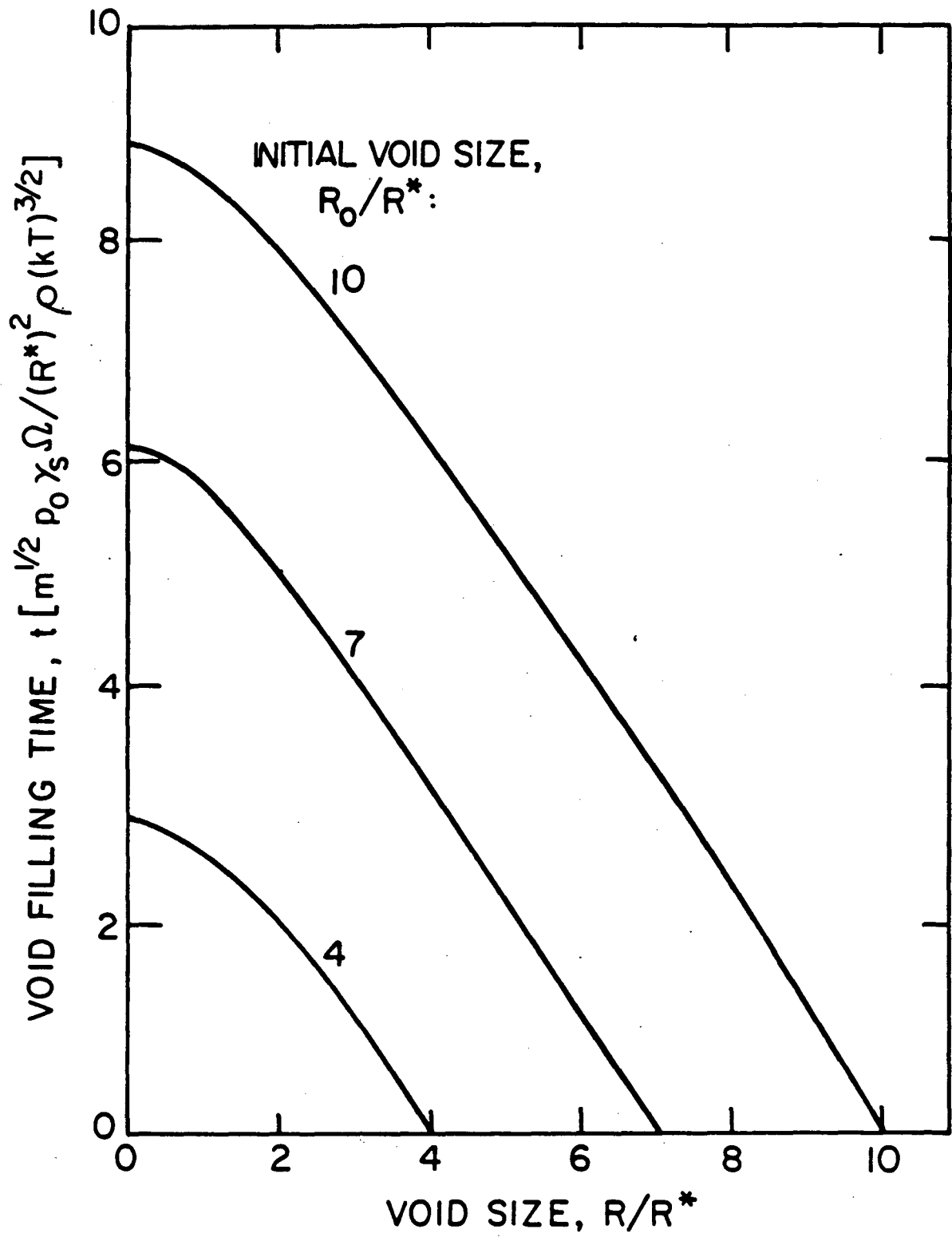
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Fig. III-9



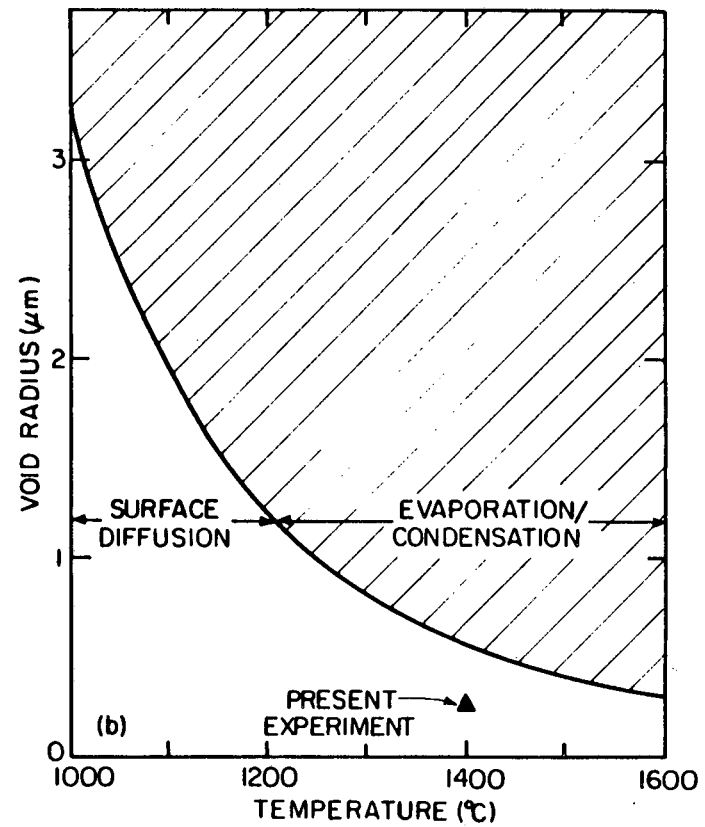
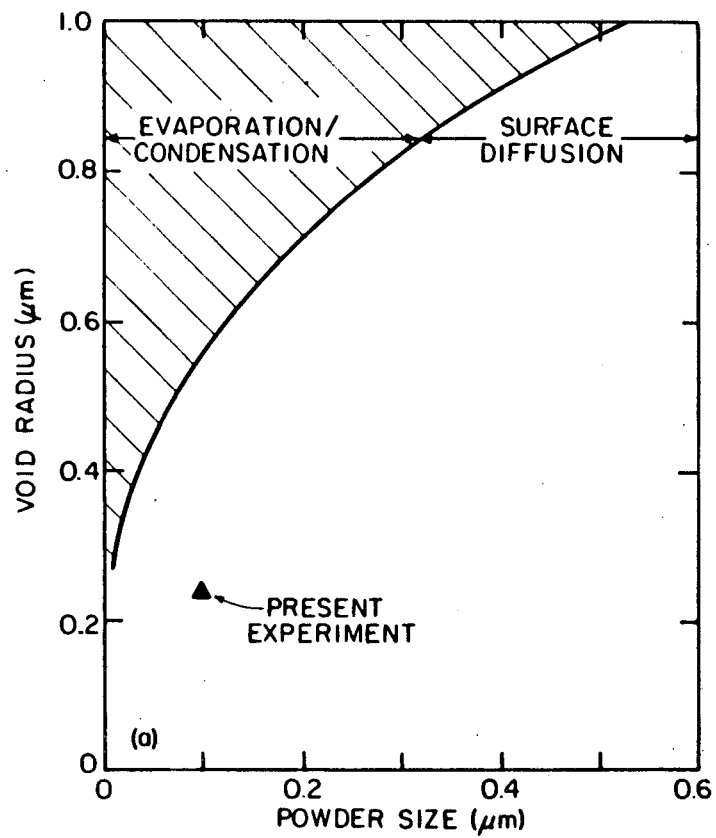
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Fig. III-10



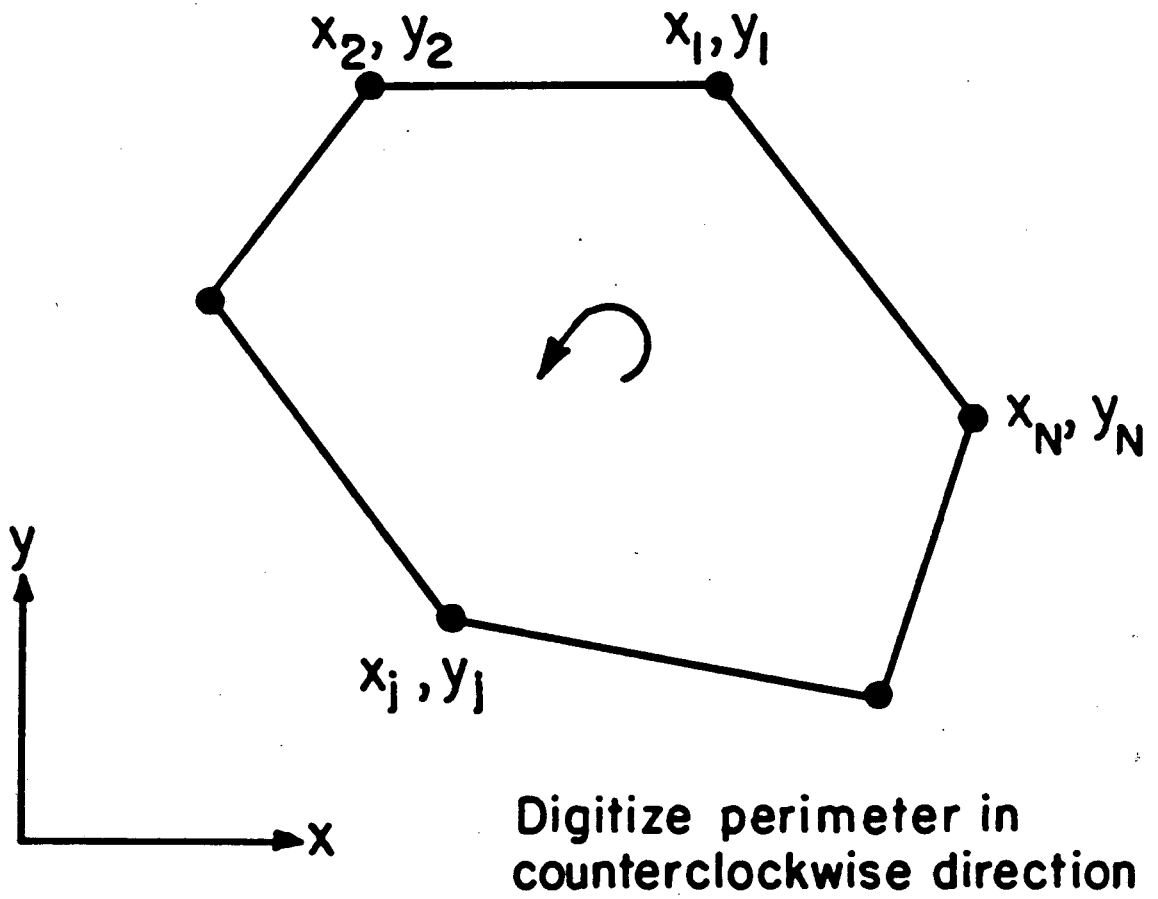
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Fig.III-11



XBL 849-7365

Fig. III-12



Digitize perimeter in
counterclockwise direction

XBL849-7366

Fig. III-13

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