8th Int'l. Symp. on the Reactivity of Solids, Gothenburg, Sweden 000-2290-179

CONF-7608104--1

NTIS MN ONLY

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It has been reproduced from the best available copy to permit the broadest possible availability.

THE STATUS OF UNDERSTANDING DIFFUSION CONTROLLED
SOLID STATE SINTERING, HOT PRESSING AND CREEP

MASTER

R. L. Coble

Massachusetts Institute of Technology

Cambridge, Massachusetts 02139

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

INTRODUCTION AND SUMMARY

Since Kuczynski's pioneering work on the development of models to predict neck growth rates in sintering by diffusion, and his experimental efforts to test their applicability, there have been numerous authors who have contributed a plethora of models covering the different stages of the process with varying assumptions regarding the geometries, the diffusion fields, and the different atomic transport paths which contribute to the overall behavior. (1-5). Ashby's recent paper is a useful source to the past modelling work on single phase materials. (6). The selection of the models cited there was based on simplicity and reasonable accuracy; both the initial and later stages of the process are covered there, although the importance of grain growth and atmosphere effects are not considered. (7,8). Experimental data on different materials, initial particle sizes, dopants, and temperature schedules have provided a relatively convincing view that for most of the range of variables, the sintering process is diffusion controlled. However, in spite of the extensive work to date, a lack of precise quantitative agreement between predicted behavior and the observed time dependences of shrinkage, size effects, temperature dependences, and dopant effects has lead to the question of what is needed: improved models; more thorough characterization of the morphology changes which occur; or should this interpretation be rejected

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EP

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

in favor of other mechanisms for the process? Plastic flow is an alternative, but is not well modelled for any stage of the process. Another alternative is that the process may be controlled by interface kinetics, but modelling has not been available for use in analysis of sintering kinetics. However, Cannon has concluded that the creep of fine grained Al_2O_3 is interface controlled. (9). The author has argued that improved characterization is one of the most important needs; it is recognized that the morphology changes which occur during sintering are complex and that the models only represent first order approximations of the behavior. (10). Because of variable particle sizes and shapes, it should not be surprising that the time dependences for initial stage shrinkage in powder compacts do not follow the prediction of models based on spheres of constant size, or that densification does not follow that predicted by intermediate stage models either, because the actual geometry is different than that assumed.

In this paper, other sources of difficulty in understanding the size effects and temperature dependences are emphasized; they principally result from the idea that rather than a single controlling mechanism a mixture of mechanisms is, in general, operative and that transformations among rate controlling ions and paths are expected. For ceramics, interpretation of dopant effects in sintering could only be done properly if the influences on the surface and boundary and lattice diffusion coefficients of both cations and anions were documented or predictable. It is emphasized below that no basis now exists to model or predict dopant effects on surface or boundary diffusion. Thus, an improved data base is still needed, on diffusion coefficients and dopant effects, as well as on the microstructure changes during sintering. The latter could provide the guidance needed for formulation of statistical models for the process. Understanding grain growth is also obviously important, but is similarly hampered by the lack of boundary diffusion data in addition to other problems. (11).

The creep behavior of numerous materials at low stresses has been found to be diffusion controlled, i.e., quasi-steady state models have been found to apply at stresses below the yield stress as will be discussed below. (9, 12, 13). It is now assumed that any difficulties which arise in interpretation of the

low stress behavior also originates from our incomplete documentation or theoretical base to interpret dopant and impurity effects on the lattice and boundary diffusivities of both species, including their temperature dependences. Also, interface kinetics control may become important at very small particle sizes.(9).

Grain boundary sliding is to be recognized as a necessary adjunct to lattice or boundary diffusion controlled grain shape changes but is not emphasized here except to note that it may be of greater importance in early stage hot pressing than in sintering.(9). Creep in dense polycrystalline materials is a simpler situation than is sintering or hot pressing. Diffusion controlled creep has been quantitatively demonstrated at low stresses and justifies the assumption above because there are no other mechanisms to which recourse could be taken. Therefore, understanding diffusional creep can be taken as a basis to conclude that diffusion also controls sintering and hot pressing for most of the range of variables (particle size, temperature, pressure, etc.) under which these operations are conducted. The basic assumption is that when the stresses in a powder compact (due to surface curvatures) are below the yield stresses the material can deform only by diffusive transport, and the rate limiting processes are either the surface defect reactions or the defect transport at surfaces, grain boundaries or in the lattice. The geometrical change occurring in sintering or hot pressing is more complicated than in creep and has precluded a precise quantitative description of the kinetics, particle size effects, temperature dependences, and diffusivity comparisons based on simplistic models. Impurity effects, initial particle shape and packing effects, space charge effects at grain boundaries, grain growth simultaneously with densification, and the pore shape evolution are other recognized factors contributing to our inability to predict the kinetics from start to finish of the sintering and hot pressing processes.

The intermediate and final stages of sintering are thought to be simpler than the initial stage, because problems associated with inadequate descriptions of broad distributions of initial particle (and therefore pore) sizes, as well as variable agglomerate densities are reduced significantly by a few percent shrinkage. Very different initial structures in compacts evolve to structures with considerable

similarity at 80 to 90% of theoretical density.

SINTERING MODELS

Numerous newcomers to this field have presumed the need to contribute new, improved models. The set now available shows inconsequential differences among the time dependences predicted for shrinkage, neck growth or densification, particle size effects, and the numerical factors associated with the respective models for any assumed mechanism of transport. Multiple modelling has been done for each of the diffusion paths, from which one may conclude that no further simplistic modelling is needed. The first order models are summarized in Table 1. Further consideration should be given, however, to the predictions and implications of the results of combined models, i.e., those in which simultaneous transport by surface diffusion, lattice diffusion and grain boundary diffusion is assumed, as Johnson has done by computer synthesis for the initial stage of sintering under constant rates of heating. (14). He showed that the predicted temperature dependence for shrinkage can be larger than that for the atomic mechanism that causes shrinkage and the time dependence is also altered from that predicted by the single models taken alone. These results provide insight as to why quantitative understanding of the observed kinetics has been so elusive. Combinations of competing mechanisms of transport can give rise to a continuously varying time dependence for shrinkage; i.e., no simple constant integer as the time exponent results as is predicted by the single mechanism models. In Table 1, the models for neck growth (X/R) and shrinkage ($\Delta L/L_0$), or densification ($\Delta \rho$) are indicated to be functions of the lattice diffusion coefficient (D_L), the surface energy (γ), the atomic volume (Ω), time (t), particle size (R), Boltzman's constant (k) and temperature (T). The coefficients n , N , and m depend on the assumed mechanism of transport; for lattice diffusion $n=4$, $m=3$ while for boundary or surface diffusion $n=6$, $m=4$.

Table 1 then indicates the important experimental variables which are used to attempt to deduce the operative atomic transport mechanism. The most important single observation is whether shrinkage (or densification) occurs: that can result from lattice diffusion or boundary diffusion, or viscous or plastic flow (when the effective stress exceeds the yield stress).

TABLE 1

SINTERING MODELS AND EXPERIMENTAL VARIABLES

Neck growth, or shrinkage,
or densification predicted

$$\frac{x}{R}^n; \frac{\Delta L}{L_0}^{n/2}; \Delta \text{ density} = F_n \cdot s \frac{ND\gamma\Omega t}{R^m kT}$$

Experimental variables:

Occurrence of shrinkage?

Yes: $D_L, D_b, n, \tau > \tau_y$

No: D_s, P^0

Kinetics:

Neck Growth
Shrinkage Rate
Particle/Grain Size Effects
Additive Effects
Atmosphere Effects
Temperature Dependence
Grain Growth Rates

With models and data, calculate $D_{\text{sint}}, \Delta Q_{\text{sint}}$

$$D_{\text{sint}} \approx D^*, \text{ and } \Delta Q_{\text{sint}} \approx \Delta Q^* \text{ for Cu, Al}_2\text{O}_3 \text{ (15)}$$

Needs:

Complete descriptions of micro-
structure evolution
Pore shapes and size distribution
Grain size distributions
Enlarged data base on diffusivities

Neck growth without shrinkage may be manifested by substantial increases in the strength of powder compacts; that can occur either from vapor transport or surface diffusion of material to inter-particle contacts. Neither of these latter mechanisms give rise to shrinkage. Quantitative measurements of the other variables listed are then used with the models to calculate the diffusivities to compare with independently measured tracer values. A common result is given at the bottom of Table 1; calculated D 's sometimes agree with the tracer diffusivities (D^*) such as for alumina or copper, but frequently the calculated D 's have been larger, and the observed activation energies also have been larger than that for the presumed diffusion mechanism.(15). The latter might arise from heating rate effects and competitive mechanisms, as Johnson has illustrated.(14).

Because of the disagreement between measured and calculated diffusivities, we have considered the possible need for transient solutions to the diffusion equation instead of the quasi-steady state solutions which are almost universally employed for solid state reactions. Because the pore and grain boundary surfaces move during the process, and the defect concentrations at all sites in the diffusion field change with time, transient solutions should formally cover the total behavior with greater precision. By computer simulation, transient solutions have been generated for a final stage model in which a spherical pore was assumed to be located within a concentric spherical shell.(16). The outer boundary simulates the grain boundaries; it was assumed to be fixed or moving at velocities typical of those observed during grain growth. The results showed that the quasi-steady state solution is approached rapidly during early time intervals that were orders of magnitude smaller than the time required for pore closure. In general, the results showed for observed values of pore and grain boundary surface velocities that the quasi-steady state solutions are adequate. Therefore, most of the behavior that is measurable in sintering experiments should be interpretable based on earlier modelling, as summarized in Table 2. Thus, the discrepancy between D 's cannot be ascribed to a failure to consider the transients for the process.

TABLE 2

SINTERING/HOT PRESSING MODELS

Transient solutions: $dC/dt = D\nabla^2 C$

Blendell, Onorato, and Coble: not necessary

Quasi-steady state: $\nabla^2 C = 0$

D_s	Kuczynski, Cabrera, Nichols, - - - -
D_L	Kuczynski, Kingery, Coble, Johnson, - - - -
D_b	Coble, Johnson, - - - -
p^0	Kingery - - - -
η	Frenkel
τ_y	Mackenzie, Shuttleworth

Various diffusion models, with different assumptions show quantitative agreement!

PROBLEMS

A summary of some of the problems in understanding sintering is collected in Table 3, where suggestions for resolving them are advanced. For the various cases in which the discrepancy in D's exist there are several possibilities. For cases in which the process is interpreted to be lattice diffusion controlled, it may be governed by boundary diffusion, particularly when small particle sizes are being used. The influences of impurities on the defect concentrations and transport in compound crystals is presumed to be understood, although recently, increased importance has been attached to association of defects, and to space charge effects at interfaces that have only recently been combined with impurity drag models to predict grain growth rates. (11,17). However, the general lack of data on grain boundary diffusion, and the influence of impurities on boundary transport will require much more work before this problem area can be discounted or quantitatively resolved. It should be noted that smaller contents of impurities could produce more substantial effects at grain boundaries than would be required to cause extrinsic behavior in the matrix crystals.

Typical lattice diffusion behavior in a metal oxide with Schottky disorder is shown in Fig. 1; an impurity cation with higher valence than the host is presumed to be present. In materials like MgO, cation diffusivities are generally found to be greater than the anion diffusivities. The expected temperature dependences for both ions are illustrated for the intrinsic and extrinsic regions. More complex behavior is expected in materials with mixed Schottky-Frenkel disorder as may be expected for Al_2O_3 or in more complex compounds such as the spinels, for which the applicability of the modeling for alkali halides is unlikely to be correct. However, for lattice diffusion it is presumed that improved characterization of the defects and complexes present (by ESR, NMR, etc.) might demonstrate the applicability of existing defect models. In contrast, we have no adequate structural models for grain boundaries or for the nature of the defects in them to interpret intrinsic or extrinsic grain boundary behavior. Further, there are insufficient experimental data on boundary diffusion to provide empirical correlations for analysis or predictions of

TABLE 3

PROBLEMS IN SINTERING, HOT PRESSING

$D_{\text{sint}} \neq D^*$, and $\Delta Q_{\text{sint}} \neq \Delta Q^*$, frequently

Geometrical complexity sintering

Documentation of microstructure evolution

Small particle sizes used $100\text{\AA} - 10\mu$

Thermodynamic approach breaks down

Statistical mechanics approach?

Grain growth

Space charge effects on boundary "drag"

Boundary diffusion documentation needed

Structures: ionic/covalent/metallic

Chemistry effects on D_b , "core", and space charge regions

Sintering covalent materials: γ_{sv}/γ_{gb}

D 's, P_0 boundary diff, liquids?

Kinetics not understood

Not expected for simple models

Microstructure evolution needed

Figure 1: Aliovalent impurity effects on D_L 's in a compound with Schottky disorder.

impurity or dopant effects on the boundary transport of both species as functions of temperature.

Another important conclusion from earlier theoretical work is noted in Fig. 1. Readey analyzed sintering by lattice diffusion (only) using a statistical mechanics approach, and considered the coupled fluxes of the different charge species (ambipolar diffusion). (18). He showed that the ion that controls the process is the slower species as would be observed in a tracer diffusion experiment (in samples with identical impurity contents). For sintering, hot pressing or creep, the slower species is enhanced by a small amount ($\sqrt{2}x$) due to ambipolar coupling.

When transport can take place by boundary diffusion in addition to lattice diffusion, the process may then take place by transport of the cations in the lattice while the anions move along grain boundaries. In this instance, Readey's conclusion that the phenomenological diffusivity governs the process must be extended to apply to all paths and ions simultaneously. Hence, the uncertainties in boundary transport in the extrinsic range become very important in governing our interpretation of the behavior, because the shrinkage may take place by any combination of paths for both species that will provide the fastest net flow. For example: lattice diffusion of both ions, or boundary diffusion of both ions, or lattice diffusion of the cation with boundary transport of the anion, or vice versa: the fastest combined path(s) operates with the slower ion in whichever path controlling the rate.

The point to be emphasized is that the sintering process is quite complicated apart from the geometrical problems. If we consider surface diffusion as well, the above schema also apply to neck growth behavior, but with lattice (or boundary) and surface diffusion paths interacting cooperatively. Since both neck growth and shrinkage phenomena must be understood, with all three diffusion paths contributing, there should be little wonder that attempts to understand the kinetics, and the temperature dependences of observed behavior have rarely been conclusive. Consider that for intrinsic and extrinsic transport of two species along three paths that there are 12 possible activation energies to be considered. For each process (neck growth or

shrinkage) for different species and paths may control the progress as the size scale is changed; eight could conceivably control each process is impurities/dopants and temperature are also changed (i.e., if D_L^O could become greater than D_L^M , etc.). In the latter case, sintering could be controlled by any of the twelve different ions, transport paths, and regimes; transitions among them are expected as neck growth takes place, or as changes in particle size, temperature, dopant concentrations, or oxygen pressures are manipulated as experimental variables.

It has been assumed that the initial stage models are applicable for shrinkage less than ~5%. However, it has not been recognized that the pressures predicted from the models exceed reasonable bounds when applied to samples made from powders of small particle size. For sintering between spheres by lattice/boundary diffusion, the minimum radius at the neck (ρ) may be equated to one-half the overlap (y) between the spheres. (19). The pressure diffusion across the neck surface (γ/ρ) may then be set equal to γ/y , and since $y/R = \Delta L/L_0$, $P = \gamma/R(\Delta L/L_0)$. The pressures calculated for two ranges of particle size ($R = 10^{-6}$, and 10^{-4} cm, with $\gamma = 10^3$ ergs/cm²) are plotted as functions of shrinkage in Fig. 2. The size ranges selected are those typical of sol-gel powders, and numerous dielectric bodies, respectively. The results show that at small shrinkage values the pressures exceed the yield stresses and plastic deformation may therefore be expected. In Al_2O_3 , the range of non-basal yield stresses from ~1200°C to 2000°C is indicated. Therefore, for shrinkage greater than 1%, the diffusion models are expected to apply. However, that covers most of shrinkage of interest. The curves are shown to turn upwards to represent, schematically, the pressure increases at later stages in the process when pore radii decrease. (6).

DIFFUSIONAL CREEP

The highlights of the results obtained on creep in oxides are intended only to justify the conclusion above: since creep is diffusion controlled at low stresses, we conclude that most of the range of sintering is also diffusion controlled. The combined lattice and boundary diffusion models as derived for an

Figure 2: Calculated pressures in initial stage sintering

TABLE 4
DIFFUSIONAL CREEP
IN A DENSE POLYCRYSTALLINE:

Metal: Lattice and grain boundary
contributions additive:

$$\dot{\epsilon} = \frac{14\sigma\Omega D_L}{kT G^2} + \frac{14\pi\sigma\Omega D_b W}{kT G^3} = \frac{14\sigma\Omega}{G^2 kT} (D_{eff})$$

Effective D for combined paths

$$D_e^i = D_L^i + \pi D_b^i W/G$$

Ceramic: Effective D in compound $M_\alpha O_\beta$

$$D_{eff} = \frac{(\alpha+\beta) D_e^m D_e^o}{\beta D_e^m + \alpha D_e^o}$$

elemental metal are presented in the first equation in Table 4. The second equation represents the uncommon terms after factoring common terms and is to be evaluated independently for anions and cations. Those values inserted in the third equation give D_{eff} for use in the expression on the right hand side of the first equation; this then covers the combined paths with ambipolar coupling of the respective ion fluxes. Note that the strain rate is linear in stress (σ), which distinguishes diffusional creep from dislocation motion controlled processes, for which higher stress dependences are expected.

The stress dependence is the first experimental variable listed in Table 5 among those used to test the applicability of the models. The second important variable is the grain size (G) dependence; the explicit effects for lattice and boundary diffusion control are given in Table 4, and their effect on the creep rate for a compound is shown in Fig. 3. It is assumed that the cations move more rapidly through the lattice than do the anions ($D_L^m > D_L^O$); either could control the rate at values fixed by the curves with slopes equal to -2. Independently, boundary transport gives rates shown by the curves with slopes equal to -3, but the assumed order is reversed, i.e.: the oxygen diffusivity in the boundary (D_b^O) is assumed to be greater than that for the cation (D_b^m). The fastest transport of both species using the combined paths, is indicated for the slower species by the dash-dot trace. As the grain size increases, evolution in control of creep is predicted from: boundary diffusion of the cation at small grain sizes; to lattice diffusion of the cation; to oxygen control in the boundary; and finally to oxygen control in the lattice at large grain sizes. The range which has been observed most frequently is for control of the process by lattice diffusion of the cations (with anions transported (faster) at the grain boundaries). Reasonable agreement has been found between the diffusivities calculated from the creep rates, and tracer values in MgO and Al_2O_3 . (9, 12, 13). At intermediate grain sizes, Cannon concludes that creep in Al_2O_3 is controlled by transport of Al in the lattice with oxygen moving along grain boundaries. (9). At small grain sizes ($G < 10\mu$) and at low temperatures, Al_2O_3 creep is controlled by Al transport at the grain boundaries. Similarly, in Fe doped MgO , Gordon et al conclude that the process changes from control by Mg transport in the lattice (at low P_{O_2}) toward control by

VARIABLES USED TO DEDUCE CREEP MECHANISMS

1. Stress: $\sigma^1 \rightarrow \sigma^4$
High stress Dislocation motion
Pore nucleation
Fracture
2. Grain Size
Diffusional creep: Explicit effects:
 G^{-2} or G^{-3}
Dislocation climb/glide: Cell structure
documentation needed
3. Temperature
Increase T, Intrinsic: D_L/D_b increases
Extrinsic: D_L/D_b increase/decrease?
Decrease T $\rightarrow$ Extrinsic range, and initial
transient dominant for overall
creep strain
4. Change P_{O_2} (Kroger-Vink) changes stoich, and
valence of impurities
5. Increase dopant $\rightarrow$ Solid solution effects: D_L 's, D_b 's
2nd phase: solid, liquid

Figure 3: Diffusional creep in a dense, polycrystalline compound as a function of grain size.

oxygen transport at the boundaries in samples with median grain sizes. (13). Intermediate exponents for the grain size effects are interpreted as being indicative of mixed control and thus substantiate the assumption of additive contributions from mixed paths for the respective ions as a valid hypothesis. The main point is that transitions from one set of controlling paths to another have been demonstrated for creep as a function of one of the variables (grain size) making quantitative interpretation quite complex.

Other variables investigated for creep include dopant effects and oxygen pressure dependencies which further support the conclusion that creep is diffusion controlled in-so-far as most of the effects can be interpreted in terms of expected changes in defect concentrations, atom mobilities, and hence creep rates. (9,12,13).

In summary, creep studies with variable stresses, grain sizes, dopants, and changes of oxygen pressure with and without dopants, and the observed temperature dependences have provided a broad range of conditions under which diffusional creep is observed and for which good agreement is obtained between calculated diffusivities and tracer values for the cation lattice diffusivities. Cannons' re-analysis of the published data for Al_2O_3 yielded a spread of only $\sim 2\times$ for the lattice diffusivities for intermediate grain sized material in contrast to the wide spread disagreement among the independent papers. (9).

It is noteworthy that diffusional creep in dense polycrystalline material is, of itself, quite complicated. Although the sintering or hot pressing behavior is recognizably more complicated, these densification processes should also be diffusion controlled in the ranges of stress, grain size, and temperature for which the creep behavior has been documented and shown to be diffusion controlled. That range covers most of the evolution in structure during sintering of Al_2O_3 , and it is presumed for many other less-well-documented materials as well. We conclude that for the initial stages of sintering of sub-micron particles, boundary diffusion is probably dominant. Lattice diffusion should take over during the intermediate and late stages in the process as a result of neck growth or grain growth. The evolution in control

of the process among paths and ions for sintering should follow the creep analogy shown in Fig. 3.

STATUS, OR CONCLUSIONS

1. Transient solutions are not needed for modelling diffusion controlled sintering.
2. Improved characterization of the microstructure evolution in sintering and hot pressing is still needed to guide realistic geometrical or statistical remodelling.
3. Numerous quasi-steady state models show quantitative agreement, and when applied to sintering data, and yield diffusivities which sometimes agree with independently measured diffusivities.
4. Steady state creep at low stresses is diffusion controlled.
5. For most of the range of variables in sintering and hot pressing at moderate pressures, diffusion must also be controlling.
6. The contributions from the independent diffusion paths are additive, and transitions in operative paths are expected with changes in neck size, grain growth, dopants, oxygen pressures, and temperature.
7. Transitions among paths have been demonstrated for creep.
8. An expanded data base on diffusivities in crystal lattices and at grain boundaries, and dopant effects upon them will be required before quantitative interpretations of the sintering behavior can be improved significantly.
9. Space charge effects at grain boundaries influence grain growth.
10. Grain boundary sliding is a necessary adjunct process to diffusional grain shape changes and may be important as an alternate to interface control by defect equilibration under presently unspecifiable conditions.

The author regrets that the space limitations preclude an exhaustive review for this broad subject and is apologetic to numerous other significant contributors to the field not cited herein.

REFERENCES

1. G. C. Kuczynski, Trans A.I.M.E., 185 (1949), 169.
2. T. L. Wilson and P. G. Shewmon, Trans. A.I.M.E., 236 (1966), 48.
3. F. Thummler and W. Thoma, Met. Rev., 115 (1969), 69.
4. R. L. Coble, J. App. Phys., 32 (1961), 787.
5. D. L. Johnson, J. Am. Ceram. Soc., 53 (1970), 574.
6. M. F. Ashby, Acta. Met., 22 (1974), 275.
7. J. E. Burke, J. Am. Ceram. Soc., 40 (1957), 80.
8. R. L. Coble, J. Am. Ceram. Soc., 45 (1962), 123.
9. R. M. Cannon and R. L. Coble in "Deformation of Ceramic Materials", Plenum Press (1975), 61.
10. R. L. Coble, Review of Understanding Sintering and Related Phenomena, Vol. 6, Plenum Press, (1973).
11. M. Yan et al., "Deformation of Ceramic Materials", Plenum Press (1975), 549.
12. G. Hollenberg and R. S. Gordon, J. Am. Ceram. Soc., 56, (1973), 140.
13. P. Lessing and R. S. Gordon, "Deformation of Ceramic Materials", Plenum Press (1975), 271.
14. D. L. Johnson in "Ultrafine-Grain Ceramics", Syracuse University Press (1970), 173.
15. R. L. Coble and T. K. Gupta, "Sintering and Related Phenomena" Gordon & Breach, N. Y. (1967), 123.
16. J. E. Blendell, P. K. Onorato and R. L. Coble unpublished research.
17. W. D. Kingery, J. Am. Ceram. Soc., 57, (1974), 1.
18. D. W. Readey, J. Am. Ceram. Soc., 49, (1966), 366.
19. W. D. Kingery and M. Berg, J. Appl. Phys., 26 (1955) 1205.

ACKNOWLEDGEMENTS

The author gratefully acknowledges helpful review of the manuscript by H. Kent Bowen, R. M. Cannon, Jr., J. E. Blendell, E. Skaar, and D. Kramer, and for financial support under ERDA Contract No. E(11-1)2390.