KFK-615

KERNFORSCHUNGSZENTRUM

KARLSRUHE

Juni 1967

KFK 615

Institut für Material- und Festkörperforschung

The sintering process

F. Thümmler, W. Thomma

GESELLSCHAFT FÜR KERNFORSCHUNG M.B.H.
KARLSRUHE

REVIEW 115

by F. Thümmler and W. Thomma

The sintering process

I. General survey

THE SINTERING PROCESS HAS A SPECIAL IMPORTANCE for three technical disciplines: powder metallurgy, ceramics, and the agglomeration of ore fines (pelletising). All these methods have been operated empirically for some time, without obtaining a deeper insight into the nature of the process. Powder metallurgy and ceramics have also developed independently to a large extent; powder metallurgy itself can be said to have been developed systematically since about 1900.

The sintering process, which is an essential factor in almost all practical applications, has been studied in closer detail only from around 1920. It was not until 1950 or thereabouts that ceramic workers began to publish extensively the results of investigations into the sintering process, particularly on the relatively simple oxide–ceramic systems. Since then the flow of publications dealing with the sintering of metals and oxides has become an avalanche. A close interaction has arisen between the fundamental research into powder metallurgy and ceramics in recent years, and the representatives of both disciplines are equally concerned in the elucidation of sintering mechanisms.

Although the present report is mainly concerned with the newer theories regarding the process, the pioneers in this field must not be forgotten. The first name that comes to mind is that of Sauerwald, who published papers on sintering processes from 1922 onwards and a general review in 1943.[1] Detailed investigations also appeared from the school of Hüttig.[2–4] Less recent reviews have been published by Balchin,[5] Dawihl,[6] and Hedvall.[7] Illustrations of the older concepts of sintering are found in the valuable books by Jones,[8] Schwarzkopf *et al.*,[9] Kieffer and Hotop,[10] Skaupy,[11] Balchin,[12] Goetzel,[13] and many others.[14] These works deal mainly with investigations into the influence of the numerous powder, pressing, and sintering parameters on the properties of the resulting sintered compact. However, they already contain statements on the principles determining the process of atom transport which plays an important part in sintering.

From 1949 onwards, stimulated by a theoretical investigation by Frenkel,[15] papers began to appear on work in which the growth of individual, defined contact zones was followed experimentally. By this means a deeper insight could be obtained into the atomistic events. These experimental and theoretical investigations carried out on models, originated in the first place with Kuczynski,[16] who has been responsible for advances over the whole field. This later period also produced many indications regarding the influence of grain boundaries on the sintering process, as well as a better understanding of sintering under pressure (hot pressing). By this time a considerable amount of information was also available on the sintering of multicomponent systems, with and without the presence of a liquid phase. It is now believed that all the factors are known that can influence the sintering process in any way or at any specific stage, and researchers are now concerned with determining the separate effects of these parameters as far as possible.[17]

In this later period numerous reviews have also appeared.[18–42] These references comprise both articles that have appeared in journals and detailed treatments in book form. The field of sintering has also been discussed in recent years at various special conferences, for example, in London in 1959.[43] During subsequent conferences in New York (June 1960[44] and May 1965[45]), Eisenach (June 1961[45a] and May 1965[45b]), Reutte/Tyrol (June 1961[45c]), Paris (June 1964[46]), and Notre Dame University, Indiana (June 1965), sintering processes also played a leading part. Finally, attention may be directed to new surveys by Coble and Burke[47] and by Fischmeister and Exner.[48]

1. Definition and delineation of the concept of sintering: Driving force and aim of the reaction

It must be admitted that the position is somewhat unsatisfactory. No definition exists at the moment that

---

Professor F. Thümmler and Dr. W. Thomma are in the Lehrstuhl für Werkstoffkunde II der Technischen Hochschule, Karlsruhe, Germany.

Metals and Materials and Metallurgical Reviews Vol. 12 (1967)

CONTENTS

takes fully into account all the theoretical and practical aspects, and at the same time delineates correctly the limits that separate sintering from neighbouring fields of study (such as pressure welding, brazing, cladding, and the elimination of shrinkage cavities and porosity by hot rolling). The list of definitions recommended by well-known powder metallurgists and compiled by Hausner[49] must be viewed from this standpoint. The various stages of sintering ranging from the loose powder filling, via the different models, to the final sintering of almost porosity-free compacts differ very widely from each other.

To be generally valid, a definition must cover all this ground and also many special cases, with the result that it becomes too complicated to be satisfactory, at any rate for practical applications. A number of essential factors exist, however. These are:

(*a*) A liquid phase is present only to the extent that it leaves a solid skeleton behind.

(*b*) A decrease in the free enthalpy of the system, which represents the driving force of the sintering process, results from:

  (i) Diminution in the specific surface area due to initiation and/or growth of contacts (necks).
  (ii) Decrease in pore volume and/or the surface area of the pores.
  (iii) Elimination of non-equilibrium states in the lattice.

(*c*) Important properties* approximate to those of the compact, porosity-free material.

On these bases, the following definition is proposed: 'By sintering is understood the heat-treatment of a system of individual particles or of a porous body, with or without the application of external pressure, in which some or all of the properties of the system are changed with the reduction of the free enthalpy in the direction of those of the porosity-free system. In this connection, at least enough solid phases remain to ensure shape stability'. However, even this condition still does not meet the requirement of distinguishing clearly between the neighbouring fields already mentioned.

The stable state, according to thermodynamic considerations, at temperatures below the melting point of any given material, is the single crystal with its equilibrium defects. At absolute zero it is the ideal, undistorted single crystal; at finite and, especially, at sintering temperatures, thermal vacancies, multiple vacancies, and dislocations constitute unavoidable lattice defects. The powder compact approximates to the stable state at elevated temperatures, with the co-operation of all the transport mechanisms concerned. The excess free enthalpy exists in the powder compact in the form of the surface energy of all interfaces, both with the atmosphere and between individual grains (grain-boundary energy), and as excess lattice energy. The lattice energy arises from the existence of excess vacancies and dislocations, together with internal stresses. The relative proportion of geometrically dependent surface energy to lattice energy is very small, even with the most finely divided powders; while the surface energy reaches only a few hundred calories per mole, the lattice energy can amount to several kcal/mole.

According to Hüttig,[50] a 'surface space' must be visualised for the powder, in which this energy is stored; this can contain the whole of the particles in the case of fine powders, and from it stems the high activity and sinterability of the finest powders. The excess free enthalpy $\Delta G = \Delta H - T\Delta S$ is made up of the enthalpy ΔH, e.g. the equivalent heat of reaction to produce all defects, and the entropy ΔS of the non-equilibrium state. (According to Torkar[51] the zero entropy of active solids can amount to $\sim 30\%$ of the fusion entropy. Thus, the powder particles cannot be viewed simply as adjacent small single crystallites).

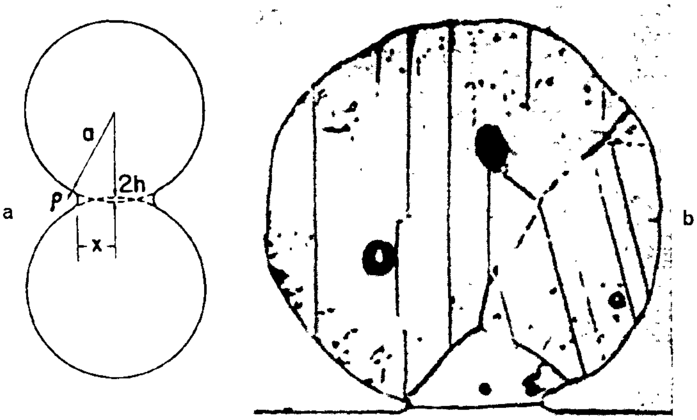
Whether the attainment of a single crystal is in fact always the object of the process is open to discussion.[52] However, this question is meaningless as far as practical sintering processes are concerned, because the sintered compact always remains polycrystalline under the conditions normally prevailing. At any rate, if too rapid and coarse a grain growth is avoided, a compact can be obtained in certain cases which, although polycrystalline, is practically free from porosity (Fig. 1), even in the absence of a liquid phase. Even massive substances cannot be transformed to single crystals by prolonged annealing alone. If the grain sizes and shapes are uniform, a true metastable state exists, which is not subject to further change except under the action of gross disturbances (deformation). Thus, the true

---

* Not necessarily all properties. For instance, expansion takes place in some circumstances when a powder mixture is heat-treated. However, if the conductivity or strength shows some increase as a result of neck growth, the process would also be termed sintering.

[Courtesy 'Compt. Rend.'

1 Almost porosity-free sintered compact: carbonyl iron, sintered in hydrogen for 765 h at 890° C. × 450. (*Ciceron and Lacombe.*[131])



[Courtesy Amer. Inst. Min. Met. Eng.

2a Geometry of a sintered contact. (*Kuczynski.*[16])

2b Sintered contact in the sphere-plate model experiment. × 640. (*Kuczynski.*[16])

objective of the sintering process is the removal of porosity. (*cf.* Fig. 6c)

Special considerations based on models can define the mechanisms in terms of the driving force. Plane microcontacts already exist in the pressed compact or even in the unpressed powder agglomerate.[53] By considering the geometry of these contacts (Fig. 2) it can be deduced that the outer (circular) edge of the contact is subjected to the tensile stress:

$$\sigma = \gamma\left(\frac{1}{\rho} - \frac{1}{x}\right) \qquad \ldots [1]$$

or, for $x/a \ll 1$ and $\rho \ll x$:

$$\sigma = \frac{\gamma}{\rho} \qquad \ldots [2]$$

which, if higher than the yield stress of the material, must lead to neck growth by plastic (or viscous) flow. Furthermore, an excess exists over the equilibrium concentration, C_0, of vacancies beneath the concave surfaces in the material, in accordance with:

$$\frac{\Delta C}{C_0} = \frac{\gamma V_0}{RT\rho} \qquad \ldots [3a]$$

as well as a reduced vapour pressure:

$$\frac{\Delta p}{p_0} = -\frac{\gamma V_0}{RT\rho} \qquad \ldots [3b]$$

This leads to vacancy diffusion into regions with a vacancy deficit (convex surfaces), or to vacancy sinks, or to an isothermal transport of material via the gas phase. In the porous sintered compact the pores, assumed to be spherical, are subjected to compressive stresses according to:

$$\sigma = \frac{2\gamma}{r_{\text{pores}}} \qquad \ldots [4]$$

Superimposing supplementary external tensile stresses on these stresses, Youssef and Eudier,[54] by extrapolating to a shrinkage O, were able to determine a hypothetical external stress that compensates the 'true sintering force'. In this way they confirmed equation [4] to a good approximation.

This experimental result provides a justification for the analogous relationships following from:

$$\sigma = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad \ldots [5]$$

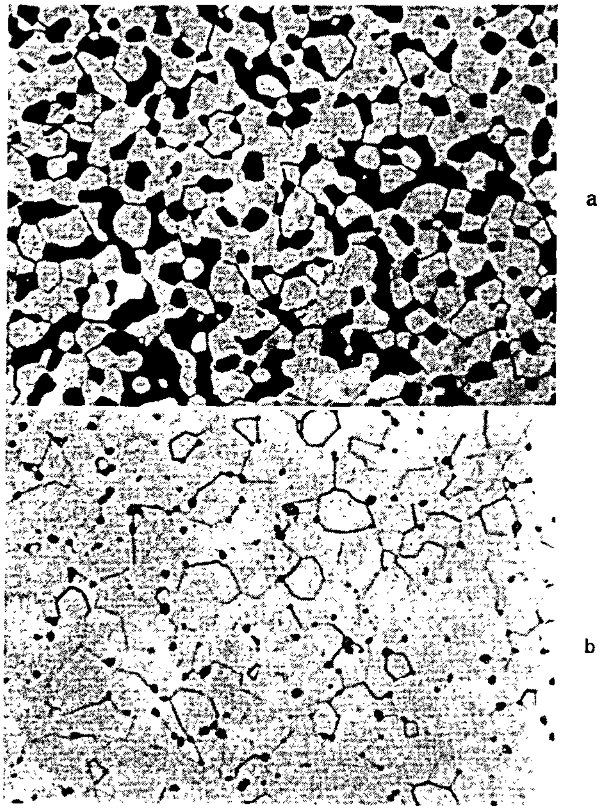
between the radii of curvature and changes in the equilibrium values of the vapour pressure (Δp) and of the vacancy concentration (ΔC). The aim of the reaction must lie in the elimination of these stresses, the equalisation of the vapour pressures, or the disappearance of the zones containing excess vacancies, resulting from atom movements.

2. The stages of sintering

Three stages can be distinguished in the course of sintering a powder agglomerate to the dense material. These merge continuously into one another, but this does not mean that it is in any way superfluous to distinguish between them.

(a) **The early stage of neck growth** Under the influence of the stresses and excess vacancies described above, neck growth proceeds according to an exponential time law. In this stage the powder particles remain as individuals, since it is still not possible for strong grain growth to take place beyond the original particle. The tensile stresses resulting from surface tension maintain the grain boundaries between two adjacent particles in the plane of contact. However, the occasional formation of new grains is possible. The midpoints of the particles approach only slightly (corresponding to a small contraction) but a marked decrease in surface activity takes place.

(b) **The stage of densification and grain growth** Fig. 3(*a*). When the x/a ratio exceeds a certain value after intensified neck growth, the separate particles begin to lose their identity. Most of the shrinkage takes place at this stage, where a coherent network of pores is formed and grain growth continues. The grain boundaries usually run from pore to pore. When ~90%



[*Courtesy 'J. Applied Physics'*.
3a Intermediate stage of sintering with pore network in Al_2O_3; b late stage of sintering with closed pores. × 125. (*Coble*.[159])

of theoretical density is exceeded the relative proportion of closed pore spaces increases rapidly, leading to the final stage of sintering (Fig. 4).

(c) **The final stage with closed pore spaces** (Fig. 3(b) The isolated pores become increasingly spheroidised. Further densification still proceeds slowly, so that it is often impossible to decide whether it has come to an end, e.g. whether the residual porosity is permanent. For a discussion of possible density regressions see Section III.

In the case where gases that have not diffused away are enclosed in these residual pores, it seems certain that further densification becomes impossible as soon as the gas pressure reaches the pressure due to surface tension. On the other hand there appears to be no reason why pores even in the interior of the grain cannot shrink further by the diffusion of vacancies, although at a correspondingly low rate (see Section II). In any event small pores in the neighbourhood of larger ones can disappear.

Quite often, for instance, at lower temperatures and in model experiments where the process is limited to neck growth, the first stage is essentially the only one reached. Under practical sintering conditions, however, where marked densification also occurs, the second stage at least is involved. The transition can take place as early as the heating-up phase; in such cases the first stage is difficult to delineate.

Based on topological considerations, in which the surfaces enclosing the powder particles and the number of contacts per particle are considered primarily, and not the interior of the particles, Rhines[55–57] defined three stages of sintering in the following way:

The 'genus' of a powder agglomerate, zero for a porosity-free massive body, is related to the number of particles and to the total number of contacts. It is numerically equal to the number of sections that must be made in a sintered compact to obtain a chain of powder particles, such that each particle may have only one contact with each of its two adjacent particles. Consequently, the genus decreases during the sintering process. The three stages are defined by Rhines as follows:

(1) The genus of the porous body remains constant (neck growth).
(2) Decrease of the genus towards zero (grain growth, decrease in the number of pores).
(3) With a constant 'residual genus', or with a slow asymptotic approach towards zero residual densification (contraction of isolated pores).

The three stages, according to Rhines, are analogous to the three phenomenologically or geometrically delineated stages of sintering already described.

3. Possible mechanisms of material transport

Table I enumerates all the conceivable mechanisms that can occur in sintering processes.

Although adhesion occurs in every type of particle contact, it is not likely to constitute the dominating principle except in impact sintering (Sauerwald[58]). Because of the extremely short effective impact period, it is unlikely that particle transport will take part in the true sense, as described below. Agglomerations with very finely divided powders and the cold welding of powders or compact bodies can also perhaps be attributed to the capture of free surface valencies and to van der Waals forces ('adhesion').

Recovery and recrystallisation alone are definitely incapable of producing a sintering process; however, they are found in powders containing severe lattice distortions, and are also concerned in the grain growth that takes place in parallel with densification, and cannot be omitted from consideration. The removal of stresses in the microcontacts is also visualised as promoting mutual binding in the initial stages.

The transport mechanisms listed in Table IB, classified into 'movements of the whole lattice region' and 'movements of individual lattice structural components', are all realistic and each is considered in various cases as representing the most important mechanism. These mechanisms might be supplemented by viscous flow; however, this is associated with the self-diffusion coefficients in accordance with:

$$\eta = \frac{kT}{D\delta} \qquad \ldots [6]$$

for amorphous substances,[15] or:

$$\eta = \frac{KTd^2}{D\gamma^3} \qquad \ldots [7]$$

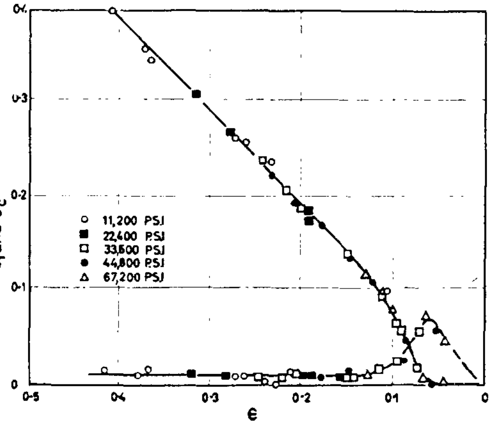
Table I. Possible elementary processes (transport mechanisms) during sintering

A	Without material transport	Adhesion	
B	With material transport (movement of atoms over increased distances)	Surface diffusion	movements of individual lattice structural components
		Lattice diffusion via vacancies	
		Lattice diffusion via interstitials	
		Grain-boundary diffusion	
		Vaporisation and re-condensation	
		Plastic flow	movements of lattice regions
		Grain-boundary slip	
C	With material transport (movement of atoms over very small distances)	Recovery or recrystallisation	

for crystalline bodies[24] ('diffusion creep' according to the Nabarro–Herring mechanism.[59,60]) This is a case of an *oriented* diffusion activated by external stresses.

Material transport via the gas phase by means of evaporation followed by re-condensation has been observed as the dominating process in some instances, e.g. with NaCl,[61,62] TiO_2,[63] and ZnO_2.[64] However, the process can produce no shrinkage. Plastic deformation can occur without the application of external forces as a result of interfacial stresses or surface tension, as mentioned above. Sintering theories based on the predominance of flow processes are no longer considered today, but they enabled the mechanisms of hot pressing to be understood. It must also not be overlooked that flow processes operate even with small external pressures.[38,39,65]

It is extremely probable that surface diffusion occurs in all sintering processes. The rounding-off of the internal and external surfaces and pores is produced by surface diffusion, which requires the least activation energy of all types of diffusion, and thus appears preferentially at low temperatures. Although it cannot cause pore shrinkage, and hence densification, several authors are of the opinion that surface diffusion is a dominating process, even when sintering with marked densification.



4 Distribution of total porosity ε between open (ε_l) and closed (ε_c) pore spaces. (*Arthur.*[383])

Grain-boundary diffusion is frequently inferred from calculated activation energies for shrinkage. A key question, still asked today, is whether grain boundaries are merely vacancy-diffusion channels, or whether they serve as actual sinks for the flow of vacancies. Important arguments, which will be discussed later, can be marshalled on both sides. However, grain-boundary diffusion *alone* cannot explain a contraction.

Interstitial diffusion has been very little studied in connection with sintering processes. It ought to be considered essentially in relation to interstitial solid solutions, because the activation energies for interstitial diffusion are usually very low. In cases where it might have a strong influence, for example, on neck growth, phase separation of the two phases must always occur. Such phenomena are unknown with interstitial solid solutions.

Lattice diffusion by a vacancy mechanism remains the last and most important mechanism to be mentioned. Vacancy gradients exist between the undistorted lattice and both curved surfaces and pore edges, between surfaces having different curvatures, and between the distorted and undistorted lattice. According to Johnson and Clarke[66] they are even found between particle centres and the centre of contact with the adjacent particles. The course of the diffusion processes during sintering is governed by the type and geometrical arrangement of the vacancy sources and sinks.

The vacancy sources and vacancy sinks to be considered are:

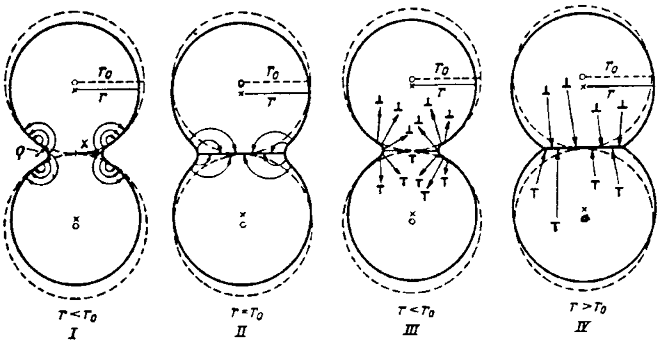
As sources	*As sinks*
(smaller) pores	grain boundaries
concave surfaces	plane or convex surfaces
(dislocations)	(larger) pores
	(dislocations)

When 'pores' and 'concave surfaces' are identified with each other in the model experiment, and when it is taken into consideration that dislocations, by climbing, can be effective both as sources and sinks, then five possibilities of material transport in the model experiment remain. Figure 5 (Ref. 48) illustrates the vacancy paths diagrammatically.

The essential participation of dislocations as sources or sinks has been disputed;[67–69] accordingly Cases III, IV, and V are improbable. The fact that contraction in the powder compact must be associated with an approach of the mid-points of the particles is a strong argument in favour of Mechanism II, although experiments have also been reported[68,69] according to which the same time law of neck growth applies with and without the presence of grain boundaries between the particles. Hence Mechanism I is also probable with a suitable geometry.

4. Possible factors of influence

The many-sided and complicated nature of the sintering process is still not adequately covered by this representation of the possible transport mechanism, because there are many factors that influence the pattern of material transport. It is useful to begin by summarising all the recognisable factors and to classify them appropriately.



[*Courtesy 'Metall'*

5 Possible diffusion paths for vacancies (arrows) in the model sintering experiment. (*Fischmeister and Exner*,[48] after Coble.)

Source	*Sink*	
I Neck surface	Particle surface	Without approach of mid-points
II ,, ,,	Grain boundary	With approach of mid-points
III ,, ,,	Dislocations	Without approach of mid-points
IV Dislocations	Grain boundary	With approach of mid-points
V ,,	Particle surface	No neck growth, therefore not considered

Thümmler[17] has published a system of classification into factors that are effective under all ideal experimental conditions (primary factors), and those that may, or may not, play a part according to the properties of the powder and the experimental conditions (secondary factors). Unfortunately, the two groups cannot be rigorously separated; for this reason the classification given in Table II will be used.

The quantities listed under (A) govern essentially the transport processes summarised in Table I and are responsible for their relative importance. (B) also includes, though these are not specifically named, the particle size, particle-size distribution, and pressing conditions; these influence particularly point (B1), but also (B2) and (B3). Groups (B) and (C) are completely decisive in many cases for the operation of practical sintering processes, and their importance cannot be overemphasised. In model experiments, on the other hand, an attempt is made to eliminate these factors or to maintain them constant. Considered as a whole, the factors listed under (B) and (C) can exert a considerable influence on the effectiveness of the transport mechanisms and the extent to which they participate in the overall process.

Table II. Possible factors of influence in the sintering process

A	Temperature-dependent properties of the material (including structure and state of bonding) 1. Free surface and interfacial energy, including the pore surfaces. 2. Diffusion coefficients (lattice, grain-boundaries, surfaces) 3. Viscosity coefficients (with amorphous substances) 4. Critical shear stresses (combined with the action of plastic flow) 5. Vapour pressure and rate of vaporisation (combined with the action of vaporisation and condensation) 6. Crystal structure and state of bonding 7. Nascent-state conditions, modification changes
B	Powder properties, pre-treatment, and sintering conditions 1. Effective integral area of contact 2. Surface activity (real surface structure) 3. Lattice activity (cold working, tensile and compressive stresses, lattice defects governed by manufacturing conditions, crystallite size) 4. Reciprocal orientation of the contact faces
C	Foreign constituents (including those introduced by the sintering conditions) 1. Soluble (homogeneously or heterogeneously present) 2. Insoluble 3. As surface layers (e.g. oxide films, soluble and insoluble, reducible and non-reducible, dissociating and not dissociating under sintering conditions) 4. Gases (adsorbed, occluded, and dissolved, and effects of the sintering atmosphere)

The importance of the individual transport principles will be described in detail in the following section. Groups (B) and (C) will be reserved for Section III.

II. Determination of the principles of transport mechanism

1. Studies on models and the importance of diffusion processes

For a theoretical and experimental approach to the determination of the mechanisms governing material transport it is first necessary to adopt certain simplifications, a fact that leads of necessity to the use of models incorporating spherical particles or circular cross-sections, and spherical or even cylindrical pores. Such models are also very amenable to experiment. The following models were used to study neck growth as a function of time: Two spheres, initially in 'point' contact (sphere–sphere model, Fig. 2 (*a*)); a single sphere lying on a flat surface (sphere–plate model, Fig. 2 (*b*)); and, for the experimental study of a very large number of individual contacts, a bar–wire model, consisting of a wire spiral wound on to a cylindrical bar. The wire–wire models (Fig. 6 (*a*)) consisting of several superimposed close-packed wire layers,[67] or of three twisted wires[70–72] (Fig. 6 (*b*) and (*c*)) have also proved very useful. The contact widths are measured, after metallographic preparation, on the micrograph.

The work of Kuczynski in this field,[16,70] which can be regarded as classical, is well known; his results are illustrated in Tables III and IV, together with those of other authors. Based on similarity considerations, Herring[73] formulated his 'scaling laws' from these model data. According to these, an equal x/a ratio with different particle diameters, a, requires a sintering time that is related to the diameter ratio according to the predominant mechanism. The Herring exponents in the equation:

$$t_2/t_1 = (a_2/a_1)^p = \lambda^p \qquad \dots [8]$$

amount to $p = 1$ for flow processes, $p = 2$ for vaporisation and recondensation, $p = 3$ for volume diffusion, and $p = 4$ for surface diffusion. They are also included in Table III and are in agreement with the difference $P = n-m$ in the Kuczynski equations. It will be seen that conclusions regarding the dominant factor in transport can be drawn from the time law of neck growth.

Table III. Equations governing neck growth in the model experiment

$$\frac{x^n}{a^m} = F(T)\ t \qquad \text{or} \qquad \left(\frac{x}{a}\right)^n = F(T)\ t\ a^{n-m}$$

Mechanism	n	m	$p=n-m$	$F(T)$	Author	Ref.
Viscous or plastic flow	2	1	1	$3\gamma/2\eta$	Frenkel	15
Evaporation re-condensation	3	1	2	$\sqrt{\frac{9\pi V_0 \gamma P_0}{2MRT}}$	Kuczynski	70
	7	3	4	—	Pines	24
Lattice diffusion*	5	2	3	$K\frac{D_v V_0}{RT}$	Kucyznski Kingery and Berg	70 61
	4	1	3	$K'\frac{D_v \gamma V_0}{RT}$	Pines	24
Surface diffusion	7	3	4	$56\frac{\gamma V_0 \delta}{RT}D_S$	Kuczynski Rockland	70 74
	—	—	—	$x^6 \ln\frac{x}{2a} \sim t$	Pines	24
	5	2	3	—	Cabrera Schwed	75 76
	3	1	2	—	Schwed	76

* In the case of lattice diffusion the numerical factor K varies according to the geometry of the model and according to the assumptions made regarding the sinks of the vacancy flow, as shown in Table IV.

Table IV. Values of numerical factors K and K' from Table III

Model	Authors			Sink of vacancy stream
	Pines[24]	Kuczynski[16,77]	Kingery and Berg[61]	
Sphere–sphere	8	—	$\frac{5\pi}{2}$	No acceptance
	—	—	80	Grain boundary
	—	—	40	Particle surface
Sphere–plate	16	40	320	Grain boundary
Bar–wire	—	$\frac{80\pi}{3}$	640	Grain boundary
Wire–wire	—	$\frac{8\pi}{3}$	—	Particle surface
	—	$\frac{16\pi\sqrt{2}}{3}$	—	Grain boundary

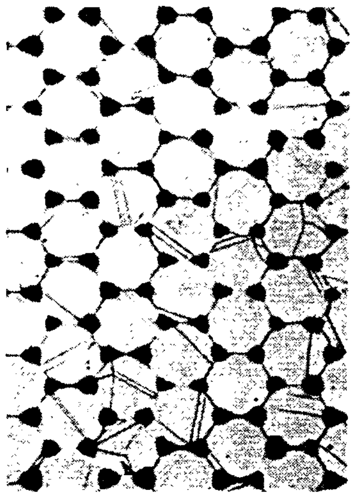
The deductions for this purpose are not consistent, however, as can also be seen from the Table; this accounts for the differences between the exponents. Exponent 7, in particular, for surface diffusion is contested, as well as the numerical constants in the case of volume diffusion, which have been recalculated by Kingery and Berg. Little attention has so far been paid to the results of Pines compared with those of Kuczynski.

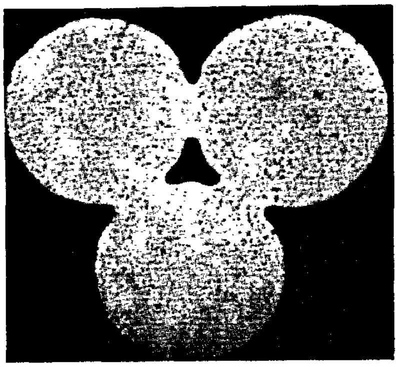
Criticism of the Kuczynski equations,* apart from the different relationships derived by Pines,[21] Cabrera,[75] and Schwed,[76] has often been confined, in the absence of a better theory, to pointing out numerical uncertainties. Thus, sometimes no definitive transport mechanism could be derived from an experimentally determined exponent, which is frequently liable to uncertainties of ± 0·5, and also appears to be temperature-dependent. The evaluation of the contact spirals of the bar-wire model and the differences between the results obtained have also been the subject of discussion.[78,79]

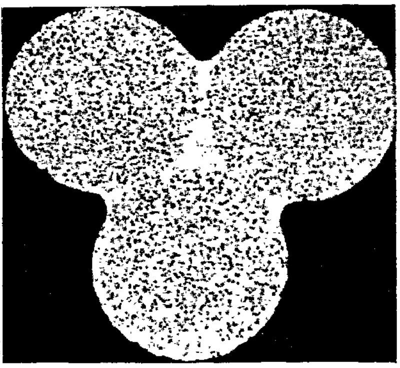
Fischmeister and Zahn[80] emphasise the prevailing lack of certainty in the numerical constants, which can lead to deviations between diffusion coefficients arrived at by direct measurement and by model experiments, respectively. Such discrepancies, in the view of Thümmler,[78] arise from non-uniform contact conditions at the start of the experiment and from a time distribution of the 'effective sintering period', resulting from initiation of points of contact *during* sintering. For this reason diffusion coefficients obtained from model experiments should preferably be termed 'mobility coefficients', because they can contain systematic defects, even although surprisingly good agreement has been found in

---

* The frequently attacked $x^7 \sim t$ relation of Kuczynski has recently been re-derived and confirmed by Rockland[74] (with $K' = 34$).







[Courtesy *'Acta Metallurgica'*

6a Wire–wire model (Cu). × 80. (*Alexander and Balluffi.*[67])
6b Model consisting of three twisted wires (Cu + Al_2O_3). × 100. (*Brett and Seigle.*[72])
6c Model consisting of three twisted wires (Cu + Al_2O_3). Note absence of Al_2O_3 particles in the necks and at the location of the original central pore. × 100. (*Brett and Seigle.*[72])

many cases with directly measured values (see the compilation of diffusion data for copper by different methods, according to Kingery and Berg[61]).

One of the main criticisms of the Kuczynski growth equations was made by de Hoff, Baldwin, and Rhines.[81] On the basis of their investigations on copper wires, the exponent n should lie between 5 and 60 according to the wire diameter, thus making the identification of a specific transport mechanism impossible. In the criticism of this work by Rieck and Rockland,[82] on the other hand, the exponent $n = 5$ was found by careful measurement to be independent of the wire diameter; these authors also confirmed the approximate constancy of the Herring factor $p = 3$ for volume diffusion.

It is, however, recognised that these model investigations have proved valuable in increasing our knowledge of the subject.

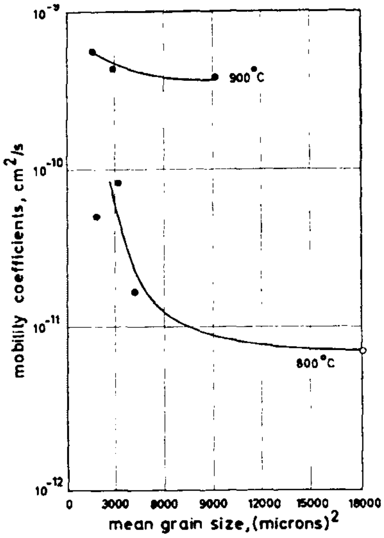
No doubts exist regarding the validity of $n = 2$ for flow processes; similarly a value of $n = 3$ for the evaporation and condensation mechanism is hardly called in question. The comprehensive factual material confirming the growth law $x^5 \sim t$ for volume diffusion also outweighs the small number of reports giving deviating results. No empirical constants are contained in the equations derived by Kuczynski and others. According to the derivations, both geometrically governed numerical factors, which vary with the different types of arrangement, and temperature-dependent material constants (lattice constants, surface tension, diffusion constants, or viscosity constants) are included. Agreement closer than an order of magnitude between theory and experiment can in general hardly be expected, especially as the temperature-dependence of the material constants in question is seldom known accurately, while secondary factors such as those listed in Table II, A and B, can also be involved. For example, the influence of grain size on the results has been detected in the bar–wire model[83] (Fig. 7).

Thus, greater deviations do not necessarily indicate the weakness of the theory.

In addition to the results[16,61,67,69,71,77,82,84,85] that gave $n = 5$ for metals, oxides have also been recently investigated. Coble[31,32] and Kuczynski, Abernethy, and Allan[86] found that volume diffusion predominated with Al_2O_3. In this instance, especially in dry hydrogen, polyhedral formation of the spherical particles was observed, which increased the difficulty of evaluation.

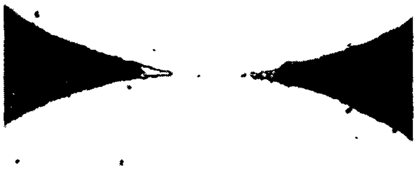
Parravano[64,87] identified volume diffusion in polycrystalline TiO_2 (900–1550° C), V_2O_5 (560–650° C), and ZnO (600–1050° C), and evaporation and re-condensation in ZnO above 1050° C, as the mechanisms governing transport. In model experiments with single-crystal spheres,[88] on the other hand, he found no constant growth exponents but the interaction of various mechanisms. In tests on single-crystal TiO_2 spheres, Whitmore and Kawai[89] reported that $n = 5$ in vacuum, corresponding to a lattice diffusion in good agreement with diffusion data on the O^{2-} ions in TiO_2. According to McQueen and Kuczynski,[90] ZnS sinters below 600° C by surface diffusion, and above 600° C by volume diffusion, the diffusion coefficients being 300 times greater in vacuum than in argon.

In the view of the present authors, the most compelling proofs of the predominance of diffusion processes have been provided by Kuczynski *et al.*[91,92] An enrichment of the more rapidly diffusing component (indium) of a homogeneous copper–indium solid solution, or of silver from copper–silver, was found to occur[91] in the contact zone by the precipitation of a second phase, and was quantitatively interpreted (Fig. 8).



[*Courtesy 'Stahl und Eisen.'*

7 Influence of grain size on the mobility coefficients calculated from model sintering experiments. Bar–wire model (Cu). (*Thümmler.*[83])



[*Courtesy 'Acta Metallurgica'.*

8 Precipitation of a second phase from an initially homogeneous Cu–In solid solution in a model experiment. × 700. (*Kuczynski, Matsumura, and Cullity.*[91])

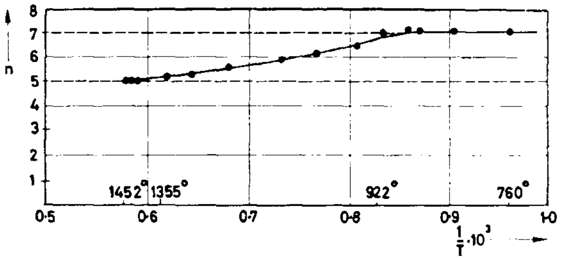
This experiment definitely eliminates flow processes and provides a further proof of the existence of excess vacancies in the contact zone. Curvatures of twin-crystal boundaries were detected[92] in copper wires; these were caused by diffusion-governed dislocation climb resulting from unequal diffusion currents in the nickel or copper wire.

Brett and Seigle[72,93] were able to exclude the action of flow or vaporisation processes for metals and saltlike substances by introducing and following inert markers in the three-wire model (e.g. nickel with 2 vol.-% Al_2O_3) and to verify the predominance of diffusion, on the ground that the markers did not migrate into the original pores (Fig. 6 (*a*) and (*b*)). In the case of glass and organic materials (cellulose acetate), on the other hand, a displacement of the marker (e.g. flow) was clearly established. This model, and the wire-coil model of Alexander and Balluffi,[67] are also very suitable for studying the later stages of sintering with spherical isolated pores. In this way Kuczynski[70,94,95] was able to account quantitatively for pore shrinkage by a diffusion mechanism. Equation [9] is valid, in the presence of grain boundaries as vacancy sinks, for the reduction in radius of cylindrical pores:

$$r_0^3 - r^3 = \frac{3\gamma V_0}{RT} D_v t \qquad \ldots [9]$$

This equation has been confirmed experimentally.

Pores in the form of tubes[69] can also shrink by a diffusion mechanism. Postlethwaite and Shaler[96] investigated the shrinkage of holes drilled in massive copper, and explained it by a flow mechanism. Silver capillaries were used by Oel[97] as models, but no single transport mechanism for the pore shrinkage could be established.



[*Courtesy Consultants Bureau.*

9 Growth exponents *n* in model sintering experiments on high-purity iron. (*Fischmeister and Zahn.*[98])

In the case of exponents $n > 5$, as well as with low activation energies, surface diffusion is assumed to be predominant. Thus Fischmeister and Zahn[80] concluded that with iron in the α-region, with an activation energy of 37 kcal/mole and $n = 7$, surface diffusion would play a predominant part, while in the γ-region with $Q = 67$ kcal/mole and $n = 5$, volume diffusion should be the principal mechanism (Fig. 9). Accordingly, and on the basis of measurements of surface diffusion from grain-boundary pits, both Fischmeister and Zahn[98] and Wilson and Shewmon[99] considered that surface diffusion must predominate, especially with large particles (i.e. with models). This is a very remarkable conclusion which will be discussed further in Section II.4.

2. Possible diffusion paths and sources and sinks of the atom and vacancy stream

The importance of the vacancy concentration gradients, which must be present in every kind of directional diffusion, and the possible sources and sinks, have already been mentioned in Section I.1. In the model experiment in which the contact plane, before grain growth becomes possible, is usually a grain boundary, an approach of the particle centres can, according to Coble[31, 32] and Kuczynski,[77] take place only when the separating grain boundary is effective as a sink. If the particle surface alone acts as a sink, the neck can certainly grow and become rounded off, without causing any approach of the mid-points (see the equations in Table V, Section II.4). Probably dislocations play a part as vacancy sinks only when they are arranged in the form of (small-angle) grain boundaries, while individual dislocations possess too small a vacancy-absorption capacity to be macroscopically effective. Only in the presence of grain boundaries in the late stages of sintering will pores be able to continue shrinking slowly through the sink action of individual dislocations until they reach a minimum radius.[70] Dislocations have also been considered theoretically by Coble[31,32] as vacancy sources with grain boundaries as sinks; this case is extremely improbable, however. The experimentally determined mid-point approach shows that grain boundaries must be the most important sinks of the flow of vacancies if the contraction is to be explained.

A second function of the grain boundaries is that of a diffusion 'short circuit' to the outer surface. Apart from these two effects Hornstra[100] presumed that grain-boundary slip and the 'climb' of the grain boundaries should enable the sintering rate to be increased by a factor of ~ 10 compared with diffusion theory. No uniform diffusion of vacancies to all sections of the grain boundary must occur in that case, but each vacancy could reach its sink by the shortest possible route without giving rise to stresses in the lattice.

The problem of the proportion of the grain boundaries acting as sinks or merely as diffusion channels has not been resolved. Brett and Seigle[101] conclude from the dimensions of grain-boundary pits along wire surfaces that no important transport of vacancies along the grain boundaries can take place in the outward direction. Apart from dislocation jogs, therefore, vacancy sinks should consist of the grain boundaries themselves, along which successive lattice planes are absorbed, so that the neighbouring grains approach one another and bring about the contraction. The interaction between vacancies and grain boundaries has been treated in detail by Burke.[103] In subsequent reports by Brett and Seigle,[93,102] it was established for copper, and for brass made porous by the vaporisation of zinc, that dislocations alone cannot contribute to pore contraction. In spite of the undoubted importance of the grain boundaries, however, it has been found in individual cases[66,102] that pores can also contract in the absence of grain boundaries, so that other sinks must also have been effective.

Hornstra[100,104] also treated the problem of sources and sinks in detail, and confirmed that dislocations cannot constitute effective vacancy sinks. It is an interesting possibility that the grain boundaries can be curved and that extremely effective vacancy sinks can be produced by grain-boundary slip. In the interior of the grain the stresses decay to values below the yield stress at a sufficiently great distance from pores. Within such regions, but with $\sigma > \sigma_{\text{yield}}$ a flow process can certainly take place, but cannot contribute to the densification.

Margerand and Eudier[105] concluded from experiments in which the porosity remained higher at the edge of sintered specimens than at the centre, that grain boundaries cannot constitute sinks, but only diffusion channels to the surface. They also concluded that internal stresses remain effective between the core and peripheral zones, which must have arisen from quenching the vacancies that are supersaturated at the exterior. The observations, according to which the periphery of sintered samples,[105] on the one hand, and the sample centre on the other,[106] is sintered preferentially to a porosity-free condition, are contradictory and increase the difficulty of a general evaluation of this fundamental problem (Fig. 10). However, the transport of all vacancies along the grain boundaries to the outside surface would mean that large samples would shrink more slowly than small ones. Practice does not bear out this assumption, so that the sink effect of the grain boundaries is more probable. Johnson and Clarke[66] postulate that only volume and grain-boundary diffusion act as transport mechanisms, that the slower (and hence the rate-determining) step is vacancy diffusion in the lattice, and that the grain boundaries between two adjacent (model) particles absorb all vacancies. The vacancy concentrations are assumed to be in equilibrium everywhere and at any given time (naturally, this can apply only for the neighbourhood of the sinks and for the undistorted lattice). It is found by calculation that the equilibrium vacancy concentration in the centre of the neck is not C_0, as beneath a plane surface, but:

$$C_0 \exp(-\gamma V_0/RT\rho) < C_0 \qquad \ldots[10]$$

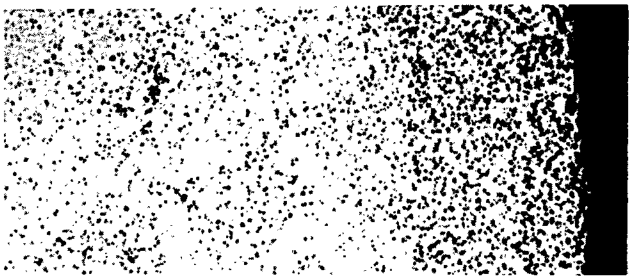
It thus follows that the vacancy-concentration gradient from the surface to the centre of the neck is in fact the steepest, and that the neck grain boundary must actually be the most effective sink. The possibility is excluded that *this* grain boundary acts as a diffusion channel to the surface, as otherwise a vacancy circulation would begin without neck growth. It is estimated that ~ 10% of all vacancies diffuse along grain boundaries for silver powder of 180 μm at 800° C and a neck width $x/a = 0{\cdot}16$. However, this estimate is based on an evaluation by Johnson and Cutler,[107] that cannot now be accepted without restrictions.

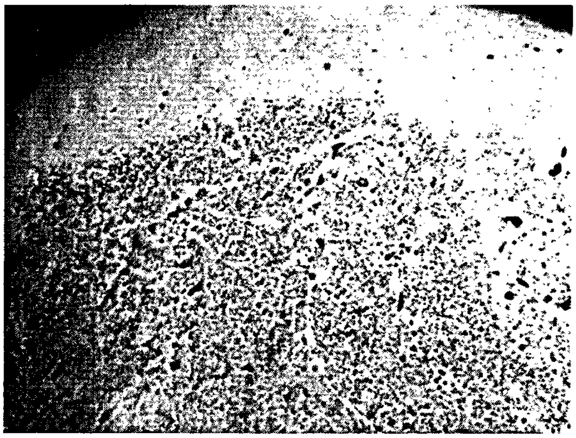
3. Other mechanisms operating as diffusion processes

In more recent work, other mechanisms have been identified as acting as diffusion processes from neck growth in the model experiment.

Evaporation and re-condensation is the predominant factor in sintering ZnO spheres at 1050–1250° C, according to Norris and Parravano.[61] The $x^3 \sim t$ law, a Herring value of $p = 2$, and the non-appearance of mid-point approach provide important evidence for this mechanism. At lower temperatures, on the other hand, volume diffusion was observed. As established by Kingery and Berg[61] on NaCl (Fig. 11 (*a*)), a vapour-phase transport mechanism is also the prevailing process when sintering MgO spheres on to NaCl plates.[62] (However, shrinkage was established in NaCl powder compacts in other work,[381,382] which also implies different transport processes.) According to Grottyoham and Herrington,[63] TiO_2 also sinters in air with $x^3 \sim t$ and $p = 2$ by this mechanism, while in nitrogen no uniform mechanism could be identified with exponents between 4 and 7.

The grain-boundary slip postulated by Hornstra[100] and Jones[108] was also considered probable by Mohanty and Bauman[109] on the basis of grinding scratches, and should play a part in the rapid heating or initial densification of powders.



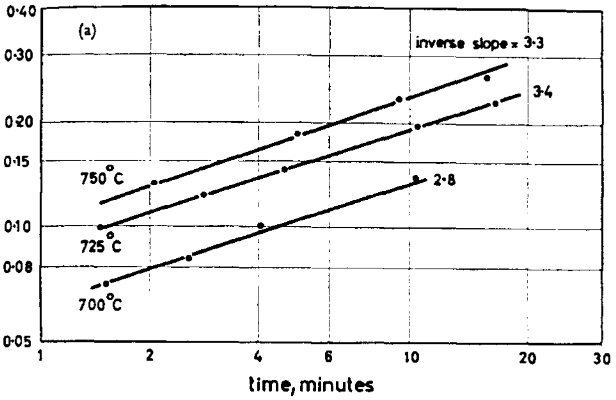


10a Preferred elimination of porosity in the interior of the specimen (Ni). × 25. (*Margerand and Eudier.*[105])

10b Preferred elimination of porosity at the edge of the specimen (Al_2O_3). × 55. (*Elyard.*[106])

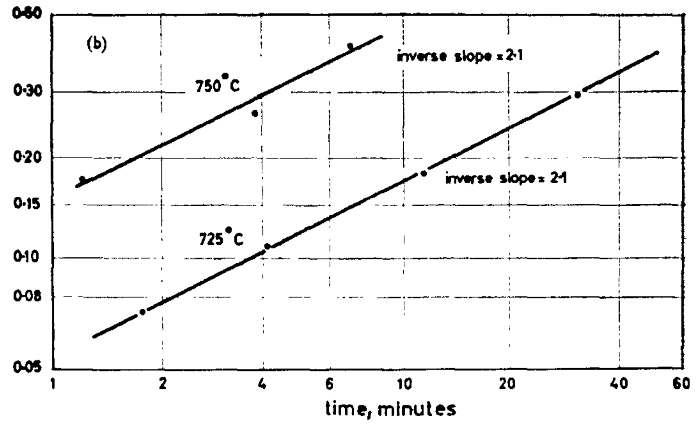
Numerous model experiments which indicate flow processes in accordance with $x^2 \sim t$ have been carried out on glass.[61,110,111] Based on the migration of markers, Brett and Seigle[71,93] also identified flow mechanisms in glass. In agreement with the relationship derived by Frenkel, viscous flow is considered in general to be predominant for amorphous substances; the results fully support this view. Flow processes have also been found in some crystalline materials, e.g. O'Bryan and Parravano[112] in TiO_3, Morgan[113] in ThO_2, and Morgan, McHargue, and Yust[114] in ThO_2–CaO solid solutions.

The flow theories of sintering for powder compacts were formulated, in particular, by Clark and White[115] and by Mackenzie and Shuttleworth.[116] Clark and White[115] derived densification equations for viscous Newtonian behaviour (without yield point) and for plastic Bingham behaviour (with yield point), which certainly provided good agreement with experiments on glass, Al_2O_3, MgO, CaF_2, and NaF with the aid of two suitable parameters, but can no longer be accepted on a critical analysis of the derivation. Mackenzie and Shuttleworth[116] deduced another densification equation from the simplifying assumption of a hydrostatic pressure over the whole of the porous body under the action of surface tensions. This should be valid for the later stages of sintering with closed pores, but surprisingly it also applies in the early stages according to Allison and Murray.[117] It has performed a useful service as regards the understanding of hot-pressing processes (see Section V), but probably is not valid as a rule for free sintering, because the yield point is not exceeded in most volume elements during the greater part of the sintering time by the action of surface tension alone. Moreover, no-



[*Courtesy 'J. Applied Physics'.*

11a Neck growth in NaCl in accordance with $x^3 \sim t$. (*Kingery and Berg.*[61])



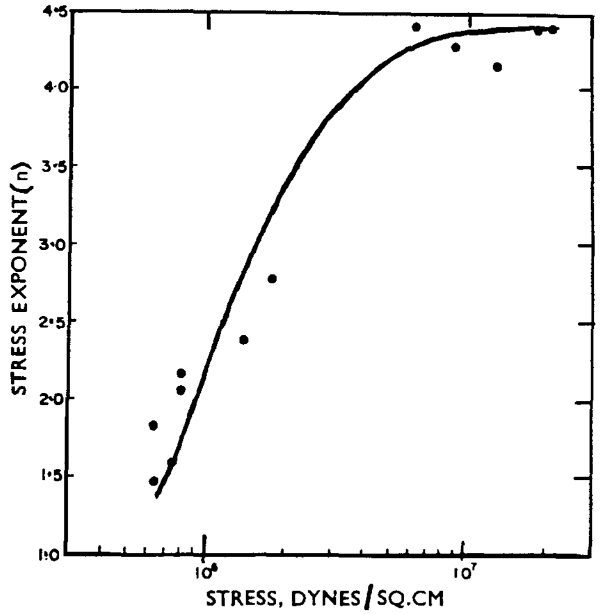
[*Courtesy 'J. Applied Physics'*

11b Neck growth in glass in accordance with $x^2 \sim t$. (*Kingery and Berg.*[61])

one has, of course, observed directly the movement of dislocations in the neck, which would cause difficulties at high temperatures.

Mention may be made in this connection of investigations by Lenel *et al.* on the influence of *small* external loads in the early stages of sintering. In experiments with coarse powders in the preliminary stages a considerable influence of the sample weight itself was established initially.[118] Under these conditions the influence of residual stresses on neck growth was also detected. It was therefore concluded that the stress given by $\sigma = \gamma/\rho$, and considered as the driving force, was not the sole factor controlling the course of the sintering process.[118,119] It was shown in further work that the activation energies, determined from the fall in electrical resistance and from the shrinkage of the sample, decreased sharply with increasing external loads.[120] This effect has already been known for some time in creep processes.[121] The part played by creep, especially high-temperature creep according to Nabarro–Herring, which may be described as an oriented diffusion, is summarised by Lenel and Ansell.[122] This mechanism functions at high temperatures and very small supplementary loads (effective stresses in the neck $< \sim 1$ kg/cm^2); contraction then proceeds according to:

$$\frac{d}{dt}(\Delta l/l_0) = \dot{\varepsilon} \sim \sigma^1 \qquad \ldots[11]$$



[*Courtesy Consultants Bureau.*

12 Increase in stress exponents from a value of 1 to 4·5 in sintering spherical copper powder, showing influence of small additional loads. (*Lenel and Ansell.*[122])

At greater stresses a transition to higher stress exponents takes place rapidly (Fig. 12), corresponding to $\dot{\varepsilon} \sim \sigma^{4\cdot5}$ in sintering copper and silver, and to $\dot{\varepsilon} \sim \sigma^4$ for two-phase copper + Al_2O_3. This stress-dependence is found in creep because of dislocation movements, cross-slip, and climb, in agreement with creep theory.[119,120,122,123] As a result of the activation energies for diffusion and dislocation climb being the same, these two transport mechanisms can be distinguished *only* by the stress-dependence of the shrinkage. These results do not contradict the diffusion theory in any way, as the $\dot{\varepsilon} \sim \sigma^1$ law indicates the predominance of an oriented diffusion at *small* stresses. The only difference between the 'classical' oriented self-diffusion and the Nabarro–Herring diffusion creep can be seen in the fact that in the latter case the stress generating the vacancy gradients can be applied, not as a result of the neck, but also 'macroscopically' from outside. Phenomenologically, the shrinkage of a powder compact can also be viewed as a slow deformation, and thus equated to a creep process.

Pines[124] also interprets the sintering process as diffusion by the Nabarro–Herring mechanism, but taking into consideration an increased diffusion coefficient due to the high degree of disorder. Pines considers the role of the dislocations to be more essential than that of the grain boundaries.

The transition of the stress exponents from 1 to the higher values at stresses > 1 kg/cm^2 signifies at the same time the transition from 'pressureless' sintering to hot pressing, where the predominance of flow processes, e.g. displacement movements, is generally accepted (see Section V).

4. Investigation of the shrinkage of powders

However valuable model experiments may be in studying sinter mechanisms, it is questionable to what extent the results obtained are applicable to the sintering of real powders, especially with a higher degree of densification. On the one hand, the complex geometry of the particle and pore arrangement, resulting from irregular shape, prevents a theoretical prediction of the shrinkage and properties of the sintered compact as a function of temperature, time, green density, &c. On the other hand, a state of increased activity exists in real powders compared with the usual model experiment attributable to the lattice distortions due to manufacturing conditions and the smaller particle sizes. Such non-equilibrium conditions and their elimination as sintering progresses often influence the process, in quantitatively unknown ways, even if qualitative information is available (see Section III).

Nonetheless an attempt has been made to transpose the theory of model sintering experiments to the kinetics of isothermal powder sintering. The starting point was again the Kuczynski equations in their original form and in the form as modified by Kingery and Berg. Equations for the mid-point approach, and hence for the shrinkage of sintered powders, are collected in Table V.

The $t^{4/5}$ law was confirmed only by Kingery and Berg;[61] otherwise relationships with $n \simeq 0{\cdot}4$–$0{\cdot}5$ were frequently established for small contractions and considered as a confirmation of diffusion mechanisms. These results are listed in Table VI.

According to the inference the validity of:

$$\Delta l/l_0 \sim t^{2/5} \qquad \ldots[12]$$

is limited to the early stages of sintering, as long as the contact zones grow in isolation and no grain growth takes place via the particles. Any conformity with this law for increased amounts of shrinkage, which is often found according to the reports cited in Table VI, must be considered accidental. Log–log plots of the isothermal contraction:

$$(\log \Delta l/l_0 = n \log t + n \log t_0) \qquad \ldots[13]$$

or of a parameter derived from it, often give straight lines with slopes between 0·4 and 0·5. This is considered to indicate the predominance of lattice diffusion ($n \simeq 2/5$); lesser slopes of $\sim 0{\cdot}3$ ($\simeq 2/7$) are interpreted on the basis of grain-boundary and surface diffusion. The activation energies to be calculated from such expressions, which often lie between the known values for grain-boundary and lattice diffusion, do not normally enable a clear identification of the transport mechanism to be made. Consequently, and in spite of a lack of knowledge of the heating-up time and a more or less marked temperature-dependence of the slopes, an activation energy is often computed the reality of which is open to question.

A mathematical analysis by Bockstiegel[125] shows that, apart from $x^5 \sim t$ (lattice diffusion) or $x^7 \sim t$ (surface diffusion), which apply for circular contacts, exponential laws also apply for mid-point approach in the case of non-circular cross-sectional contacts:

$$\frac{\Delta l}{l_0} \sim t^{\frac{2}{\alpha\beta+1}} \qquad \ldots[14]$$

but that the constants α and β depend in an unknown way on the real geometry. Consequently, the resulting exponent $n = 1/(\alpha\beta + 1)$ does not enable any conclusion to be drawn regarding the principle governing transport. Furthermore, the fact that isothermal shrinkage experiments can seldom be evaluated in a completely satisfactory manner by a simple exponential law over long periods of time and wide ranges of temperature, led Johnson and Cutler[107] to derive modified exponential laws. Thus, the sintering contacts between adjacent particles can probably not be considered to be purely circular, as in the model experiment. Deviations of the powder from a spherical shape and the existence of a particle *size-distribution* account for this fact. The 'non-ideal' sintering in the first phase is transformed after a certain isothermal sintering time to 'ideal' behaviour; this is defined by the equation:

$$\frac{\Delta l}{l_0} = \left(K \frac{\gamma V_0 D}{RTa^p}\right)^m t^m \qquad \ldots[15]$$

This contains the following constants for volume and grain-boundary diffusion with grain boundaries as vacancy sinks:

	K	p	m
Volume diffusion:	$31/\pi^2$	3	0·46
Grain-boundary diffusion:	$50b/7\pi$	4	0·31

(b = thickness of grain boundaries.)

By adjusting two parameters, δl and δt, the shrinkage curve is drawn as the best straight line through the measured points:

$$l = (l_0 - \delta l)\left[1 - \frac{K\gamma V_0 D}{RTa^p}\right]^m (t - \delta t)^m \qquad \ldots[16]$$

Table V. Equations for mid-point approach in the sphere–sphere model

Authors	Coble[31]	Kuczynski and Ichinose[77]	Kingery and Berg[61]
Grain boundary as vacancy sink	$\frac{\Delta l}{l_0} = -\left(2\frac{\gamma D_v V_0}{RTa^3}\right)^{\frac{1}{2}} t^{\frac{1}{2}}$	$\frac{\Delta l}{l_0} = -\left(\frac{\pi\gamma D_v V_0}{3\sqrt{2}RTa^3}\right)^{\frac{2}{5}} t^{\frac{2}{5}}$	$\frac{\Delta l}{l_0} = -\left(10\sqrt{2}\,\frac{\gamma D_v V_0}{RTa^3}\right)^{\frac{2}{5}} t^{\frac{2}{5}}$
Particle surface as vacancy sink	—	$\frac{\Delta l}{l_0} = 0$	$\frac{\Delta l}{l_0} = -\frac{n}{8}\left(40\frac{\gamma D_v V_0}{RTa^3}\right)^{\frac{4}{5}} t^{\frac{4}{5}}$ (n no. of contacts per particle)

δt and δl have the meaning of a heating-up time or heating-up shrinkage; they cannot be determined by measurement, but only graphically.

The following relationship should also apply for equal proportions of volume and grain-boundary diffusion:

$$\frac{d}{dt}\left(\frac{\Delta l}{l_0}\right) = \frac{\Delta l/l_0 + \dfrac{16\pi b D_B}{100 a D_v}}{\dfrac{7\pi^2 R T a^3}{100\gamma D_v V_0}\cdot\left(\dfrac{\Delta l}{l_0}\right)^{2\cdot 20}} \qquad \ldots[17]$$

By transforming this equation in accordance with:

$$\left(\frac{\Delta l}{l_0}\right)^{2\cdot 2}\cdot\frac{d(\Delta l/l_0)}{dt} = A\frac{\Delta l}{l_0} + B \qquad \ldots[18]$$

it is possible to determine diffusion coefficients and activation energies from the slope A and ordinate section B of this representation,[107,126] (For further papers see Table VI.)

A shrinkage equation with three empirical constants is also given:

$$(\Delta l + \beta)^n = l_0^n K'(t - t_s) + \beta^n \qquad \ldots[19]$$

with $n = 3\cdot 13$ for grain-boundary diffusion and $n = 2\cdot 08$ for volume diffusion.

Such densification equations containing several constants are unsuitable for elucidating the mechanism of material transport. The determination of shrinkage data by an exponential law always succeeds when empirical corrections are used which optimise the representation in log–log form as straight lines.

Pines[24] summarised older empirical shrinkage equations. The representations according to:

$$\frac{d}{dt}\left(\frac{\Delta V}{V_0}\right) = Me^{-\beta t} \qquad \ldots[20]$$

$$\frac{\Delta V}{V_0} = A\,(1 - e^{\alpha t}) + Bt \qquad \ldots[21]$$

and

$$P = P_0\,(qmt + 1)^{-1/m} \qquad \ldots[22]$$

have little information value. However, Pines postulated the general validity of a shrinkage law of the simplified form:

$$l(t) = m(T) + n(T)\sqrt{t} \qquad \ldots[23]$$

in which $m(T)$ signifies the heating-up shrinkage, or any other given pre-contraction, and t the isothermal sintering time. This $\sqrt{t}$ law originated from the diffusion laws on the assumption of the 'diffusion activity' decreasing according to:

$$D \sim 1/\sqrt{t} \qquad \ldots[24]$$

(See also the work by Geguzin and Ovcharenko.[128]) In fact, the various results can be represented satisfactorily in this way, especially when the shrinkage is followed on the same sample at different, successive temperatures.

Occasionally the densification is represented better with parameters other than the directly measured shrinkage:

$$\Delta l/l_0 \text{ or } \Delta V/V_0 \simeq 3\,\Delta l/l_0$$

Thus 'standardised' values with a maximum value of 1 are utilised in sintering up to the theoretical density:

$$\frac{l_0 - l_{\text{sint.}}}{l_0 - l_{\text{theoret.}}} \text{ or } \frac{V_0 - V_{\text{sint.}}}{V_0 - V_{\text{theoret.}}}$$

and also the parameter ranging from 0 to ∞:

$$\frac{V_0 - V_{\text{sint.}}}{V_{\text{total}} - V_{\text{theoret.}}}$$

In recently published work Torkar, Oel, and Illigen[129] start from the reaction kinetics, in which the decrease in porosity is viewed as 'material exchange' of a chemical reaction of the n^{th} order. Corresponding to this view, they derived a 3rd order reaction for the sintering of VC:

$$\frac{dP}{dt} = -kP^3 \qquad \ldots[25a]$$

or

$$kt = \tfrac{1}{2}\,(1/P^2 - 1/P_0^2) \qquad \ldots[25b]$$

No uniform activation energies or predominant mechanisms could be identified in VC over the whole range of temperatures investigated.

Numerous densification laws that have so far been established are listed in Table VI. Where no equation is given, the expression

$$\Delta l/l_0 = [A\exp(-Q/RT)t]^n \qquad \ldots[26]$$

was always used and exponents n and activation energies Q were determined from it.

As the exponents and activation energies are frequently given as time- and temperature-dependent, it must be doubtful what conclusions regarding the transport mechanisms can be drawn from such equations.

Some reports will now be discussed which not only give a clear indication of diffusion mechanisms but also state the type of transport (grain-boundary or volume-diffusion, and character of the sources and sinks).

Kuczynski[95] establishes that sintered samples can be produced to the theoretical density after a second pressing, although stresses in excess of the yield point must previously have been applied in the neighbourhood of the residual pores, and further densification must have taken place without pressing if the flow theory is valid. However, further densification could be produced only with the formation of new grain boundaries by plastic deformation. This must signify that the shortening of the diffusion paths to the nearest sink or short-circuit channel must have a decisive effect.

Most of the densification occurs with the start of grain-boundary displacement from the neck, e.g. from the time at which grain growth *via the individual powder particles* becomes possible. In this second stage of

Table VI. Shrinkage and densification equations

Authors	Ref.	Material	Particle size	Quantity measured	Temperature range, °C	n	Q, kcal/mole	Remarks
Oxley and Ciceron	130	Fe	20 µm	Δl	710–880	0·2—0·33	36	H_2 Following in sequence
					710–880	−0·50	36	
					920–1000	+0·40	69	—
					710–750	+0·20	182	Vacuum
					750–880	−0·50	44	
Ciceron and Lacombe	131	Fe	20 µm	Δl	<740	+0·2	78	T-dependent
						+0·33	53	
					750–90	+0·20	36	Following in sequence
						−0·50	35	
Ciceron	132	Fe	20 µm	Δl	710–800	+0·20	182	
					800–880	+0·20	46	Following in sequence
						−0·05	42	
					910–1000	+0·40	69	—
Pinteau, Ciceron, and Lacombe	133	U	<44 µm	Δl	600–668 (α)	+0·40	40 ±4	
					668–775 (β)	+0·40	56 ±5	
					800–900 (γ)	+0·50	29 ±3	
					900–1000 (γ)	−0·50	16 ±3	
Pinteau, Ciceron, and Lacombe	134	U	15–20 µm	Δl	800–920	0·40	39	Valid only up to 3% shrinkage
Hampe	135	U	—	$\Delta l/l_0$	850–1075	0·50	33·8	Extremely low in oxide
Forss	136	Fe	75 µm	$\frac{\rho_s-\rho_0}{\rho_{th}-\rho_0}$	800, 900	1·0 – 1·25	24	n, Q vary with time
Okamura, Masuda, and Kikuta	137	Cu	<50 µm	$\frac{V_0-V_s}{V_0-V_{th}}$	550–720	0·33	24	—
Borchert and Carl	138	Co	< 3 µm	$\Delta l/l_0$	716–1038	$n > 0$	—	3 stages following in sequence
						lg t	3;24 – 29	
						$n < 0$	58 – 61	
Borchert and Rieger	139	Th	50–70 µm	$\Delta l/l_0$	832–1425	+0·75	12 – 68	4 stages following in sequence; Q is T- and t-dependent
						+0·46		
						+0·22		
						−0·48	34 ± 5	
		Th	10–15 µm	$\Delta l/l_0$	832–1425	−0·51	35 ± 4	
Tikkanen	140	Ni	4–10 µm	$\frac{V_0-V_s}{V_s-V_{th}}$	800–1202	0·50	29·5 – 33	Carbonyl nickel; Q increases with annealing temperature; Q is dependent on Δl
		Ni	40 µm	$\frac{V_0-V_s}{V_s-V_{th}}$	1268–1355	0·50	62	Atomised nickel powder
Tikkanen and Ylasaari	141	Ni	5 µm	$\frac{V_0-V_s}{V_s-V_{th}}$	750–1200	0·60	25 – 0·4	Carbonyl nickel
Tikkanen and Mäkipirtti	142	Co	7–30 µm		665–885	0·50	70·5	—
		Ni	1–20 µm	$\frac{V_0-V_s}{V_s-V_{th}}$	882–1215	0·86	26·7	Carbonyl nickel
		Cu	2–50 µm		910–1010	0·62	46	—
		Fe	3–20 µm		730–890 1380–1460	0·65	30	Carbonyl iron
		90%W+ 10% Ni	W1–7 µm		1020–1250	0·80	70·9	—
Mäkipirtti	143	W-Ni-Cu	W 2 µm Ni 6 µm Cu 12 µm	$\frac{V_0-V_s}{V_s-V_{th}}$	893–1321	0·50 – 1·50	55·3 – 146·7	n and Q dependent on T and on composition
Kothari	144	W	0·3–1 µm	$\frac{V_0-V_s}{V_s-V_{th}}$	1100–1500	0·20	101 ± 2	
			1–8 µm			0·20	101 ± 2	
			10–18 µm			0·33	72 ± 2	

Authors	Ref.	Material	Particle size	Quantity measured	Temperature range, °C	n	Q, kcal/mole	Remarks
Kothari	145	W	3 µm	$\frac{dV}{dt}$; $\frac{V_0-V_s}{V_s-V_{th}}$	1100–1500	0·18 – 0·23	102 ± 2	Different evaluation of data possible
		W	3 µm	$\frac{\rho_s-\rho_0}{\rho_{th}-\rho_0}$	1100–1500	—	—	Logarithmic law
Kothari and Waring	146	Fe + Cu	Fe 10–20 µm Cu 30–45 µm	$\frac{V_0-V_s}{V_s-V_{th}}$	950–1250	0·25 – 0·33	64·5	n and Q are dependent on Cu content
Johnson and Clarke	66	Ag	< 150 µm	$f\left(\frac{\Delta l}{l_0}\right)$	800, 900	(0·48)		Evaluation according to equation [18]
Rhines, deHoff, and Rummel	147	Cu	74–88 µm	$\frac{V_s-V_{th}}{V_0-V_{th}}$	805–1011	0·06 – 0·40	—	$\frac{V_s-V_{th}}{V_0-V_{th}} = \exp^{-}(kt^n)$
		Ni	74–88 µm	,,	1000–1300		—	
Amato, Colombo, and Protti	148	UO_2	1–2 µm	$\frac{\Delta l}{l_0}$	710–930	0·40	61·5 – 70·5	Q is dependent on O : U ratio; Q decreases with rise in temperature
Kostic and Ristic	149	UO_2	< 63 µm	$\frac{\Delta V}{V_0}$	800–1300 800–1300	$n = n_0 - mT$ $n = 0·11$ $n = 0·05$	— 2·5 < 1100° 12 > 1100°	n and Q are strongly temperature dependent
Bannister	150	BeO	0·2 µm	P	1290–1600	– 0·40	116	n is temperature-dependent from 1600° C
Aitken	151	BeO	0·41 µm	$\Delta l/l_0$	> 1200	0·30	—	Calcining: 900° C
			0·65 µm	$\Delta l/l_0$	> 1200	0·50	—	
			0·91 µm	$\Delta l/l_0$	> 1200	0·40	—	1000°, 1250° n decreases with time
Daniels and Wadsworth	152	ThO_2	—	$\Delta l/l_0$	750–900	0·41	22	Curved lines
Daniels and Wadsworth	127	ThO_2	100Å	$\frac{\Delta l + \beta}{l_0}$	777	0·31 – 0·33	—	Evaluation according to equation [19] with scatter; both groups usable for representation
		Al_2O_3	0·3–0·5 µm		1414	0·4 – 0·5	—	
Johnson and Cutler	107	Al_2O_3	0·2–1 µm	$\frac{l}{l_0-\delta l}$	1200–1600	0·31	142	Evaluation according to equation [16]
			3–5 µm					
			1–20 µm	,,				
Bruch	153	Al_2O_3	0·3 µm	P	1400–1900	–0·40	150	n is dependent on green density $n < 0·4$ for high ρ_0
Keski and Cutler	154	Al_2O_3	18–22 µm	$\Delta l/l_0$	1400–1550	0·31	140	
		Al_2O_3 + MnO				0·46	140	
Jorgensen	155	Al_2O_3	0·3 µm	$\Delta l/l_0$	1300–1650	0·40	—	Curved lines
Hagel, Jorgensen, and Tomalin	126	Cr_2O_3	0·14 µm	$f(\Delta l/l_0)$	1050–1300	0·46	109·9	Evaluation according to equation [18]
		Cr_2O_3	0·14 µm	$\Delta l/l_0$	1050–1300	0·50	101·6	Evaluation according to Table V (*Coble*[31])
				$\Delta l/l_0$	1050–1300	0·40	123	Evaluation according Table V (*Kingery and Berg*[61])
Anderson	156	$BaTiO_3$	0·03–0·1 µm	$\Delta l/l_0$	700–1100	0·31 ± 0·03	112 ± 9	
Iwasaki	157	Pb (Ti, Zr) O_3	—	$\Delta l/l_0$	1160–1240	0·30 – 0·50	60 – 140	According to Ti : Zr ratio
Cech and and Bronkal	158	$MoSi_2$ + Al_2O_3 SiO_2	—	$\Delta l/l_0$	—	—	—	Early stages logarithmic
				$\Delta l/l_0$	—	0·20	—	Late stages
Ammar and Budworth	382	NaCl	< 53 µm	$\Delta\rho/\Delta_0$	619–737	0·50 – 0·56	—	Strong influence of particle size and green density

sintering, as proved from micrographs (Fig. 3 (*a*)) and porosity measurements, the pores form a continuous channel system along the grain boundaries[159] and are to a large extent open. The grains are considered to be uniform in shape and size, namely, as tetradecahedra (14-polyhedra), octahedra with all the corners truncated by four-sided pyramids. Pores in the form of a circular cylinder lie along all the edges of these bodies (Fig. 13). The solution of the diffusion equation with this geometry is as follows, on the assumption of grain boundaries as vacancy sinks, for the decrease of porosity P:

$$dP/dt = -K\frac{D_v\gamma V_0}{d^3RT} \qquad \ldots[27]$$

(d = grain size, proportional to the length of the edge of the polyhedron).

The range of validity is ~ 50–90% of the theoretical density, i.e. before high proportions of closed pores or extremely coarse grains have been produced.

Together with the grain-growth law in isothermal sintering:*

$$d^3 - d_0^3 = K'(T)\,t \qquad \ldots[28]$$

the following applies for the decrease in porosity:

$$P = P_0 - K''\frac{D_v\gamma V_0}{RT}\ln\frac{t+K'''}{t_0+K'''} \qquad \ldots[29]$$

$$(\text{for } t = t_0 : P = P_0)$$

or, if $d \gg d_0$:

$$P = P_0 - K''\frac{D_v\gamma V_0}{RT}\ln t/t_0 \qquad \ldots[30]$$

The relationships formulated above were confirmed by Coble himself[159] on Al_2O_3 (with and without MgO additions).

In supplementary work Coble and Gupta[165] were also able to account for the discrepancy of 2–4 orders of magnitude in the value of the diffusion coefficient of aluminium in Al_2O_3 and copper in copper (Fig. 14).

Instead of tetradecahedra, dodecahedra (12 regular pentagons as boundary faces) have also been used as grain shapes in calculations. It has been shown that the numerical factors in the densification equation depend only to a small extent on grain shape. In place of the original factor $K = 10$, the corrected calculation gives:

$K = 288$ for dodecahedra
$K = 335$ for tetradecahedra

After re-correction of the grain size a value of $K = 720$ has also been obtained,[166] by means of which a good agreement with actual diffusion data was found for copper and Al_2O_3.

However, activation energies of densification cannot be determined from the integrated equation, because $Q_{\text{densification}}$ appears to be approximately equal to $Q_{\text{grain growth}}$ (Bannister,[150] Bruch,[153]). Kingery and François[164] proved in a discussion of equation [28] that the activation energy for grain growth in the sintered compact must be consistent with that for densification, but that it has nothing to do with the activation energy for grain growth in the massive porosity-free material. Grain growth and densification control each other and possess the same activation energy.[167] Only when dP/dt is determined for a constant density or constant grain size (which is equivalent, according to Coble and Gupta,[165] and also according to our own measurements) can it be used to calculate an activation energy for densification. The Coble densification equation has been confirmed in several reports since its publication. Fischmeister[168] found that the Coble grain-growth and densification laws were applicable to 8-μm iron powder. Thümmler and Thomma[163] confirmed both equations on finely divided cobalt and nickel powders, both separately and as mixtures (Fig. 15 and 16). In an attempt to represent the contraction data by exponential laws, they obtained satisfactory straight lines in all cases in accordance with:

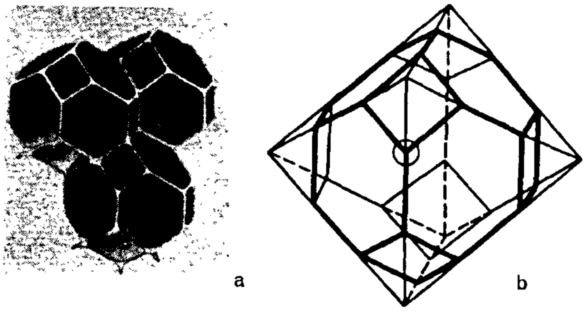
$$\log \Delta l/l_0 = \log K + n \cdot \log t \qquad \ldots \quad [31]$$

The slopes (n) depended on the material, mixing ratio, and temperature, and varied between + 0·3 and − 0·8. Thus a logarithmic representation produced the most satisfactory results empirically before Coble's work was published.

Morgan and Welch[169] also found a logarithmic shrinkage law for oxides (MgO, Al_2O_3, SnO_2, TiO_2, and Nb_2O_5) at temperatures below 1400° C, and in some cases over very long periods and for different degrees of porosity. They obtained the relationship:

$$dl/dt = -kt/ \text{ with } k = k_0 \exp(-Q/RT) \quad \ldots \quad [32]$$

where k is constant if the temperatures are not too high. Deviations at higher temperatures are probably associated with coarse grain formation. Logarithmic shrinkage behaviour was also found by Brown for very fine MgO, CaO, and NiO powders,[170-172] and by Duder-



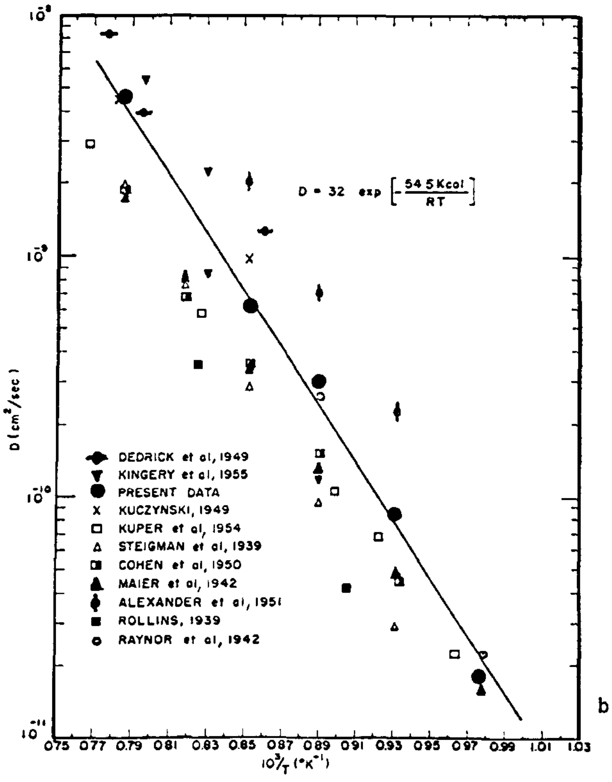
[*Courtesy 'J. Applied Physics'*
13 a. Geometry of tetradecahedron.
b. Position of cylindrical pores along the edges of the tetradecahedron. (*Coble.*[159])

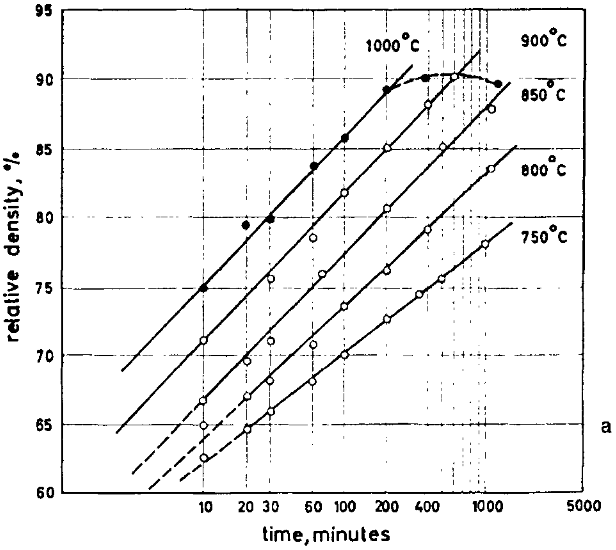
---

*Theory and experiment have frequently confirmed the applicability of the expression:

$$d^2 - d_0^2 = K(T)t$$

for grain growth in the recrystallisation of massive metals. In porous sintered compacts the pores have an inhibiting action on grain growth. Hausner[160] introduced a correction term into the above equation; this term contains the pore radius and total porosity. Exponential laws with smaller exponents have often been observed; a particularly good approximation was given[161–163] by an empirical law: $d^3 - d_0^3 = K'(T)t$. This expression has recently been established theoretically by Kingery and François.[164]





[*Courtesy American Ceramic Society.*

14a Logarithmic densification of copper powder compacts. (*Coble and Gupta.*[165])

[*Courtesy American Ceramic Society.*

14b Self-diffusion of copper according to different authors and methods of measurement. Heavy symbols (●) mark values calculated according to equation [27]. (*Coble and Gupta.*[165])

stadt and White[173] for very fine BeO powders. Ram *et al.*[174] reported the same behaviour for UO_2 powder of -74 μm size at 950–1500° C in hydrogen, with $Q = 102 \pm 10$ kcal/mole, which is in good agreement with the activation energy of 108 kcal/mole for uranium ion self-diffusion. Smith[175] and Vasilos and Smith[176] confirmed the logarithmic law on finely divided molybdenum and tungsten powders of 2–6 μm (Mo) and 0·45–0·88 μm (W) particle sizes.*

For the finest powders with diffusion paths that are short, and remain so, a generally valid logarithmic contraction law is therefore extremely probable. If it is found, the mechanism of volume diffusion would also appear to be confirmed. However, a discrepancy with an older and widespread view becomes immediately evident, i.e. that grain-boundary and surface diffusion predominate with the finest powders. For example, Tikkanen[140,141] deduces grain-boundary diffusion from calculations of the activation energy from contraction data, while the predominance of surface diffusion is presumed to some extent by other authors,[98,99] provided that the sintering temperature is not too high. Fedorchenko *et al.*[177] also explain the powder contraction as a consequence of surface diffusion.

It must be emphasised, however, that a low activation energy alone is still not a clear indication of surface or grain-boundary diffusion, even when *a uniform time law* exists over the whole range of temperatures and contractions under consideration. Even when volume diffusion predominates, much higher atom mobility than that corresponding to 'true' volume diffusion can exist, because of the numerous non-equilibrium states. Relevant investigations have been reported by Geguzin,[128] by Lange *et al.*[178] and by Aucouturier *et al.*[179] on sintered compacts. The activation energy for diffusion processes, composed of Q_f, for formation and Q_m, for migration of vacancies, lies in such a case far below the 'standard' value in the distorted lattice. Finally, the shrinkage is much higher in very fine than in coarse powders, a fact that is directly opposed to the predominance of surface diffusion.

It must be assumed, on the other hand, that surface diffusion plays a greater part with coarse-grained and coarsely crystalline powders, i.e., when the diffusion paths for vacancies to the next sink are too wide. In such cases only the vacancies near to grain boundaries or surfaces can contribute to the densification process. This is in agreement with the small shrinkage of such powders.[140] The results obtained by Fischmeister and Zahn[80,98,168] confirm this view completely. Surface diffusion contributes in the early stages to the elimination of very active surfaces and in the later stages to the rounding-off of pores.

III. Further factors influencing sintering

1. General

Numerous possibilities exist of influencing the promotion or inhibition of sintering, either deliberately or otherwise. These include all the 'secondary' factors listed in Table II under B and C, which relate both to

---

* Because of a criticism by Jorgensen[155] of the derivation of the Coble densification equation, Coble still uses only equation [27]. We believe, however, that the derivation is correct and must lead to the logarithmic densification equation [29] or [30], provided that the grain-growth equation [30] is valid.

powder and processing criteria. (Of the aspects mentioned under A, the influence of structure, state of bonding, and of modification changes has not so far been considered). An extensive amount of mostly qualitative, factual material also exists in this field, which it is difficult to arrange in a simple scheme. Often several of the conceivable factors act simultaneously, and this increases the problem of assessment. It must be the aim of all relevant experiments to determine the parameters individually as far as possible. Investigations have been undertaken from time to time with the object of obtaining a technically utilisable, sinter-promoting action, e.g. by the influence of aggressive gas atmospheres or of small additions of foreign substances. The concept of 'activated sintering' was developed in this connection.

Although some of these phenomena belong to the field of multicomponent systems (Section IV), the influence of oxide layers, sintering atmospheres, and deviations from stoichiometry will be treated in this section. The promotion or inhibition of a sintering process, which naturally consists of the exercise of a positive or negative effect on transport processes, can take place in the following ways:

(*a*) The surface or contact conditions between the particles are altered.
(*b*) The activation energies of the transport mechanisms are raised or lowered.
(*c*) The number of particles capable of migration is changed.
(*d*) The type of particle transport or of transport path is changed.

It is by no means always possible to state which of these factors exerts a promoting or inhibiting impulse.

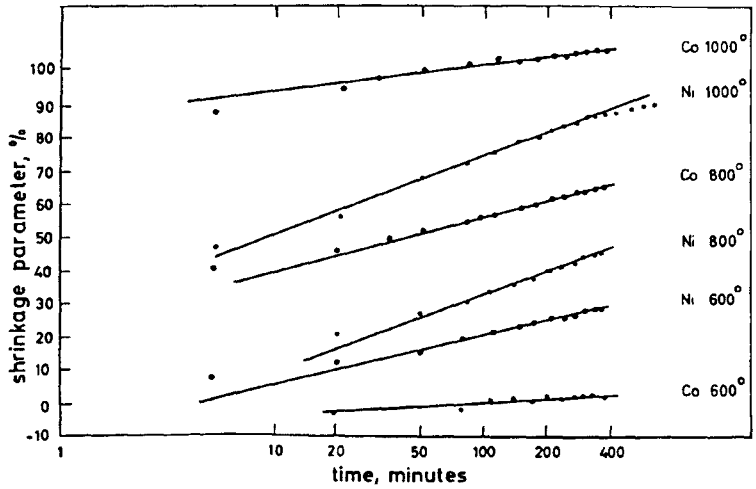
2. Effect of structure, state of bonding, and modification changes

Clearly, a general structural influence will not have to be investigated in the case of in a pure material, as it can exist only in an equilibrium state at one temperature. On the other hand, a comparison between metals possessing cubic, hexagonal, and tetragonal lattices shows that the temperature at the start of sintering, referred to the relevant melting point, increases with decreasing symmetry, i.e. the sinterability decreases correspondingly.[180,183] This could be due to the occurrence of non-metallic homopolar bonding constituents, at any rate with less closely packed structures. These results are still uncertain in relation to the low-melting-point metals lead, tin, cadmium, and zinc, because when comparisons were made the effect of the thinnest surface films was not completeley excluded; this is recognised as being particularly strong in the case of tin.[181]

With oxides and other compounds, the bonding conditions are much more complex owing to the existence of heteropolar and homopolar bonds. Structural influences were not explicitly investigated. In studying nitrides of the transition metals Samsonov *et al.*[182] established qualitatively an influence of electron-density distribution in the *d*-shells. Furthermore, the loss of nitrogen during vacuum sintering should bring about an increasing proportion of ion bonding and promote dense sintering.

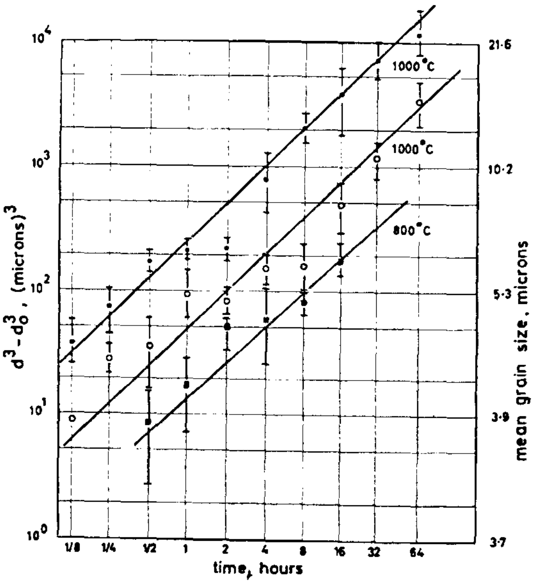
Bron[183] treated crystal-chemical relationships in the sintering of mixed oxides and oxide mixtures, and found that extending the lattice and loosening the bonding promoted sintering as a result of excess disordering. Results on organic materials (anthracene, terphenyl, hydroquinone, nylon, &c.), are very informative in this connection: these materials sinter very badly or almost not at all, which is explained by the fact that the diffusing units are very large, so that the self-diffusion coefficients are extremely small.[184,185]

With suitable metals the various modifications and the influence of the transformation can be investigated. It must be borne in mind that other properties also alter during the transformation and that sintering



[Courtesy Consultants Bureau.

15 Logarithmic contraction of very fine cobalt and nickel powders. (*Thümmler and Thomma.*[163])



[Courtesy Consultants Bureau.

16 Grain growth during the sintering of nickel powder compacts (at 1000° C, different green densities). (*Thümmler and Thomma*[163])

contacts can be destroyed or distorted by reason of volume changes. Detailed investigations have been undertaken, especially on iron. Observations based on the chemistry, according to which transformations, decomposition, &c., should always promote sintering,[186] are not confirmed for iron, however. Various authors[80,98,130–132,168,188,189] deal in detail with the sintering of iron in the α- and γ-regions. Sintering proceeds much more slowly in the γ-region than in the α-region, in analogy with the pattern of the diffusion coefficients. A further basis for this can be found in the grain growth during the α–γ transformation, so that many pores are enclosed in the interior of larger grains. The irreversible destruction of sintering contacts, which are often not formed again after re-transformation, is also an influencing factor. The different proportions of volume, grain-boundary, and surface diffusion in the two modifications and the additional defects which are probably produced after transformation make an exact interpretation more difficult. Hampe[190] found similarly with uranium that existing sintering contacts were destroyed in the α–β and β–γ transformations.

3. Effect of powder activity

The total activity of the powder particles is composed of the surface and lattice activities. The surface activity is directly related to the particle size and shape, and hence to the specific surface. It cannot be rigorously separated from the lattice activity, because the 'surface space' according to Hüttig[50] extends into the interior of the particle. Finally, fine particles, irrespective of how they were obtained, always possess both a high surface activity and an increased activity in the form of irreversible disorder of the most varied types. However, it seems reasonable to start by considering the influence of surface activity separately. Various, mostly older, papers exist on the overall influence of powder activity[191,192] in which many phenomena are described. More recent reports have been published by Murray,[193] Blackman,[194] and Torkar and Perlhefter.[195]

(a) **Surface activity**

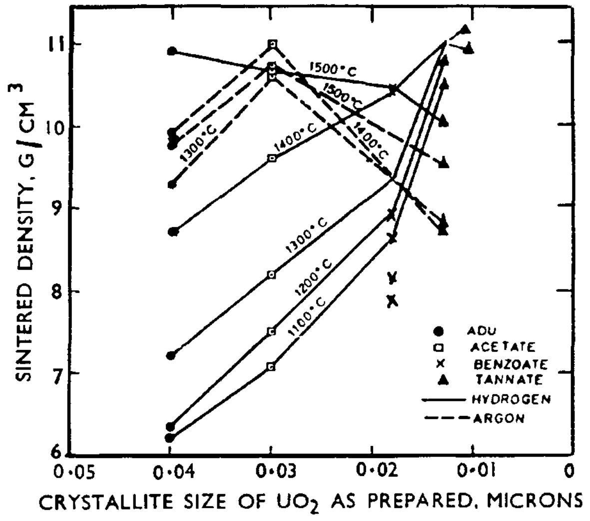
Powders with a high surface activity are often characterised by sharp surface irregularities, as well as by a high specific surface area. In every case the atoms are particularly mobile on surfaces having a strongly convex curvature, which leads to the initiation of sintering at very low temperatures with such powders. Thus, sintering phenomena were observed in gold powders, with a particle dia. of ~ 0·01 μm, at ~ 150° C, from the changes in resistance and in the reflecting power for infra-red radiation.[196] Relationships exist between the specific surface area and the sintering behaviour which have been investigated for iron, nickel, cobalt and chromium, or their oxides, by Royen[197] and Fedorchenko and Kostyrko.[177] An increase in surface values naturally gives lower sintering temperatures and a higher shrinkage. While the surface activity is likely to be the deciding factor at the start of sintering, it is very probable that the lattice activity contributes to the effect as sintering progresses. All the surface phenomena in powder manufacture, pressing, and sintering have been summarised by Eremenko and Nizhenko.[198]

Apart from the specific surface area, other properties have been utilised to characterise the surface activity of very fine powders, such as catalytic behaviour, adsorption and desorption, oxidation, exo-electron emission, electron-microscope characterisation, and so on.[199] All these can be used to control the reproducibility of powder manufacture.

(b) **Lattice activity**

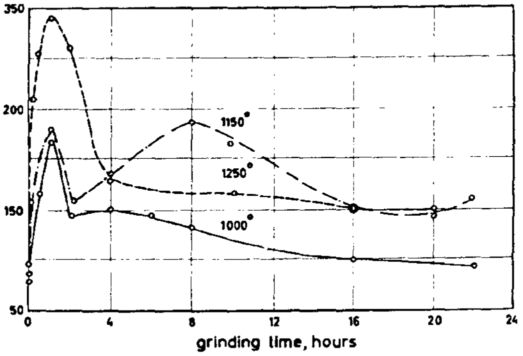
(i) *Particle and crystallite size*

It is generally known that finer powders give higher shrinkage than coarser material and that favourable distribution functions improve the apparent powder density, tap density, and green and sintered density; on the other hand, fine powders give lower apparent and green densities. The atomic processes in fine materials usually take place more rapidly and easily during sintering, because surfaces, grain boundaries, and all lattice distortions are present within a more restricted space, and hardly any undistorted regions exist. The finest powders, especially in the pressed state, also have a large 'integral contact area' per unit volume, provided that their surface is not too severely fissured. Oxide powders produced by the calcining of metal salts, together with the metal powders obtained from them by hydrogen reduction, become more widely dispersed and therefore more active with decreasing calcining and reducing temperatures. Particle sizes of < 0·1 μm are obtained in this way. The specific surface areas of oxides so prepared reach up to 100 m²/g. The very numerous investigations on the shrinkage of powders manufactured by different processes cannot be described in detail here; some recent papers are given in Refs. 113, 200, 201, and 202. Variations in shrinkage behaviour between mixtures of different iron powders have been reported.[203] Extreme effects were found with MgO.[24] In many investigations on powders adequate consideration has certainly been given to the particle parameters, but the crystallite sizes (to be determined



[*Courtesy Springer-Verlag.*

17 Influence of crystallite size on the sintered density of UO_2 powders of different origins. (*Moorthy and Rao.*[207])



[*Courtesy 'Ber. Deut. Keram. Ges.'*

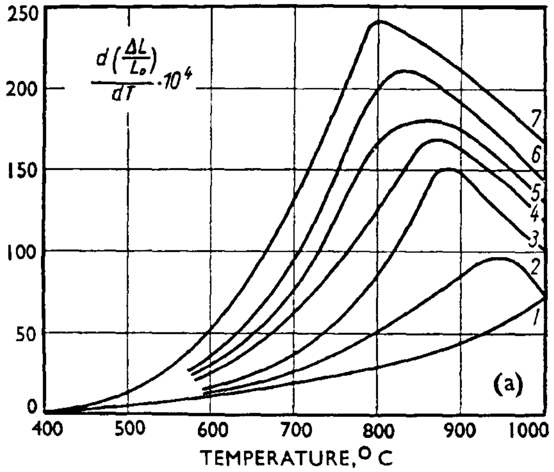
18 Influence of grinding time on the compressive strength of aluminium silicate sintered compacts. (*Naeser, Scholz, and Fiedler.*[210])

by X-ray methods) have seldom been taken into account. Reports on this aspect have been published by Oel,[204–206] and by Moorthy and Rao.[207] The crystallite size must have a considerable influence on the effectiveness of grain boundaries as sinks for vacancies. Fig. 17 shows an example of such an effect. It has been established[208] that powder from single-crystal particles exhibits slight grain growth at high sintering temperatures, while polycrystalline particles show a strong grain growth, corresponding to their higher activity.

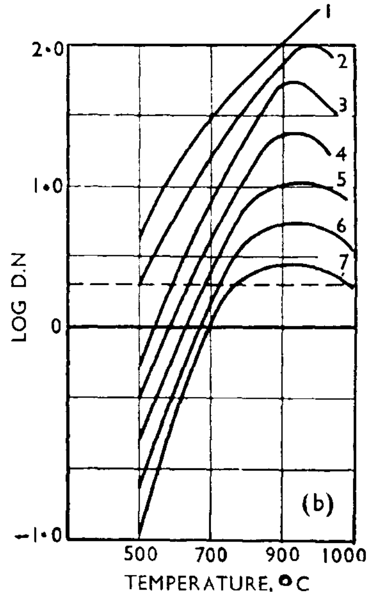
(ii) *Lattice defects, dislocations; Internal stresses*

Non-equilibrium states within the volume (excess vacancies, dislocation arrangements, and internal stresses) also arise from the method of powder production; excess energy can be introduced into powders, especially by cold working, i.e. *grinding*. Fundamental work on this aspect has been reported by Naeser *et al.*[209,210] A periodic dependence of the activity is found, not only for sintering processes but also for many kinds of chemical reaction, on the duration of grinding or rolling, with maxima and minima (Fig. 18). The strength values are particularly affected during the sintering of oxides. This is interpreted by assuming an interaction of lattice distortions and healing of the distortions during deformation; but the exact mechanism has not been explained. An increase in densification with grinding time is also shown.[211] It is established[212] that Al_2O_3 powder is more active when ground for a longer time after calcining at a high temperature than when ground for a shorter time to the same particle size after calcining at a lower temperature. Lattice defects due to grinding thus appear to be effective for a longer period in the case of Al_2O_3 than in that of metals with a high recrystallisation capacity at lower temperatures.

The results on the influence of *deformation-induced* stresses in metals are not in agreement. Thus, Torkar and Perlhefter[195] state that the stresses are eliminated at temperatures much lower than those at which densification begins, and are thus without practical importance as far as sintering processes are concerned. It is not the deformation-controlled primary recrystallisation (which is much more important in metals than in oxides, &c.[213]), but the secondary recrystallisation (grain growth, controlled by the grain-boundary energy) that influences the sintering process. However, this picture seems to be over-simplified, especially since it has been found that even when complete freedom from stresses has been achieved, excess lattice disorder that increases the diffusion period is still effective for some time. Bokshtein[214] found for the diffusion of tin in massive nickel after 12% elongation that the volume diffusion at 700° C, but without an intermediate anneal, was increased by a factor of 7; after an intermediate anneal at 900° C the factor was 4·6, while it was still 1·2 after annealing at 1200° C. Cold deformation acts on D_v even after prolonged



a



b

[*Courtesy 'Physics Metals Metallography'.*

19a Shrinkage rate d/dt ($\Delta l/l_0$) of electrolytic copper powder compacts at different heating-up rates:
(1) 5, (2) 2, (3) 0·8, (4) 0·4, (5) 0·2, (6) 0·1, (7) 0·05 degC/sec. (*Geguzin and Ovcharenko.*[128])

[*Courtesy 'Physics Metals Metallography'.*

19b Diffusion data ($D.N$; N = number of pores per unit volume) calculated from Fig. 19a; values increase with increasing heating-up rate, owing to the slow removal of lattice distortions. (*Geguzin and Ovcharenko.*[128])

annealing at high temperatures. Thümmler, in experiments on cold-worked copper[83] at 750° C on the bar–wire model, found that the mobility coefficients were increased by up to two orders of magnitude; an influence is still detectable at higher temperatures (see Fig. 7). It is doubtful whether such effects can be transposed to a greater extent to metal-powder compacts in practice, because an inhibiting impulse is introduced by the poor compressibility of deformed powder.

Geguzin *et al.*[215,216] investigated the shrinkage kinetics of electrolytically deposited copper powder, which also shows severe internal stresses. Marked maxima were found in shrinkage rates at certain temperatures, according to the heating-up rate (Fig. 19 (*a*)), from which sharply increased diffusion coefficients for the distorted crystal lattice can be calculated. Geguzin and Ovcharenko[128] also report model sintering experiments on the wire–wire model with electrolytically coated copper wires. The neck growth and the diffusion coefficients calculated from the Pines equation (Table IV) are much higher than in the model experiment with uncoated copper wires, e.g. by a factor of 100 at 750° C, 15 at 870° C, and 4 at 1020° C. Increased values were still found after 20 h at 1020° C. In spite of the absence of chemical concentration gradients diffusion porosity is found preferentially along grain boundaries. A similar result was obtained by Pines and Sirenko;[218] pores were formed on the side of the less distorted lattice as the dislocation densities are lower there (the dislocations here should be effective as vacancy sinks!). Even a smaller excess of vacancies is then sufficient for the separation of pores, because of unequal dislocation currents. The dislocation density is higher on the more severely distorted side of the diffusion specimen, so that the effective supersaturation in vacancies is less.

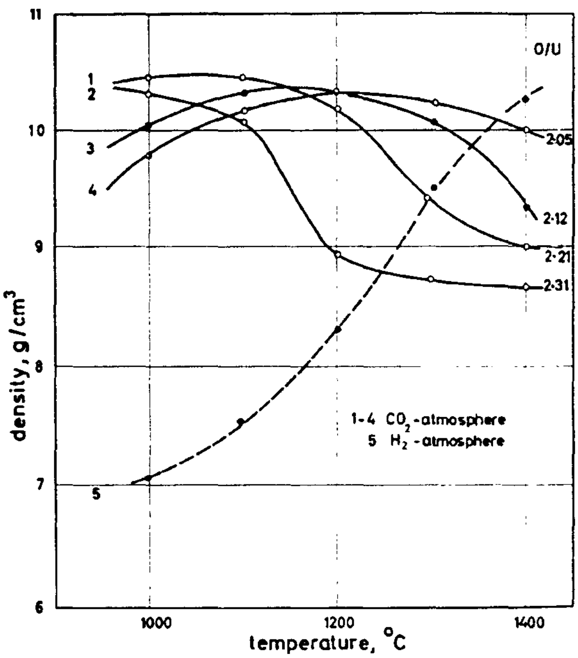
Diffusion measurements on porous sintered compacts in the non-equilibrium structure are also of interest in this connection.[178,179,219] The discrepancy, which is often considerable, between true diffusion coefficients and mobility coefficients calculated from sinter models can possibly be explained on these grounds. According to Aucouturier *et al.*[179] and Guiraldenq[219] the activation energies for grain-boundary diffusion are 39 in massive α-iron, 30 in porous α-iron, and 40·3 or 36·7 kcal/mole, respectively, in the γ phase. There is no sudden discontinuity in the α–γ transformation. In the volume diffusion of iron in porous nickel Q_{Fe} is 10 kcal/mole lower than in massive nickel, and 13 kcal/mole lower in porous than in massive cobalt. Hässner[220] summarises the criteria according to which of the effectively measured diffusion coefficients are identical with the true D_v This shows that the conditions:

$$\sqrt{2D_v t} \gg 2d \qquad \ldots[34]$$

and

$$d\,D_v \gg \delta D_b \qquad \ldots[35]$$

must be fulfilled simultaneously. If the grain size is not too fine (according to [35]), or has a sufficiently high product $D_v t$ (according to [34]), volume diffusion will be predominant. In the porous structure D_b and hence the ratio D_v/D_b can evidently be far higher than in the massive metal.



[Courtesy 'Ber. Deut. Keram. Ges.'.

20 Influence of deviations from stoichiometry in UO_2 on the sintered density in CO_2 and H_2. (*Müller.*[223])

4. The influence of stoichiometry

A special type of change in lattice activity becomes possible, for example, with oxide compounds, as a result of the presence of non-stoichiometric states in the cation or anion sub-lattice. Excess oxygen is present in uranium dioxide (UO_{2+x}) at elevated temperatures in the form of interstitial atoms, which are extremely mobile.[221] (UO_{2+x}) sinters more easily than the stoichiometric oxide under many, if not all, conditions.[222,223] Temperatures for optimum densification were found, above which lower values are again obtained (Fig. 20). The cause of this regression is not known with certainty; possible causes are the formation of gas in the interior or intensified grain growth at the higher temperature. However, the sinter-promoting influence is rapidly removed in hydrogen. The time law of grain growth in sintering is found to be a function of the O:U ratio and the sintering atmosphere.[224] It must, however, be noted that, especially with UO_2, the influence of oxygen and particle size often cannot be separated rigorously, because the finer particles often have a higher O:U ratio.

A sinter-promoting influence of excess zinc (1–6 ppm) has been found with ZnO, but not in all cases.[225–227] An intensified zinc self-diffusion with an excess of zinc is postulated. The composition of an oxide, at any rate of the surface layers, can also be controlled by the sintering atmosphere; this is very evident in the sintering behaviour of Al_2O_3.[86,228] This is referred to in Section III.6b. Equations have been formulated[229] which should be applicable, with deviations from stoichiometry, for the effective diffusion coefficients. Blackman[194] and Parravano[87,88] have published reviews on the influence of stoichiometry.

5. The influence of corpuscular radiation

Heavy particles, e.g. neutrons above a certain energy level, expel lattice constituents from their regular positions. This means that allowance must be made for additional vacancies; the steady-state concentration is dependent on the flux and, because of the parallel healing processes, is strongly temperature-dependent. Dienes,[230] for example, refers to their influence on the sintering process. An increase in the diffusion leading to sintering is caused in this way, especially at low temperatures. Apart from isolated observations, however, no experimental material on this subject is available. UO_2 sinters under neutron bombardment at temperatures as low as 200° C, and properties are observed at 600° C which show no further changes after a subsequent long-time anneal outside the reactor at 900° C.[231] McBride and Clinton[232] investigated the change in specific surface area of ThO_2 powders after irradiation with a flux of $2{\cdot}5 \times 10^{13}$ n/cm²/sec, and at temperatures up to 100° C, for 489 days, and found a very marked decrease. It is concluded that accelerated material transport takes place, especially with crystallites of < 2000 Å. Larger crystallites were less affected. However, these results cannot be directly transposed to the behaviour of non-fissionable materials.

6. The influence of foreign constituents

The sintering process can be affected in various ways by foreign atoms and foreign constituents, which can be present in different forms and are to some extent unavoidable. The influence of sintering atmospheres and aggressive gases has also to be considered in this connection. A very important part is played in practice by oxidised surface layers. These factors are described below.

(a) **Oxide layers**

If the layers are reducible or soluble, or dissociated during sintering, a promoting effect is observed up to certain layer thicknesses. This was found by various authors[233-237] for copper and iron, where the most effective layer thicknesses lie between 400 and 500 Å and 400–600 Å, respectively. The spongy surface metal present after decomposition of the oxides is more active than the massive metal, which is free from oxide from the start. Rutkowski[238] recorded a sinter-promoting effect with metal/oxide mixtures (Cu–CuO, Fe–Fe_2O_3, W–WO_3), as long as the water vapour formed and other enclosed gases could be removed sufficiently easily. Dienst and Werner[239] found a lower heat of activation of sintering with pre-oxidised powders. The unfavourable action of thicker layers evidently depends on too great a deterioration in the contact conditions due to an increase in the specific volume.

Oxides that are not removable under sintering conditions have in general an inhibiting effect*, because they act as diffusion barriers. The fact that aluminium powder, for example, cannot be densified to give usable compacts by cold pressing and sintering is generally known, as well as the poor sintering characteristics of stainless steel under 'ordinary' conditions. The causes are the Al_2O_3 or high Cr_2O_3 contents of the surface layers. Similar effects have been reported with uranium,[240] where UO layers have a more inhibiting effect than UO_2. Hampe[135,190] found that the temperature at which a strength increase takes place is $>$ 200 degC lower with an O_2 content of $\sim 0{\cdot}01\%$ than in a powder with $0{\cdot}06\%$ O_2. The differences disappear at higher temperatures. Apart from these results and a few values given by Magdanz and Sauerwald[235] practically no quantitative data are known to exist. Friemel, Knacke, and Stranski[181] showed that extremely thin, even in some cases, monomolecular oxide and adsorption layers, can have a strongly inhibiting effect with tin. Clearly such factors exert a particularly marked effect in low-melting-point metals, as all the sintering temperatures that can be used for these metals are very low with reference to the properties of the layer (contact SnO_2–SnO_2).

(b) **The influence of sintering atmospheres**

An extremely important influence is exerted by the sintering atmosphere. Inert or reducing gases in the case of metals, and inert, reducing, and oxidising media in the case of ceramics, can cause fundamental differences. Additions of aggressive or nascent gases promote the reactions. Only a few reports can be discussed in this connection. Reviews on the influence of the atmosphere have been published by various authors[241-243] (see also Ref. 17, pp. 407–415).

The fact, established in Section 6a, that the sintering process is in general inhibited in metals with non-reducible oxide layers, also implies that a significant oxygen partial pressure (e.g. impure or moist hydrogen, argon, &c.) gives poor results in such cases. This indicates the use of vacuum sintering, e.g. with beryllium or other highly reactive metals, although conditions must be established that prevent too much vaporisation. The rate of vaporisation depends not only on the sintering temperature, but also in practice on the geometry of the sintering vessel, the packing density, and the temperature distribution. The material to be sintered can also be covered with suitable powdered substances.

Vaporisation of the sintered compact is undesirable primarily because of losses of material and changes in shape, and in some cases because of changes in composition. Certainly a sinter-inhibiting effect is associated with vaporisation, when the inner surfaces undergo a marked reaction with the gas phase and do not contribute to the internal transportation of material. On the other hand a selective vaporisation of impurities is very advantageous in many cases (tantalum, niobium), e.g. suboxides. Small amounts of auxiliary metals used as aids to sintering can also be vaporised again out of high-melting-point metals and carbides in a high vacuum.

In removing enclosed or adsorbed gases from the compact a vacuum is often superior to other sintering atmospheres, because such gases govern the final density, especially in the later stages of sintering, or make further densification more difficult (see also Section V). The phenomenon of 'over-sintering', i.e. a decrease in density in spite of further sintering, must be attributed, at least

---

* See Section IV for the promoting effect of certain oxide additions in the later stages of sintering.

in many cases, to the effects of entrapped or newly generated gases.

Sintering was frequently promoted by the addition of aggressive gases such as chlorine and HCl, and of especially reactive nascent hydrogen (for example, by the decomposition of TiH_2). In such cases new sinter-active surfaces are continually formed, thus accounting for the promotion of sintering. Attempts were made to utilise such an 'activated sintering process', especially for iron powder metallurgy, and good results were obtained with regard to the density and the magnetic and mechanical properties (e.g. a much higher elongation). Investigations in this direction have been made by Eudier,[244] Korovsky,[245] and Andrievsky and Fedorchenko,[246] who later summarised all the aspects of activated sintering.[247] Chlorine-containing sintering atmospheres promote the sintering process in the case of iron and steel by the formation of volatile or low-melting-point metal halides, especially in the early stages. This is supported by the fact that the strength properties determined by neck growth, such as tensile strength and elongation, are improved to a greater extent than the densification. Stainless-steel powder behaves in the same way, according to Andrievsky and Solonin,[248] while Eisenkolb[249] found no sinter-promoting effect in atmospheres containing chlorine, except when nascent hydrogen from titanium hydride was used. Processes employing aggressive gases or additives cause difficulties in practice, however, because of the increased danger of corrosion.

The influence of oxygen partial pressure in the sintering of oxides is obvious, because surface deviations from stoichiometry, and consequently the degree of disorder, can be increased (or eliminated). This effect is often investigated with uranium oxide. The maximum sintering temperature is frequently necessary in dry hydrogen to obtain given density values, while lower temperatures are sufficient in moist hydrogen, argon, and nitrogen.[250,251] In steam the oxide can also be sintered to very high densities at temperatures as low as 1300° C.[252,253] All sinter-promoting atmospheres give products with an O: U ratio significantly $> 2{\cdot}00$ (e.g. $2{\cdot}05$–$2{\cdot}15$) which is unfavourable for use as a nuclear fuel. If the advantage of over-stoichiometric sintering is to be utilised, therefore, a reducing anneal in dry hydrogen must be carried out subsequently.

It has been found[255] that the greatest sintering rate is observed in oxides with a variable valency (CuO) when the dissociation pressure and atmospheric partial pressure are the same. It is also understandable in this connection that Cr_2O_3 in vacuum or nitrogen gives better densification than in oxidising atmospheres.[256]

7. The influence of pressing

The main factors to be investigated are:

(*a*) Raising the 'integral contact area' per unit volume, thus producing an increase in green density.

(*b*) Introduction of elastic and plastic deformation.

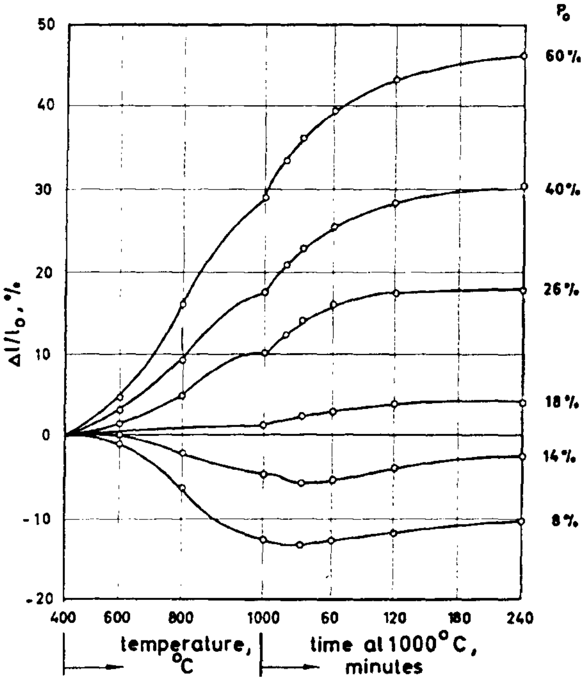
(*c*) Deformation or cracking of surface layers.

(*d*) Inclusion of air and gases.

A large number of empirical investigations into the dependence of various material properties on the pressing conditions have been reported in the literature. These refer both to the sintered and the unsintered state, and general relationships have been established. Discussion of these is outside the scope of the present review, however. Papers dealing with the separate assessment of the above points with reference to the sintering process are much less common. Thus, there are hardly any reviews dealing with the way in which the integral contact area grows with increasing compacting pressure, or how the specific surface area of the powder decreases. Undoubtedly these relationships are very different for metallic and ceramic powders. Regarding point (*b*) Lenel *et al.*[257] established for copper compacts that the residual stresses are responsible for the early shrinkage from 210 to ≮ 400° C. The actual densification, characterised by a temperature-dependence, takes place only above 650° C, e.g. after the stresses have been largely eliminated. This view is confirmed by Lenel *et al.*[120,123] Matsumura[258] also states that the actual sintering process is not influenced by the compacting stresses, as these are eliminated too rapidly.

Model experiments on cold welding during compacting were conducted by Nicholas.[259] The essential result is that the oxide layers are cracked, not by the compacting pressure itself, but only by the relative movement of the faces against each other. This result does not of course cast any doubt on the importance of the increased surface of contact.

The inclusion of gases at high compacting pressures is of great importance. The growth phenomena during sintering, which are associated with gas inclusion in some cases, have been known qualitatively for some time, and were investigated more accurately by Pines, Sirenko and Sukhinin.[260] The effect becomes greater with decreasing initial porosity; under the conditions of Fig. 21 no shrinkage is observed with copper powder



[*Courtesy 'Zhur. Tekhn. Fiziki'.*

21 Influence of initial porosity on the shrinkage or expansion of copper powder compacts. Left of diagram: heating-up to 1000° C; right of diagram: isothermal sintering at 1000° C. (*Pines, Sirenko, and Sukhinin.*[260])

beyond 14% porosity, but only growth. The effect is more marked with finer than with coarser powder. Given very careful heating-up this disturbance is usually less, as the pores are not really closed and the gas can still be evolved slowly.

In the case of die-compacted powders shrinkage is usually found to be different in directions parallel and vertical to the direction of pressing. This is a consequence of the density distribution in the compact and the unequal distribution of contact area in the various directions. The ratio of radial and longitudinal shrinkage is dependent on compacting pressure, sintering temperature, dimensions, and the method of supporting the specimen; however, the ratio can neither be predicted nor fully interpreted.

Even in unpressed (e.g. vibrated) powders, such anisotropies in shrinkage exist. Relevant investigations have been reported by Lenel, Hausner, and their coworkers,[118,119,261–264] who infer from the results that the force of gravity exerts an influence on the sintering process.

If a high initial density is obtained without the use of a compacting pressure, e.g., by vibration with a suitable particle-size distribution, the influence of the high density can be studied separately, without interference from factors (*b*)–(*d*). In this case the sinter density is dependent to a greater extent on the particle size and distribution and the powder activity than for compacted powders. By maintaining close tolerances, however, surprisingly high densities (> 95%) can be attained; this has been demonstrated with beryllium, for example.[265,266]

IV. Sintering of multicomponent systems

1. General

It is an undisputed fact that in multicomponent systems, with and without a liquid phase present, the decrease in free surface energy (γ_A, γ_B) or in interfacial energy γ_{AB} is a precondition for the commencement of sintering. According to Pines,[267] a condition for mutually insoluble systems is;

$$\gamma_{AB} < \gamma_A + \gamma_B \qquad \ldots [36a]$$

With

$$\gamma_{AB} > \gamma_A + \gamma_B \qquad \ldots [36b]$$

no sintering of the A–B contacts takes place, although the A–A and B–B contacts sinter together in every case. If the condition stated in [36*a*] is valid, a distinction must still be drawn between

$$\gamma_{AB} > |\gamma_A - \gamma_B| \qquad \ldots [36c]$$

and

$$\gamma_{AB} < |\gamma_A - \gamma_B| \qquad \ldots [36d]$$

While contacts build up in case [36*c*] with an approach of the mid-points up to a 'critical distance' only, complete sintering is possible in case [36*d*] given sufficient sintering time. The component with the lower γ will completely surround the other component by surface diffusion. This gives the state of lowest free energy (see also Ref. [198]). The lower the value of γ_{AB} the greater is the driving force, in every case. It must be emphasised that the interfacial energy controls the process even without the formation of liquid phases; the effect is more clearly marked in the presence of a liquid phase only because of the phenomenon of wetting. Strictly speaking, the absence or presence of wetting can also be defined between solid phases.

2. Without solubility of the components

In this case, according to Pines and Sukhinin[267] and Goodison and White[268] the sintering characteristics are a quadratic function of the mixing ratio. The number of similar types of A–A or B–B contacts, compared with the number of A–B contacts, determines the behaviour of the system exclusively. With the same proportions by volume C_A and C_B (assuming equal particle size and shape), and the same statistical distribution, the A–B contacts are the most frequent and their influence on the overall sintering behaviour is a maximum. Pines expresses the shrinkage η by the following equation:

$$\eta = \eta_A C_A^2 + \eta_B C_B^2 + 2\eta_{AB} C_A C_B \qquad \ldots [37]$$

with

$$C_A + C_B = 1 \qquad \ldots [38]$$

Here η_A and η_B signify the shrinkage behaviour of components A and B under the same conditions, e.g. the behaviour of A–A or B–B contacts alone; their number is a function of the square of C_A and C_B. η_{AB} is the proportion of shrinkage due to the A–B contacts.

An analysis of equation [33] shows that for:

$$\eta_{AB} = 1/2\ (\eta_A + \eta_B) \qquad \ldots [39a]$$

a simple linear dependence on shrinkage is obtained, while for

$$\eta_{AB} > 1/2\ (\eta_A + \eta_B) \qquad \ldots [39b]$$

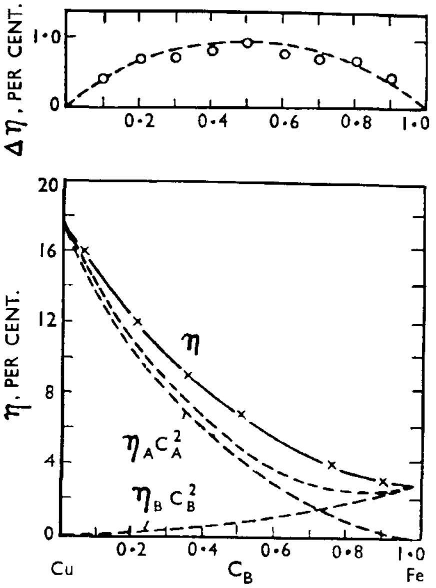
convex parabolas are formed, e.g. intensified contraction of the mixtures, and concave parabolas result for

$$\eta_{AB} < 1/2\ (\eta_A + \eta_B) \qquad \ldots [39c]$$

corresponding to decreased shrinkage of the mixtures. According to definition, therefore, case [39*a*] represents the behaviour of an 'ideal mixture'. The quadratic relationship [37], which is also valid for the strength of sintered compacts, has been verified on several systems (Cu–W, Cu–Mo, Cu–Fe) (Fig. 22) and was even extended to three-component systems (Pines *et al.*[267,269,270–272]). With an 'inactive' component (B), which does not sinter even at the temperature in question, η_B and η_{AB} can become zero. This is expressed, for example in the sintering of Cu–Mo and Cu–W mixtures, by a sharp drop in the strength, extrapolated to zero porosity, with increasing molybdenum and tungsten contents (Fig. 23).

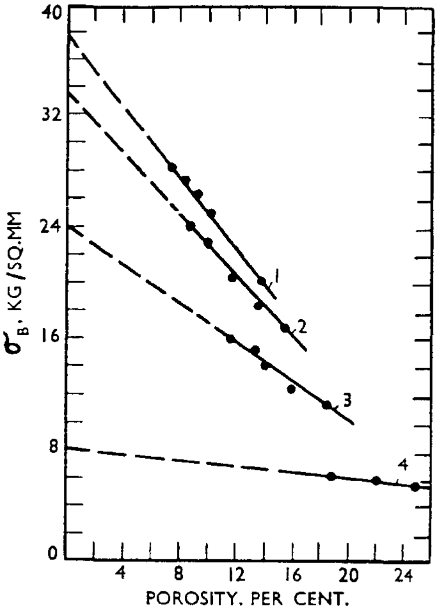
According to its derivation, equation [37] should apply only for immiscible systems; this must not be understood unconditionally, because the term η_{AB} directly reflects the behaviour of the A–B contact, which can also act as a promoting or inhibiting factor during the formation of solid solutions or intermetallic phases (see Williams and Jones.[273]).

The values γ_A, γ_B, and γ_{AB} are of decisive importance for the magnitude of η_{AB}, as mentioned above. Oxide cermets are typical cases in which the components are insoluble or only slightly soluble. However, no investigations into the validity of equation [37] have been published, apart from the case of the cermet system Cr-Al_2O_3 in which, according to Modl-Onitsch,[274] because of the difference in melting points, only the chromium sinters to any extent up to 1450° C, and both $\eta_{Al_2O_3}$ and $\eta_{Cr-Al_2O_3}$ are zero.



[*Courtesy 'Zhur. Tekhn. Fiziki'*.

22 Total shrinkage (η) of copper/iron mixtures subdivided into component contractions $\eta_A C_A^2$ and $\eta_B C_B^2$ and (top)'$\Delta\eta = 2\eta_{AB}C_AC_B$, according to equation [37]. (*Pines and Sukhinin.*[260])



[*Courtesy 'Zhur. Tekhn. Fiziki'*.

23 Tensile strength σ_B as a function of porosity P for copper/tungsten and copper/molybdenum powder mixtures.
(1) Pure Cu; (2) Cu + 5%W or Mo; (3) Cu + 20%W or Mo;
(4) Cu + 35%W or Mo. (*Pines and Sukhinin.*[260])

On the other hand, the quadratic concentration-dependence of the shrinkage was found in some insoluble oxide mixtures: Goodison and White[268] showed this for Cr_2O_3–SiO_2 and $MgCr_2O_4$–Mg_2SiO_4.

A considerable improvement takes place in the sintering behaviour and chemical properties of oxide cermets when a limited interaction (wetting, solubility, or chemical reaction) between the components can be achieved.[275] This can be brought about in many cases by introducing an 'auxiliary phase' which reacts towards both sides. Thus, improvements were observed with Cr-Al_2O_3 cermets in the presence of Cr_2O_3, which can easily be formed, e.g., by slightly oxidising sintering atmospheres.[274,276]

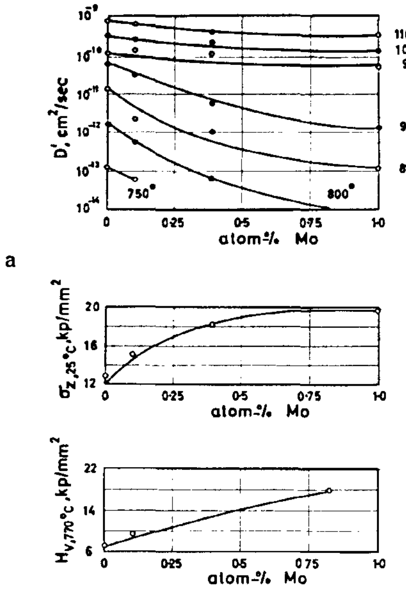
3. With mutual solubility of the components

It is necessary to differentiate in general between:

(*a*) Sintering homogeneous solid solutions (without a concentration gradient),
(*b*) Sintering with simultaneous homogenisation,
(*c*) Sintering with the decomposition of solid solutions.

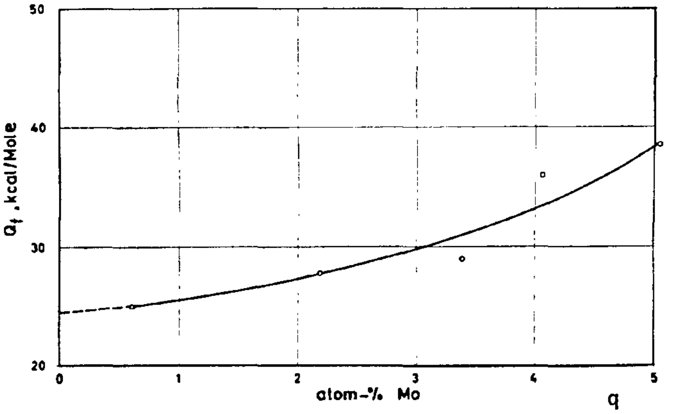
Thümmler[277] dealt with the sintering of dilute, homogeneous solid solutions, in comparison with the pure base metal, and studied the systems Fe–Sn, Fe–Mo, Fe–Ni, and Cu–Sn with up to ~2 at.-% of the second metal. The bar–wire model was adopted. The sintering behaviour is closely related to the physical and thermodynamic properties of the solid solutions (Fig. 24). In cases of higher strength and hardness values, which originate from the bonding forces in the lattice and which in the system Fe–Mo, for example, give a higher formation energy for vacancies,[278] a marked inhibition of sintering by the second metal is observed. There are still no data available as to whether an increased atom mobility, such as that observed in systems on a silver basis,[279] produces the reverse effect. The segregation phenomena reported in Ref. (91) are of great interest (see Section II.1).

Sintering with the simultaneous formation of solid solutions is much more difficult to survey, and is accompanied in some cases by unexpectedly large-scale effects. Many reports have been published on this aspect of sintering, because the sintering of ordinary powder mixtures often involves mutual dissolution. A great deal of work has also been carried out with the aim of activating the sintering process by small additions. The first investigations originated from May,[280] Butler and Hoar,[281] Balchin,[12] and Agte and Vacek.[282,283] Strongly inhibiting or promoting effects of the second component were observed, according to the materials used, sintering conditions, and stage of sintering. Here the deciding factor is not the solid-solution formation, as such, but the different partial diffusion coeffi-



[Courtesy '*Planseeber. Pulvermet*'.

24a Top: Mobility coefficients D' in the model sintering experiment using Fe–Mo solid solutions.
Middle: tensile strength (σ_z) of Fe–Mo solid solutions at room temperature.
Bottom: High-temperature hardness (H_v) of Fe–Mo solid solutions at 770° C. (*Thümmler.*[277])



[Courtesy '*Physics Metals Metallography*'.

24b Formation energy of vacancies (Q_f) in Fe–Mo solid solutions. (*Mokrov.*[278])

cients occurring in each case in practice. New vacancies are constantly being produced in this way. These can assist the process by increasing the effective atom mobility, provided that they remain 'dissolved' in the lattice. If they coagulate to form new pores, they naturally have an inhibiting action by producing the well-known Kirkendall effect. All the facts indicate that with an ideal mixture (which does not exist in practice in any system) the sintering behaviour must fall linearly between that of the pure components, as long as lattice diffusion is predominant. Examples of a promoting action are also cited in Ref.[12],[282],[283], and were found by Thümmler[277] in the systems Fe–Ni, Co–Ni, and Ag–Cu in model experiments with electrolytic deposition of the second metal,* in many oxide systems (see Section IV.5), and in tungsten with small additions of metals of the iron group.†

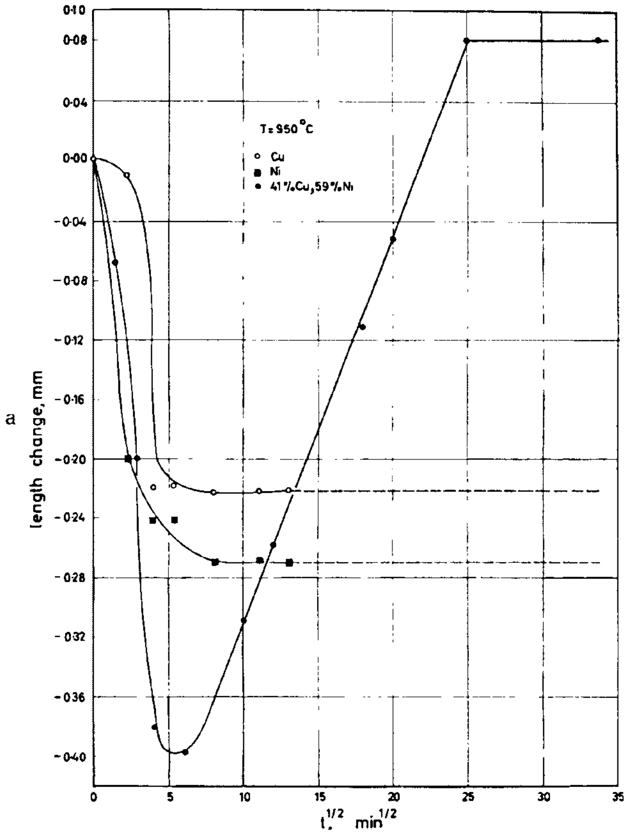
More recently the inhibited sintering characteristics of powder mixtures, e.g. in the Cu–Ni system, have been investigated. Under certain conditions expansion phenomena were observed instead of contraction (Fig. 25*a*). According to Fisher and Rudman,[284] these are directly related to the degree of homogenisation (Fig. 25*b*). Huntz and his co-workers,[285] Lund *et al.*,[286] and Rao[287] also found either inhibited shrinkage or expansion in Cu–Ni. Torkar *et al.*[288,289] utilised magnetic methods to follow the progress of homogenisation, and were able to determine frequency distributions for the solid-solution compositions existing after various sintering treatments. From the activation energies of 10·3–26 kcal/mole measured in several investigations it is concluded that the homogenisation is determined by grain-boundary and surface diffusion rather than by lattice diffusion. At higher temperatures and in the later stages of sintering the values are increased. It must be emphasised once again that volume diffusion too can exhibit a lower activation energy in distorted lattices, and also that homogenising is not to be equated with the sintering process itself (neck growth and pore contraction).

Raichenko and Fedorchenko[290] derived a solution of the diffusion equation for the homogenisation of a powder mixture with unlimited miscibility, in which the volume increase arising from the Kirkendall effect was also calculated. The progress of homogenisation as determined by X-ray methods corresponds approximately to the calculated result, at least as far as the time required for a high degree of homogenisation is concerned. However, the calculated increase in volume is less than the experimental value, ranging from 30 to 90% of the experimental results. This is attributed to other factors that can also cause volume increases, such as preferential gas evolution *during* the formation of solid solutions. Other changes in properties during sintering with homogenisation were also calculated by Raichenko[291] and gave results in good agreement with experimental data. Thümmler and Thomma[163] studied a system with solution characteristics *approaching* the ideal, namely Co–Ni in the form of very fine powder mixtures. The early stages of sintering and homogenisation, in which no vacancy coagulation had so far taken place, were examined dilatometrically, and better sintering of the mixtures was found here (Fig. 26). In the later stages poorer sintering was observed under many conditions than with the pure components (but no expansion) (Fig. 27). The behaviour of individual contacts, especially their asymmetrical shape, their constraint or contact frequency, was demonstrated with models by Kuczynski and Stablein on Au–Ni and Fe–Ni[292,293] and by Thümmler and Thomma[163] on Co–Ni, in relation to the experimental layout (Fig. 28). The maximum radius of curvature is always

---

* Here the influence of the change in disorder of the electrodeposited layer itself could be eliminated.

† However, the mechanism of promotion is somewhat different here (see below).

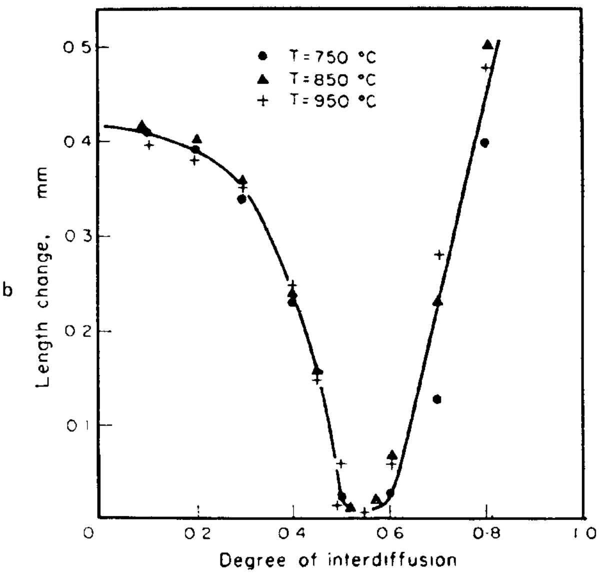


[*Courtesy 'Acta Metallurgica'*·

25a Shrinkage and expansion of copper, nickel, and a mixture of 41% Cu and 59% Ni. Because of the Kirkendall effect the expansion follows a $\sqrt{t}$ law. (*Fisher and Rudman.*[284])

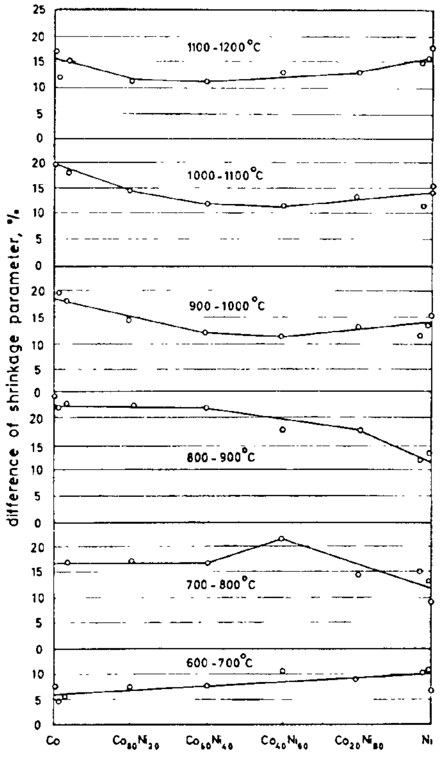
found in the metal or solid solution with the higher atom mobility. The depressions that are formed can be defined as 'surface pores' and correspond to the Kirkendall pores in the real powder compact.*

In Co–Ni, cobalt layers were found to promote cobalt sintering and inhibit nickel sintering: this was an indication of higher atom mobility in the nickel-rich solid solution and was in agreement with diffusion measurements.[295,296] A much higher contact frequency was also found in the nickel-bar–cobalt-wire model than with the cobalt-bar–nickel-wire arrangement. Because the decrease in radius of small particles is more marked in material exchange than the growth in radius of large particles, this result also indicates that nickel is the more mobile component (cf. Fig. 28*b* and Ref. [292], and [293]. It is also recognised how sensitively sinter contacts respond, both in the model and in the finest powders, to small deviations from ideal solution characteristics, where results are visible which are not obtained in a normal diffusion arrangement with a flat contact. Superimposition of the neck-governed and diffusion-



[*Courtesy 'Acta Metallurgica'*.

25b Relation between change in length in copper/nickel powder mixtures and the degree of homogenisation. (*Fisher and Rudman.*[284])

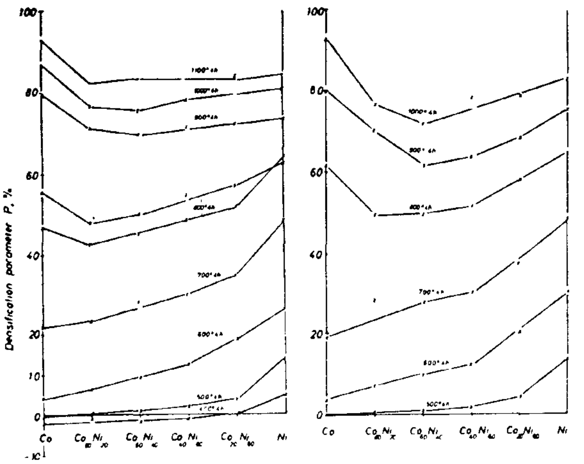


[*Courtesy Consultants Bureau.*

26 Shrinkage of cobalt/nickel powder mixtures during slow heating-up:
600–700° C: indifferent behaviour (no marked homogenisation)
700–900°C: sintering promoted (commencement of homogenisation).
900–1200° C: sintering inhibited (progressive homogenisation). (*Thümmler and Thomma.*[163])

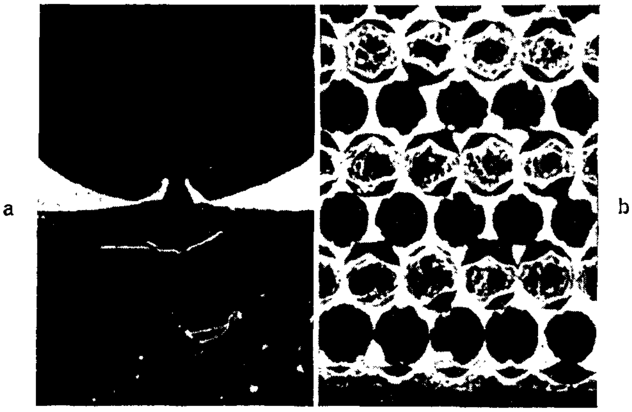
---

* In powder compacts Kirkendall pores can hardly be distinguished from 'normal' pores, because pores can act both as sources and sinks for vacancies. Only in diffusion experiments where porous bodies of different compositions are brought into contact can conclusions be drawn, from the different levels of porosity on the two sides of the contact area, regarding the type and magnitude of the Kirkendall effect.[294]



[*Courtesy Consultants Bureau.*

27 Inhibition of sintering of cobalt–nickel powder mixtures compared with the pure metals; concave concentration-dependence curves. (*Thümmler and Thomma.*[163])



[*Courtesy Elsevier.*

28 a Single asymmetrical model contact (Ni bar/Au wire) with higher diffusion of gold. × 320.
b Section through a wire–wire model (Au–Ni) after necking-down of most of the Au/Ni contacts and mechanical separation of the Au/Au contacts. × 240. (*Kuczynski and Stablein.*[292, 293])

governed excess vacancies occurs at the sintering contact.[163]

Other systems investigated in which similar effects of hetero-diffusion are visible are nickel–ferrochrome[297] and Fe–Ge.[298]

The marked promotion of tungsten sintering by small additions of metals of the iron group, especially nickel, must be considered as a special case, in which the temperature of extensive densification can be decreased by ~ 1000 degC, e.g. to 1100° C. The nickel is best introduced by means of salt solutions, since a surface coating of each tungsten particle is the most effective. The best possible result is achieved only by this geometry.

Vacek[282,299] obtained nearly theoretical density with additions of 0·25% nickel. Brophy *et al.*[300] illustrated the 'sinter-promoting' effect obtained with porous tungsten sprayed in the plasma arc, by infiltrating with nickel–zinc alloys, vaporising the zinc, and 'sintering' the tungsten/nickel mixture. Prill *et al.*[301] have discussed in a review the phase relationship between tungsten and the added metals. According to them, metal additions should be effective only up to the point where a continuous surface layer is formed on the tungsten particles; a further addition appears to have no effect. Tungsten diffusion in these layers should be rate-determining, because tungsten is soluble in the added metals but these metals do not dissolve in the tungsten. Larger additions have a very minor effect, or may even prove inhibiting if intermetallic phases, with a high bonding energy are formed. This last viewpoint is new and has not so far been considered by any other author.

Only one paper[304] exists on the influence of the decomposition of solid solutions; this refers to amalgamated copper surfaces. A sinter-promoting effect was observed at 750–900° C due to the decomposing copper amalgam. The effect is reminiscent of the influence of reducible oxide layers. Owing to the low solubility of mercury in copper the amalgam consists partly of intermetallic phases.

4. With the formation of new phases (reaction sintering)

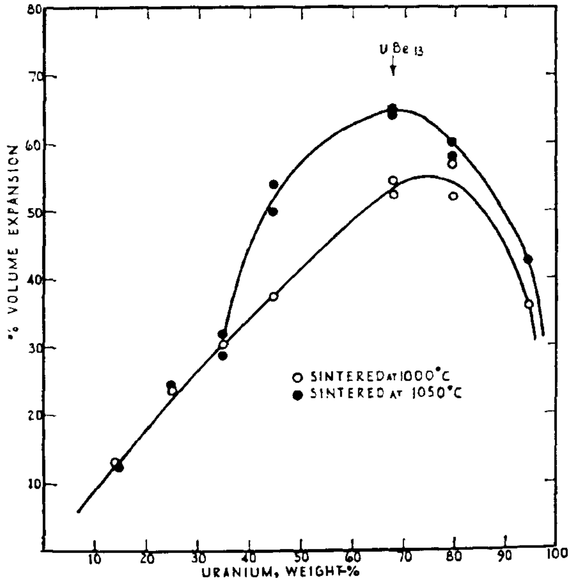
The formation of new phases during sintering is associated in many cases with particularly marked expansion phenomena, as established by Raub and Plate[305] and Duwez.[306] The compacts disintegrate completely in some cases; the manufacture of sound shapes from the phases is successful only when the reaction and sintering are carried out in separate stages or when sintering under pressure. Williams and Jones[273] sintered various uranium- and beryllium-containing mixtures and found the greatest expansion with compositions corresponding to the phases (Fig. 29). Volumetric expansion is greatest in the direction of pressing, as the number of points of contact is greater than in the perpendicular direction. Since the mobility of the different kinds of atoms varies considerably in many phases, the large diffusion porosity is understandable. With a high degree of brittleness the internal stresses always associated with the Kirkendall effect are not plastically eliminated and the product disintegrates. Kriek *et al.*[307] and Goodison and White[268] reported a similar behaviour for mixtures of MgO with Al_2O_3, TiO_2, and SiO_2.

By using specific pressure-sintering conditions, sound and fairly pure phases can be manufactured by such 'reaction sintering', for example, UC from uranium and carbon mixtures.[308,309] Sintering is carried out at ~~the internal stresses always associated with the Kirken-~~ ~ 1000° C at 1·5–3 metric tons/cm². In certain cases a permanent external pressure is not necessary, for instance, with mixtures of oxides and metals, which react by a thermit process with a considerable evolution of heat to form a cermet.[301,311] However, the occurrence of a liquid metal phase is probably a decisive contributory factor in this case. By adding the oxides produced the process can be so controlled that the reaction temperature is adjusted to a suitable level without fusing the metal. These special cases have received less attention as far as the sintering process is concerned.

5. Oxide mixtures

A separate discussion of oxide mixtures appears to be justified by the fact that a great deal of work has been published, e.g. with the aim of obtaining better densification of oxides that are difficult to sinter by making suitable additions. Furthermore, the phenomena observed cannot be related directly to the metals. Older work has been covered by a number of authors.[151,250,252,307,313-320] These papers relate to the sintering and grain growth of MgO, Al_2O_3, BeO, ZnO, and UO_2, with many additions. It is still not possible to derive from them any generally valid indications regarding the sintering of mixtures. Blackman[194] surveyed the various factors of influence and emphasised the importance of having a knowledge of all possible parameters, such as impurities, crystallite size and distribution, deviations from stoichiometry and homogeneity and their relationship to the existence of excess vacancies. It is to be expected from the diffusion theory of sintering that *insoluble* additions made in the early stages of densification will hardly promote sintering on geometrical grounds (constriction of the diffusion cross-section, 'passivity' of A–B contacts), while they can have a marked sinter-promoting effect in the later stages owing to the inhibition of grain growth. This is very often observed; for example in the case of Al_2O_3,[155,212,321] BeO[282] and $BaTiO_3$,[323] with small additions of a second oxide in each case. MgO additions to Al_2O_3, which resulted in almost theoretical densification and to the development of the well-known 'Lucalox', were considered to be insoluble and therefore grain-growth-inhibiting.[159] Westbrook *et al.*[321,322] found, on the other hand, that a process of dissolution and reprecipitation must take place. It was established by hardness measurements in the vicinity of grain boundaries that the initially disperse oxide addition is enriched uniformly at the grain boundaries, and that its concentration falls off rapidly towards the interior of the grains. This observation throws a completely new light on all the work that deals with grain-growth inhibition and hence the promotion of sintering by second phases.

With *soluble* additions attention must be given to the problem of how the solid solution forming *in situ* alters its diffusion characteristics. According to older concepts the change in defect concentration due to foreign ions with different valencies should play the most important part, as in the oxidation theory of Wagner, Hauffe, and others. However, this model is inadequate for many reasons, one being that equivalent additions often exert a considerable influence. Probably considerations of the bonding character, the lattice parameters, and the solubility limits play a complex part. Thus sinter inhibition due to the addition of TiO_2 to Al_2O_3 is attributed to lattice contraction, and sinter promotion achieved with additions of Cr_2O_3 to lattice expansion.[212] However, this basis alone cannot be considered adequate. Bron[183] summarised crystal-chemical relationships (valency, ion radii, lattice energy, temperature at the commencement of sintering) and also came to the conclusion that additions with a larger cation radius accelerate the sintering process owing to expansion of the lattice and the development of excess vacancies. In the case of a single-phase CaO–SrO solid solution, on the other hand, Brown[17] found a sinter-inhibiting effect associated with the lattice expansion due to decreased atom mobility. He was unable to reach a similar conclusion[170] with MgO + V_2O_5, but he observed strong grain growth from 1250° C upwards, which may be related to the occurrence of a liquid phase. Small amounts of liquid phases are probably often present, but remain unnoticed in most cases in investigations of the type under consideration because of their low concentrations.



29 Maximum expansion of uranium–beryllium powder mixtures with the phase composition UBe_{13}. (*Williams and Jones.*[273])

Felten[324] investigated the influence of a large number of oxides on the sintering of BeO. Titanium and alkaline-earth oxides formed liquid phases with BeO and promoted densification and grain growth; oxides of different valences—except B_2O_3—only promoted densification without affecting grain growth. Additions of MgO and ZrO_2, enhance[173] the sintering of BeO by inhibiting grain growth. Nicholson[325] observed in the investigation of grain growth in MgO + V_2O_5 that the same grain-growth law ($d^3 = kt$) applied with additions of 1 and 2 at.-% vanadium with occurrence of a liquid phase and with 0·1% vanadium without a recognisable liquid phase; he believed that even in the case of 'pure' oxides amounts of as little as 200 ppm of foreign constituents could possibly influence the sintering process by the formation of small quantities of liquid phases. Also working with MgO, but using nickel additions, Oel[326] established that grain growth was inhibited by nickel in the liquid phase. On the other hand, Sjodahl and Westbrook[322] hold the view, as do Jorgensen and Westbrook[321] that although dissolution and precipitation processes promote sintering in the boundary layers, no fundamental difference (with small additions) can exist between sintering with and without the presence of a liquid phase.

It is recognised that neither the general occurrence of small amounts of liquid phases nor their effect are clearly established by these investigations.

Ruh *et al.*[327] reported that sintering can be shown to be promoted *only* above the solubility limit *and* above the solidus curve of ZrO_2, with titanium, chromium, and zirconium. In all other cases, where according to the phase diagram no liquid phase can occur, *no* promotion of sintering is found.

Additions to UO_2 that facilitate sintering are 0·1 wt.-% platinum[328] with two-stage sintering as in Ref. [222], and V_2O_5, Nb_2O_5, CaO, and especially TiO_2.[329] A new phase is formed with TiO_2 that is liquid at sintering temperatures, so that this oxide should be particularly effective. Below 1400° C, on the other hand, no marked solid-solution formation takes place in the solid state. Fluorine impurities, which can originate from the UF_6 'route' necessary for enriched uranium, have a strongly inhibiting effect on sintering. Inhibition is found to be less frequent in oxide mixtures than in metals; this is probably due mainly to the slower rate of diffusion in the oxides. The condition of electron neutrality certainly prevents substantial excesses of anion or cation vacancies, which are essential for the occurrence of a marked Kirkendall effect with the formation of pores. Thus, it is understandable that inhibition of sintering is found mostly in insoluble systems in the early and middle stages, while sintering is often promoted in soluble systems.

6. Sintering processes in the presence of a liquid phase

This field occupies a special position compared with sintering without the formation of a liquid phase. This is attributable to the ease of diffusion in melts, and to the possibilities of re-ordering of the phase remaining solid in the melt and of rapid dissolution and re-precipitation. The marked promotion of densification in metals and oxides, which are otherwise difficult to sinter, by small additions of liquid phases is connected with these processes, and is therefore not surprising. While the facts often indicate the predominance of diffusion in the solid state, the above-mentioned mechanisms play the main part in liquid-phase sintering, at least for a large portion of the densification process. Based on phenomenological observations, which go back to earlier work by Lenel *et al.*[330,331] and Gurland and Norton,[332] it is considered by Kingery[333–335] that three stages can appropriately be distinguished:

(1) *Rearrangement* of the particles of the residual solid phase by viscous flow in the liquid phase. The random, and thus in no sense the most beneficial, arrangement of the grains after mixing and pressing is improved, to the accompaniment of rapid shrinkage. A growing amount of liquid phase increases the densification, as 'friction' is diminished. Geometrical considerations, assuming spherical particles, offer the possibility of complete densification by this process alone if >35 vol.-% of liquid phase is present. Wetting of the grains by the melt is the most important assumption in this connection, while solubility still plays no part. Naidich *et al.*[336,337] point out that, because of the shape of the meniscus, densification takes place more rapidly with improved wetting. The forces of attraction between two spherical particles, between which a concave lenticular liquid phase is situated, depends on their respective amounts. Coarse powder particles and small quantities of liquid should lead to greater forces of attraction.

(2) *Dissolution and reprecipitation processes.* For these to take place, at least a limited solubility of the solid in the liquid phase is necessary, otherwise this stage of densification is completely absent. Densification occurs more slowly than in the rearrangement stage, because the transport of material must proceed by means of dissolution and diffusion in the melt. Small grains with strongly convex curvatures then disappear, while the larger ones assume a more regular shape. The driving force for material transport results from the increased compressive stresses and hence from the enhanced chemical potential and higher solubility in the contact zones. The solid substance is then carried away and precipitated again at locations of lower stress. This results in an approach of the mid-points of the particles, and therefore in shrinkage. The grain shape so formed, which is illustrated in Fig. 30, suggests a higher packing density than with the spherical grain.

In cases of complete wetting (angle of contact $\simeq 0$) the grains remain separated by films of liquid.

30 Grain shape of sintered heavy metal (93% W, 5% Ni, 2% Cu) after (a) 1 or (b) 6 h at 1400° C. (*After Price, Smithells, and Williams.*[384])

(3) *Coalescence.* In the case of incomplete wetting (angle of contact $< 90°$) the solid grains are partly in contact without the interposition of the melt. After the conclusion of Stage 1, processes such as those found when sintering without a liquid phase take place; these later become rate-determining and lead to slow further densification with a simultaneous decrease in driving force.

A non-wetting liquid phase (contact angle $> 90°$) is ineffective or inhibiting and usually exudes partially from the sintered compact in the form of droplets.

The quantitative treatment of these processes is due to Kingery.[333,334] Since then many experimental results have been obtained which bear out his findings, although quantitative agreement was not obtained in all cases. in particular, the relationship:

$$\frac{\Delta l}{l_0} = k\, r^{-1}\, t^{1+x} \qquad \ldots[40]$$

applies for the stage of rearrangement with $1 + x \simeq 1$. The corresponding relationship for the stage of dissolution and reprecipitation is:

$$\frac{\Delta l}{l_0} = k'\, r^{-4/3}\, t^{1/3} \qquad \ldots[41]$$

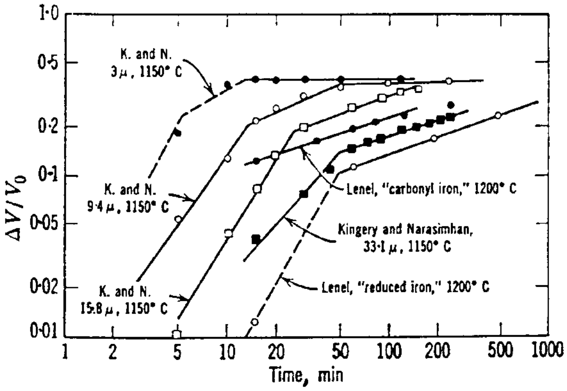
where r = initial particle size, provided that diffusion in the liquid film is rate-determining and a spherical grain is present. Figure 31 shows shrinkage curves for iron–copper compacts, in which the straight-line sections correspond to the slopes 1 and 1/3 of equations [40] and [41]. Figure 32 shows the agreement of the grain-size-dependence with theory. According to Fischmeister and Exner,[48] the exponent with a prismatic grain geometry should be $n = 1/5$, compared with $n = 1/2$ according to Eremenko *et al.*[338] Such a $\sqrt{t}$ law, on the other hand, would never be clearly established; but it is certainly very difficult to identify exponents between 0·2 and 0·5 accurately enough to enable conclusions to be drawn regarding the predominant mechanism, expecially as the transition from the t^{1+x} law takes place continuously and the subsequent densification in the third stage shows no abrupt transition. For example, exponents up to $1 + x = 5$ were also found in the rearrangement state.[338] Furthermore, Fischmeister and Exner,[48] using different methods of evaluation, reported that an exponent $n = 1$ instead of $n = 1/3$ can also exist. Hence equation [41] is not adequately confirmed by Kingery's experiments.

Cech[339] described the rearrangement stage as a viscous-flow process, and distinguished between open and closed pores, which should behave differently according to $\Delta l/l_0 \sim \log t$ or $\Delta l/l_0 \sim t^4$. Further shrinkage of the closed pores in the final stage should take place by outward diffusion of the enclosed gases and should be characterised by the equation $\Delta l/l_0 \sim t^{1/3}$. Cech confirmed these equations for several systems.

No equations were formulated by Kingery for Stage 3; but it is presumed that the conditions are the same as when sintering without a liquid phase. The decreasing rate of densification with time could again be attributed entirely to grain growth and would consist of volume diffusion.

All the relationships derived apply only in the absence of closed pores, filled with gas which cannot easily diffuse. A final density of $< 100\%$ is to be expected in this case, according to the equation:

$$P_R = \left(\frac{p_0 r_0}{2\gamma_L}\right)^{3/2} P_0 \qquad \ldots[42]$$



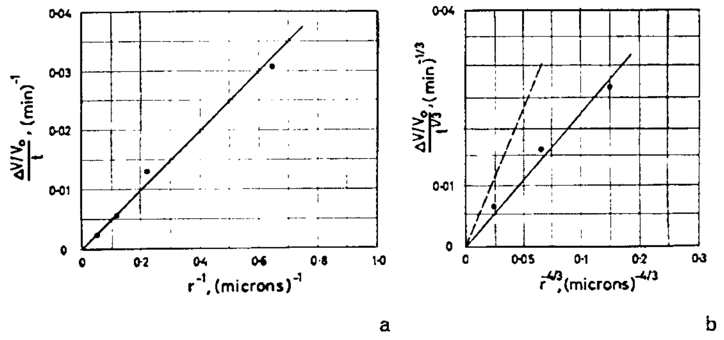
[*Courtesy 'J. Applied Physics.'*

31 Densification during sintering of iron–copper powder compacts with a liquid phase present. Slopes of straight-line portion $\simeq 1$ and $\simeq 1/3$ according to equations (40) and (41). (*After Kingery.*[334])

where P_R = residual porosity, P_0 = initial porosity, p_0 = initial gas pressure, r_0 = initial pore radius, and γ_L = surface tension of the melt. Similar relationships exist for hot pressing. Pines *et al.*[260] found a deterioration in the sintering behaviour of copper containing 3–5% Pb, Sn, Cd, or Bi with rise in compacting pressure (up to 4·2 metric tons/cm^2), as this favoured the formation of enclosed pore spaces in the presence of a liquid phase (see also Cech[339]). With regard to the grain growth of the solid phase, it was established by Parikh and Humenik[340] that the original grain size remained essentially unaltered with complete wetting (WC–Co),* while growth took place with partial wetting. It follows that the grain growth proceeds largely without the influence of the liquid phase.

The view has been held for some time that the phase remaining in the solid state forms a coherent frame or skeleton. This has been detected, for example, in the system WC–Co by dissolving-out the cobalt from finished sintered compacts. The residual WC has considerable shape stability and strength. However, this cannot be directly explained when complete wetting takes place during sintering, and it must be considered questionable whether a WC framework is already present *during* sintering. For the cooled product, Dawihl[342,343] postulates the existence of a 'composite framework', in which the thin layers of the binder, bonded by capillary action, are present and can be dissolved out only with difficulty by acids.

Essentially different conditions are present when the liquid phase disappears during sintering by dissolving in the component that remains solid. This is the case in the systems Fe–Cu and Cu–Sn. Here, a growth component is found in addition to the contraction; this has the technological advantage of enabling closer dimensional tolerances to be maintained in the manufacture of copper-alloyed sintered iron, and is also of great importance with sintered bronze. The diffusion of the (iron-saturated) copper into the iron skeleton causes expansion of the skeleton, while pores remain at the sites of the copper particles (Fig. 33). The increase



a

b

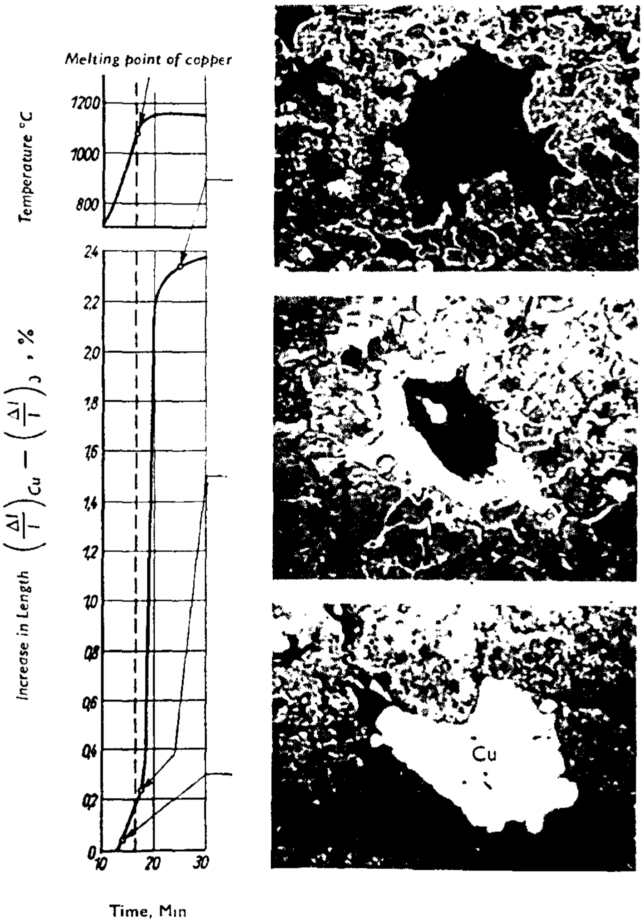
[*Courtesy 'J. Applied Physics'.*

32 Dependence of contraction in liquid-phase sintering on the particle size. a $\Delta V/V_0 \sim r^{-1}$; b $\Delta V/V_0 \sim r^{-4/3}$. Broken line calculated from equation [41]. (*Kingery and Narasimhan.*[334])

---

* According to Gurland and Norton,[332,341] growth of the WC particles is still observed under certain conditions, at least with low cobalt contents.

in volume reaches its maximum with copper contents corresponding to saturation of the γ-iron with copper at the temperature in question (e.g. ~ 8% at 1150° C). In both the systems mentioned expansion or shrinkage can be controlled by the addition of, e.g., 1% graphite. In the case of Fe–Cu the proportion of liquid phase is increased in this way by the formation of a ternary eutectic (less expansion); with Cu–Sn the solid–solid sintering is inhibited by mechanical separation of the components (increased expansion). A number of investigations on this subject have been conducted.[344–349] Nishijima[349] confirms that complete densification can be readily attained only when the liquid phase remains in existence throughout the sintering process. On the other hand, when completely solid solutions are formed during sintering, pores remain behind, because a type of Kirkendall effect (preferential penetration of one phase into the other) always takes place in such a case.



a

b

[*Courtesy 'Stahl und Eisen'*.

33 Behaviour of Fe + 7·5% Cu compacts:
a Increase in temperature and length with time.
b (bottom): Initial state: Cu particle in Fe matrix.
(middle): Diffusion of Cu in Fe matrix with formation of pores.
(top): Pore in place of the original Cu particle and marked increase in length.
(*Bockstiegel.*[347]) × 105.

V. Hot pressing

Pressure and heat are applied simultaneously for the manufacture by powder metallurgy of particularly large, heavy parts, as well as in cases where satisfactory results are unobtainable by the usual method of cold pressing followed by sintering. The boundary between sintering and hot pressing, from a scientific point of view, must be drawn at effective stresses of ~ 1 kp/cm^2, according to the results reported by Lenel and his co-workers,[120,122,123] where small external loads (in the early stages of neck growth) alter the sintering mechanism. Flow processes undoubtedly predominate over wide ranges of densification in hot pressing. Under the temperatures and at the pressures of a few hundred kilogrammes per square centimetre that are employed in practice, and when the 'supporting cross-section' in the porous compact, i.e. the existing contact area, is considered, the yield point is exceeded in most materials and plastic deformation takes place.

The theoretical treatment of this field is still relatively new and the older work was aimed mainly at the attainment of high-density products. For this reason reviews[350–352] dealing with this subject have appeared only recently. The expressions derived by Mackenzie and Shuttleworth,[116] which were originally developed for normal sintering, have proved to be a suitable starting point in many cases for a theory of hot pressing.

Accordingly, spherical, isotropically distributed pores are considered as if they are under a hydrostatic pressure that decays with increasing distance from the pore. This leads to viscous or plastic flow, corresponding to the equations:

$$\gamma = \frac{\tau}{\eta} \qquad \ldots[43]$$

or for $\tau > \tau_c$

$$\gamma = \frac{\tau - \tau_c}{\eta} \qquad \ldots[44]$$

where γ is the shear rate, τ the effective shear stress, η the viscosity, τ_c the critical shear stress.

If the distance between the pores becomes so great in the later stages of densification that no zones intersect in which $\tau > \tau_c$, densification will cease and the residual porosity is permanent. The original densification equation according to Mackenzie and Shuttleworth is as follows:

$$\frac{dP}{dt} = -\frac{3\gamma}{2\eta r_p} P\left(1 + \frac{\sqrt{2}\,\tau_c r_p}{2\gamma} \ln P\right) \ldots[45]$$

where P is the porosity and r_p the pore radius.

Murray, Rodgers, and Williams[353] supplemented equation [45] by a term corresponding to the external pressure, and obtained:

$$\frac{dP}{dt} = -\frac{3}{4\eta}\left(\frac{2\gamma}{r_p} + \sigma\right) P \left(1 + \frac{\sqrt{2}\,\tau_c}{\frac{2\gamma}{r_p} + \sigma} \ln P\right) \qquad \ldots[46]$$

For the case where the external pressure σ outweighs the surface-tension term $2\gamma/r_p$, equation [46] is simplified to:

$$\frac{dP}{dt} = -\frac{3\sigma}{4\eta} P \left(1 - \frac{\ln P}{\ln P_R} \right) \qquad \ldots [47]$$

where P_R is the above-mentioned residual porosity at a sufficiently large distance between the pores.

According to McClelland,[354] complete integration of equation [47] is possible. If in addition $\sigma \gg \tau_c$, the residual porosity P_R is eliminated and a simple logarithmic densification law is obtained in integrated form:

$$\ln P/P_0 = -\frac{3\sigma}{4\eta} t \qquad \ldots [48]$$

where P_0 is the initial porosity.

Kovalchenko and Samsonov[355] found a similar pressure-sintering equation by the rheological method, according to the continuum theory of the elastic, plastic, and viscous behaviour of the solid bodies and their dispersions in each other:

$$\frac{dP}{dt} = -\frac{3\sigma}{4\eta} \frac{P(1-P)}{1-aP} \qquad \ldots [49]$$

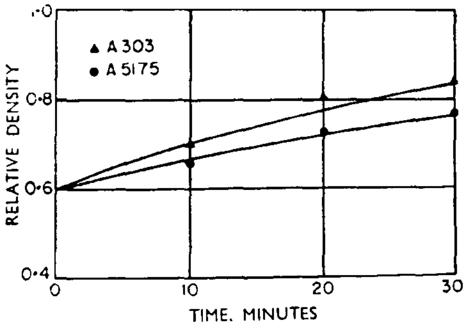
which also leads to equation [48] for $a = 1$.

Equation [48] has been confirmed satisfactorily by Mangsen, Lambertson, and Best[356] (Fig. 34), Vasilos,[357] and Jaeger and Egerton.[358]

In other cases agreement is not so good, especially with regard to the question of final density and the extent to which τ_c can be disregarded.[354,359] Experimental difficulties, such as determination of the effective pressing period and the problem of temperature equalisation in rapid heating, also play a part. McClelland[354,359] therefore modified equation [47] by introducing an effective pressure:

$$\sigma_{\text{eff}} = \frac{\sigma}{1 - P^{2/3}} \qquad \ldots [50]$$

which, because of the porosity, is higher than the pressure applied externally, referred to the specimen diameter. This correction is in contradiction to the model of the Mackenzie–Shuttleworth theory of the hydrostatic pressure on spherical pores; but since it can apply only in the later stages, correction [50] can also be viewed as a phenomenological adjustment.



[*Courtesy Amer. Ceram. Soc.*

34 Testing equation [48] in the hot pressing of Al_2O_3 at 1450° C. Measured values and calculated curves are in agreement (*Mangsen, Lambertson, and Best.*[356])

The asymptotic residual porosity accordingly becomes

$$(1 - P_R)^{2/3} \ln P_R = -\frac{\sigma}{\sqrt{2}\tau_c} \qquad \ldots [51]$$

A second correction to equation [48] was also given by Kovalchenko and Samsonov.[355] This correction—in a similar way to that applied by Coble in normal sintering—took into account for the first time the significance of grain growth. The Nabarro–Herring mechanism was used, which connects the viscosity coefficient η (in viscous flow), obtained formally from creep tests, with the diffusion coefficient D_v and the grain size d.

With:

$$\eta = \frac{RTd^2}{10 D_v V_0} \; (V_0 = \text{molar volume}) \qquad \ldots [52]$$

and $a = 1$ in equation [49], it follows from:

$$\frac{1}{P}\frac{dP}{dt} = -\frac{3\sigma}{4\eta} \qquad \ldots [49a]$$

that:

$$\frac{1}{P}\frac{dP}{dt} = -\frac{15}{2} \frac{\sigma D_v V_0}{RT} \frac{1}{d^2} \qquad \ldots [53]$$

in which the grain size d increases with time according to:

$$d^2 = d_0^2 (1 + bt) \qquad \ldots [54]$$

Equation [54] is in agreement with the grain-growth law for massive metals and has been confirmed by Lersmacher, Roeder, and Scholz[360] in the hot pressing of carbides. Grain-growth inhibition by pores, which furnishes (perhaps accidentally) a $t^{1/3}$ law in sintering, has not so far been observed.

The following relationship is obtained from equations [53] and [54]:

$$P = P_0 (1 + bt)^{-k\sigma} \qquad \ldots [55]$$

with:

$$k = \frac{15}{2} \frac{D_v V_0}{a_0^2 RTb} \qquad \ldots [55a]$$

In addition to equation [55] various empirical hot-pressing equations exist, also with a hyperbolic time-dependence. Westermann and Carlson[361,362] found for Pb–Sn alloys at 150–200° C:

$$P \sim t^{-n} \qquad \ldots [56]$$

By converting the results obtained by McClelland and Whitney[363] (on tin at room temperature), Scholz and Lersmacher[350] were able to establish the same simple hyperbolic equation [56]. The exponents and constants are not capable of interpretation, however.

A modified empirical densification equation was used by Scholz and Lersmacher[350] based on their own work[364–366]

$$P = P_0 (1 + \beta t)^{-n} \qquad \ldots[57]$$

with two empirical constants β and n (Fig. 35). This agrees formally with equation [55]. Thümmler, Ondracek, and Dalal[385] confirmed equation [57] in certain ranges of time, temperature, and pressure during hot pressing of uranium nitride.

Only in the first-mentioned, theoretically derived equations was the hot-pressing mechanism, i.e. flow processes, taken into consideration. The other relationships do not enable any direct conclusions to be drawn regarding the mechanism of material transport. Certainly, the existence of a temperature-dependent limiting density is an indication of flow processes with a temperature-dependent yield point; nevertheless results exist according to which the residual porosity is independent of the hot-pressing temperature.[367]

This behaviour is interpreted on the basis of the predominance of slip, fracture, and reordering processes over plastic deformation. Felten[368] and Hashimoto[369] also consider that such processes predominate, especially in the early stages of hot pressing. Possibly this behaviour is also connected with the fact that the start of rapid grain growth inhibits further diffusion-controlled densification in the late stages, as observed by Lersmacher and Scholz, and by Thümmler, Ondracek, and Dalal. The two opposing effects, namely, decreasing residual porosity with rising temperature owing to a fall in the critical shear stress, and higher porosity at elevated temperatures after marked grain growth, could explain by their combined action the behaviour observed by Chang and Rhodes.[367] As in the case of normal sintering, it must now be regretted that the study of isothermal densification techniques undertaken in earlier work was not accompanied by the investigation of the grain growth that took place simultaneously.

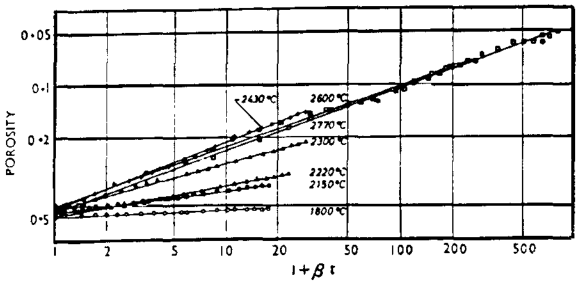
Deviations from the equations formulated above were attributed by McClelland[354,359] to the existence of three stages, similar to those found during sintering in the presence of a liquid phase, and to which no common law can apply:

(1) Stage of rapid densification ('micro-flow', presumably by re-ordering of the powder particles at the first application of pressure under the high pressures at the first small-area contacts.)

(2) Stage of retarded densification (predominance of plastic flow according to equation [48] or [51]).

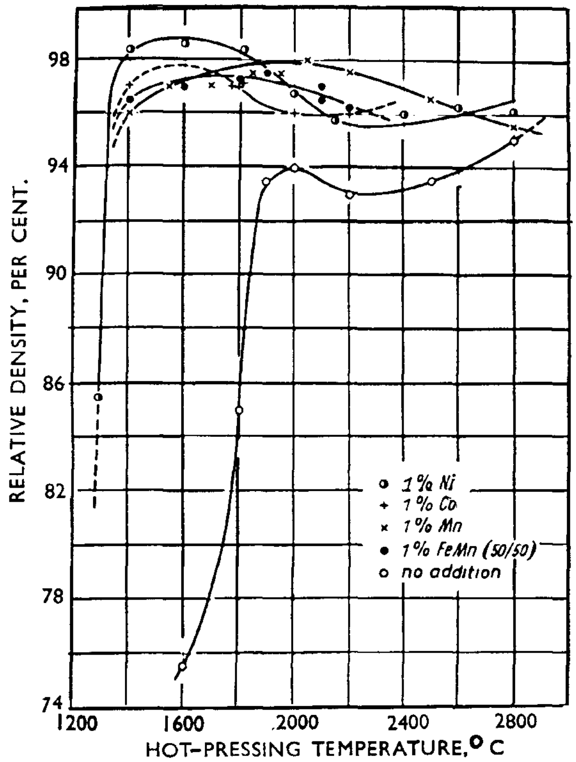
(3) Diffusion-controlled gradual approach to the limiting density, probably according to the Nabarro–Herring mechanism, together with a grain-size influence.

Vasilos and Spriggs[370] obtained complete densification when hot pressing Al_2O_3 and MgO between 1100 and 1700° C at 300–700 kp/cm², and derived a densification law $\rho \sim \log t$ valid up to 95% of theoretical density. In evaluating the densification curves according to the Nabarro–Herring equation the calculated diffusion coefficients are in good agreement with the directly measured values. In every case it is concluded that diffusion processes play a part in the late stages. Rossi and Fulrath[351] also reported a Nabarro–Herring mechanism with Al_2O_3 at temperatures between 1150 and 1350° C and pressures between 150 and 450 kp/cm² in the final stage, and activation energies corresponding to self-diffusion of Al^{3+}. Enclosed gases, especially water vapour, should govern the residual porosity, which could be eliminated by a suitable pretreatment of the powder.



[*Courtesy Academic Press.*

35 Testing equation [57] in the hot pressing of TaC. (*Scholz.*[366])



[*Courtesy 'Arch. Eisenhüttenwesen'.*

36 Effect of small additions of foreign metals on the hot pressing of TaC; 300 kp/cm², 1 h. (*Lersmacher and Scholz.*[364])

Under similar conditions, on the other hand (Al_2O_3, 1100–1500° C, 70–450 kp/cm²) McClelland and Zehms[359] found final densities that were related to the temperature-dependent critical shear stress in accordance with equation [51], and in which an Arrhenius relationship was established for τ_c with Al_2O_3 and BeO. Coble and Ellis[371] followed up the problem of the mechanism (diffusion or plastic flow) by investigations on Al_2O_3 single-crystal spheres of 0·7–1-mm dia. at 1530° C and with loads of 76–952 g. Neck growth rapidly came to an end, and equilibrium was established by a strengthening mechanism.

Salkind, Lenel, and Ansell[372] followed the neck growth of loose silver powders at 300° C under different loads, and found, by means of conductivity measurements, stress-dependent activation energies from which the occurrence of plastic flow by the movement of dislocations, especially cross-slip, was inferred.

Smith and Vasilos[373] concluded for the pressure-sintering of copper at 300–600° C, from a $\rho \sim \log t$ law, that plastic flow by itself cannot be effective below 400° C, because higher densities were attained than those corresponding to the flow theory of McClelland. At temperatures greater than 400° C, however, flow processes should be dominant.

When pressure-sintering USi_2 at 1300–1450° C Accary and Caillat[374] established three different stages, which were described by:

$$\Delta l/l_0 = a_0 t^{2/5} + b_0 \qquad \ldots[57a]$$

$$\Delta l/l_0 = a_1 \log t + b_1 \qquad \ldots[57b]$$

$$\Delta l/l_0 = a_2/\sqrt{t} + b_2 \qquad \ldots[57c]$$

The first term is absent in the reactive sintering of $(U + Si)$ because the reaction takes place with expansion before densification. The equations were not interpreted, but the log t law is again found in the second stage of densification.

Kingery, Woulbronn, and Charvat[375] showed in the investigation of liquid-phase sintering with the use of additional pressure, that the $\Delta l/l_0 \sim t^{1/3}$ law (equation [41]) ceases to be applicable for the stage of dissolution and reprecipitation, since these processes no longer play a part under external loading in comparison with the densification-controlling flow processes. In the rearrangement stage a law $\Delta l/l_0 \sim t^n$ is applicable, with $n = 0{\cdot}17 - 0{\cdot}58$, after which equation [48] applies irrespective of the proportion of liquid phase.

Interesting 'model hot-pressing' experiments have been reported by Garber and Polyakov.[376] In these, the resistance to tearing of contacts between massive aluminium blocks pressed together at 300–600° C was determined. The increase in strength with time is also accomplished in two stages, the first and more rapid stage being controlled by plastic-deformation mechanisms and the second, slower one by diffusion processes.

There is no doubt from all the experimental work that flow processes predominate, especially in the intermediate stages of densification. But, the more recent work indicates clearly the simultaneous action of diffusion processes, especially in accordance with the Nabarro–Herring mechanism, in the later stages of the process.

Naturally, the results on one material cannot be transposed to another. It has also been stated from time to time[377] that the effect of certain factors, such as powder activity, small proportions of foreign substances, &c., is not as strongly marked as when sintering without external pressure. On the other hand, results have been reported[366,378,379,380] which show a very strong influence of foreign atoms on carbides of various degrees of purity with metal additions of up to 1%. However, these influences may well be attributable to the presence of a liquid phase (Fig. 36).

References

1. F. Sauerwald, *Kolloid Z.*, 1943, **104**, 144.
2. G. F. Hüttig, *ibid.*, 1941, **97**, 281; 1942, **98**, 6, 263.
3. G. F. Hüttig, *Arch. Metallkunde*, 1948, **2**, 93.
4. G. F. Hüttig and R. Kieffer, *Angew. Chem.*, 1952, **64**, 41.
5. M. Yu. Balchin, *Vestnik Metalloprom.*, 1936, **16**, (17), 87.
6. W. Dawihl, *Stahl u. Eisen*, 1941, **61**, 909.
7. J. A. Hedvall, *Arch. Metallkunde*, 1947, **1**, 296.
8. W. D. Jones, 'Principles of Powder Metallurgy'. **1937:** London (Edward Arnold).
9. P. Schwarzkopf *et al.*, 'Powder Metallurgy'. **1947:** New York and London (Macmillan); *Powder Met. Bull.*, 1949, **4**, 28, 64; 1950, **5**, 4.
10. R. Kieffer and W. Hotop, 'Pulvermetallurgie und Sinterwerkstoffe' 2nd edn. **1948:** Berlin (Springer-Verlag).
11. F. Skaupy, 'Metallkeramik' 4th edn. **1950:** Weinheim/Bergstrasse (Verlag Chemie).
12. M. Yu. Balchin, 'Poroshkovaya Metallurgiya'. **1948:** Moscow: (Machgiz); 'Pulvermetallurgie'. **1954:** Halle (Saale) (Wilhelm Knapp).

13. C. G. Goetzel, 'Treatise on Powder Metallurgy', Vols. I–III. **1949–1952:** New York and London (Interscience Publishers).

14. Ref. [17], Vol. II, p. 916.

15. J. Frenkel, *J. Physics* (*U.S.S.R.*), 1945, **9,** 385.

15*a*. J. A. Hedvall 'Einführung in die Festkörperchemie,' p. 241. **1952:** Braunschweig (Vieweg).

16. G. C. Kuczynski, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **185,** 169; *J. Appl. Physics*, 1950, **21,** 632.

17. F. Thümmler, 'Fortschritte der Pulvermetallurgie' (edited by F. Eisenkolb), Vol. I, p. 329. **1963:** Berlin (Akademie Verlag).

18. A. J. Shaler, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **185,** 796.

19. H. G. Crone and J. H. McKee, *Brit. Coal Utilisation Research Assoc. Monthly Bull.*, 1950, **14,** 329.

20. J. P. Roberts, *Metallurgia*, 1950, **42,** 123.

21. F. Sauerwald, cited by E. Thilo, 'Aktuelle Probleme der physikalischen Chemie'. **1953:** Berlin (Akademie Verlag).

22. G. A. Geach, *Progress Metal Physics*, 1953, **4,** 174.

23. M. Eudier, *Bull. Soc. Franç. Minéral Crist.*, 1954, **77,** 1126.

24. B. Ya. Pines, *Uspekhi Fiz. Nauk*, 1954, **52,** 501; (translation, **AEC–TR 5563, 2/15,** 1963).

25. R. F. Walker, *J. Amer. Ceram. Soc.*, 1955, **38,** 187.

26. J. A. Hedvall, *Ceramic Age*, 1955, **65,** 13.

27. F. Thümmler, 'Die neuere Entwicklung der Pulvermetallurgie' (edited by F. Eisenkolb), p. 108. **1955:** Berlin (VEB Verlag Technik).

28. D. R. Wilder, 'High-Temperature Technology' (edited by J. E. Campbell), p. 235. **1956:** New York (John Wiley); *Ames Lab., Iowa, Rep.* (**IS–460**), 1962; *Electrochem. Technol.*, 1963, **1,** 172.

29. T. J. Gray, 'The Defect Solid State', p. 93. **1957:** New York and London (Interscience Publishers).

30. R. A. Andrievsky, *Voprosy Poroshkovoi Met. Prochnosti Materialov* (Kiev), **1958,** 54.

31. R. L. Coble, *J. Amer. Ceram. Soc.*, 1958, **41,** 55.

32. R. L. Coble, 'Kinetics of High-Temperature Processes' (edited by W. D. Kingery), p. 147. **1959:** New York (John Wiley).

33. H. J. Oel, *Z. Metallkunde*, 1960, **51,** 53.

34. W. D. Jones, 'Fundamental Principles of Powder Metallurgy'. **1960:** London (Edward Arnold).

35. H. Schreiner and F. Wendler, *Z. Metallkunde*, 1961, **52,** 218.

36. J. White, 'Science of Ceramics' (edited by G. H. Stewart) Vol. I, p. 1. **1962:** Vol. II, p. 305. **1965:** New York and London (Academic Press); *J. Brit. Ceram. Soc.*, 1965, **3,** 155.

37. G. Ciceron, *Silicates Ind.*, 1963, **28,** 383.

38. F. V. Lenel and G. S. Ansell, *Indust. and Eng. Chem.*, 1963, **55,** 46.

39. F. V. Lenel, 'Fundamental Phenomena in the Material Sciences' (edited by L. J. Bonis and H. H. Hausner), Vol. I, 'Sintering and Plastic Deformation', p. 3. **1964:** New York (Plenum Press).

40. L. L. Seigle, *Progress in Powder Metallurgy*, 1964, **20,** 221; *Metal Powder Ind. Fed. Proc.*, 1964, **20,** 221.

41. I. Kalning, *Monatsber. deut. Akad. Wiss.*, 1964, **6,** 225.

42. N. C. Kothari, *Danish Atomic Energy Commission, Met. Section, Risö-Rep.* (**89**), 1964.

43. *Powder Met.*, 1959, (**3**), 86–171; discussion, 1959, **4,** 126.

44. 'Powder Metallurgy' (edited by W. Leszynski). **1961:** New York and London (Interscience Publishers).

45. 'Modern Developments in Powder Metallurgy' (edited by H. H. Hausner), Vol. I: 'Fundamentals and Methods'. **1966:** New York (Consultants Bureau).

45*a*. 'Berichte über die II Internat. Pulvermet. Tagung (Eisenach. 1961)' **1962:** Berlin (Akademie Verlag).

45*b*. *Ibid.* (Eisenach. 1965).

45*c*. Pulvermetallurgie in der Atomkerntechnik' (4 Plansee Seminar 1961). **1962:** Vienna (Springer Verlag).

46. International Symposium on 'Métallurgie des Poudres' (Paris, 1964). **1966:** St.-Germain en Laye (Editions Métaux).

47. R. L. Coble and J. E. Burke, 'Progress in Ceramic Sciences' (edited by J. E. Burke), Vol. III, p. 197. **1963:** Oxford (Pergamon Press).

48. H. Fischmeister and E. Exner, *Metall*, 1964, **18,** 932; 1965, **19,** 113, 941.

49. H. H. Hausner, *Planseeber. Pulvermet.*, 1963, **11,** 59.

50. G. F. Hüttig, see Ref. [2] and Ref. [27], p. 145 (footnote).

51. K. Torkar, 'Reactivity of Solids' (edited by J. H. de Boer), p. 400. **1961:** Amsterdam (Elsevier).

52. Ref. [27], pp. 110–111 (discussion).

53. Ref. [27], p. 111.

54. H. Youssef and M. Eudier, *Mém. Sci. Rev. Mét.*, 1963, **60,** 165.

55. F. N. Rhines, *Plansee Proc.*, **1958,** 38.

56. F. N. Rhines, *Proc. Metal Powder Assoc.*, **1958,** 91.

57. R. T. de Hoff, R. A. Rummel, and F. N. Rhines, Ref. [44], p. 37.

58. F. Sauerwald, *Z. physikal. Chem.*, 1958, **209,** 206.

59. C. Herring, *J. Appl. Physics*, 1950, **21,** 437.

60. F. R. N. Nabarro, 'Report of Conference on Strength of Solids', p. 75. **1948:** London (Phys. Soc.).

61. W. D. Kingery and M. Berg, *J. Appl. Physics*, 1955, **26,** 1205.

62. A. Rozner and G. C. Kuczynski, *J. Amer. Ceram. Soc.*, 1962, **45,** 92.

63. A. C. Grottyoham and K. Herrington, *ibid.*, 1964, **47,** 53.

64. L. F. Norris and G. Parravano, *ibid.*, 1963, **46,** 449.

65. F. V. Lenel, *Soviet Powder Met.*, **1964,** (6), 523.

66. D. L. Johnson and T. M. Clarke, *Acta Met.*, 1964, **12,** 1173.

67. B. H. Alexander and R. W. Balluffi, *ibid.*, 1957, **5,** 666.

68. L. Seigle, 'Kinetics of High-Temperature Processes (edited by W. D. Kingery), p. 172. **1959:** New York and London (John Wiley).

69. A. L. Pranatis and L. Seigle, Ref. [44], p. 53.

70. G. C. Kuczynski, Ref. [44], p. 11.

71. J. Brett and L. Seigle, *Acta Met.*, 1963, **11,** 467.

72. J. Brett and L. Seigle, *ibid.*, 1966, **14,** 575.

73. C. Herring, *J. Appl. Physics*, 1950, **21,** 301.

74. J. G. R. Rockland, private communication; *Acta Met.*, 1966, **14,** 1273.

75. N. Cabrera, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188,** 667.

76. P. Schwed, *ibid.*, 1951, **191,** 245.

77. H. Ichinose and G. C. Kuczynski, *Acta Met.*, 1962, **10,** 209.

78. F. Thümmler, *Wiss. Z. TH Dresden*, 1954–55, **4,** 1045.

79. H. Rutkowska and B. Olenderek, 'Berichte über die II. Internat. Pulvermet. Tagung (Eisenach, 1961), p. 77. **1962:** Berlin (Akademie Verlag).

80. H. Fischmeister and R. Zahn, *ibid.*, p. 93.

81. R. T. de Hoff, D. H. Baldwin, and F. N. Rhines, *Planseeber. Pulvermet.*, 1962, **10,** 24.

82. G. D. Rieck and J. G. R. Rockland, *ibid.*, 1965, **13,** 3.

83. F. Thümmler, *Stahl u. Eisen*, 1958, **78,** 1134.

84. I. Zaplatynskyj, *Planseeber. Pulvermet.*, 1958, **6,** 89.

85. A. L. Pranatis, L. S. Castleman, and L. Seigle, *Sylvania Electric Products Rep.* (**SEP–247**), 1956/57.

86. G. C. Kuczynski, L. Abernethy, and J. Allan, *Plansee Proc.*, **1958,** 1.
    G. C. Kuczynski, Ref. [45], p. 332.
    G. C. Kuczynski, L. Abernethy, and J. Allan, 'Kinetics of High-Temperature Processes', p. 163. **1959:** New York and London (John Wiley).

87. G. Parravano, *ASTIA Rep.* (**AD-602529**), 1963.

88. G. Parravano, *ibid.*, (**AD-207974**), 1957–1958.

89. D. H. Whitmore and T. Kawai, *J. Amer. Ceram. Soc.*, 1962, **45,** 375.

90. H. J. McQueen and G. C. Kuczynski, *ibid.*, p. 343.

91. G. C. Kuczynski, G. Matsumura, and B. D. Cullity, *Acta Met.*, 1960, **8**, 209.

92. G. C. Kuczynski and P. Stablein, 'Reactivity of Solids' (edited by J. H. de Boer), p. 91. **1961:** Amsterdam (Elsevier).

93. J. Brett and L. Seigle, *U.S. Atomic Energy Commission Publ.* (**GTR-20**). 1961–1963.

94. G. C. Kuczynski, *Acta Met.*, 1956, **4**, 58.

95. G. C. Kuczynski, *Powder Met.*, 1963, (**12**), 1.

96. A. W. Postlethwaite and A. J. Shaler, 'The Physics of Powder Metallurgy' (edited by W. E. Kingston), p. 189. **1951:** New York and London (McGraw-Hill).

97. H. J. Oel, *Z. Metallkunde*, 1960, **51**, 53.

98. H. Fischmeister and R. Zahn, Ref. [45], Vol. II, p. 12.

99. T. L. Wilson and P. G. Shewmon, *Trans. Met. Soc. A.I.M.E.*, 1966, **236**, 49.

100. J. Hornstra, *Physica*, 1961, **27**, 342.
H. G. van Bueren and J. Hornstra, 'Reactivity of Solids', p. 112. **1961:** Amsterdam (Elsevier).

101. J. Brett and L. Seigle, *Sylvania Electric Products Rep.* (**SEP-259**), 1960–1961.

102. J. Brett and L. Seigle, *Acta Met.*, 1963, **11**, 467.

103. J. E. Burke, *J. Amer. Ceram. Soc.*, 1957, **40**, 80.

104. J. Hornstra, Ref. [46], p. 97.

105. R. Margerand and M. Eudier, *Powder Met.*, 1963, (**12**), 17.

106. C. A. Elyard, *ibid.*, p. 50, Fig. 2.

107. D. L. Johnson and I. B. Cutler, *U.S. Atomic Energy Commission Rep.* (**TID 17007**); *J. Amer. Ceram. Soc.*, 1963, **46**, 541.

108. W. D. Jones, *Acta Met.*, 1959, **7**, 222; Ref. [34], p. 392.

109. A. Mohanty and E. Bauman, *ibid.*, 1963, **11**, 84.

110. Ya. E. Geguzin, *Doklady Akad. Nauk U.S.S.R.*, 1953, **92**, 45.

111. G. C. Kuczynski and I. Zaplatynskyj, *J. Amer. Ceram. Soc.*, 1956, **39**, 349.

112. H. M. O'Bryan and G. Parravano, Ref. [44], p. 191.

113. C. S. Morgan, cited in *U.S. Atomic Energy Commission Publ.*, (**ORNL-3160**), 1960–1961, p. 39.

114. C. S. Morgan, C. J. McHargue, and C. S. Yust, *ibid.*, **ORNL(-P-427)**, 1961; *J. Brit. Ceram. Soc.*, 1965, **3**, 177.

115. P. Clark and J. White, *Trans. Brit. Ceram. Soc.*, 1950, **49**, 305.

116. J. K. Mackenzie and R. Shuttleworth, *Proc. Phys. Soc.*, 1949, [B], **62**, 833.

117. E. B. Allison and P. Murray, *Acta Met.*, 1954, **2**, 487.

118. F. V. Lenel, H. H. Hausner, O. V. Roman, and G. S. Ansell, *Trans. Met. Soc. A.I.M.E.*, 1963, **227**, 640.

119. F. V. Lenel, *U.S. Atomic Energy Commission Publ.*, (**TID 18324**), 1963.

120. F. V. Lenel, Ref. [46], p. 105.

121. I. Ya. Dekhtyar, *Doklady Akad. Nauk U.S.S.R.*, 1951, **80**, 875.

122. F. V. Lenel and G. S. Ansell, Ref. [45], p. 281.

123. J. G. Early, F. V. Lenel, and G. S. Ansell, *Trans. Met. Soc. A.I.M.E.*, 1964, **230**, 1641.

124. B. J. Pines, *Physics Metals Metallography*, 1963, **16**, 55.

125. G. Bockstiegel, *Trans. Amer. Inst. Min. Met. Eng.*, 1956, **206**, 580.

126. W. C. Hagel, P. J. Jorgensen, and D. S. Tomalin, *General Electric Research Lab. Rep.*, (**65-RL-3939M**), 1965.

127. A. U. Daniels and M. E. Wadsworth, *U.S. Atomic Energy Commission Publ.*, (**TID 21624**), 1965.

128. Ya. E. Geguzin and N. N. Ovcharenko, *Physics Metals Metallography*, 1959, **8**, 70; 1960, **9**, 53, 58.

129. K. Torkar, H. J. Oel, and A. Illigen, *Ber. Deut. Keram. Ges.*, 1966, **43**, 162.

130. M. Oxley and G. Ciceron, *Internat. J. Powder Met.*, 1965, **1**, 15.

131. G. Ciceron and P. Lacombe, *Compt. Rend.*, 1955, **240**, 427.

132. G. Ciceron, *ibid.*, 1957, **244**, 2047.

133. B. Pinteau, G. Ciceron, and P. Lacombe, *Mém. Sci. Rev. Mét.*, 1964, **61**, 787.

134. B. Pinteau, G. Ciceron, and P. Lacombe, *ibid.*, 1961, **252**, 1149.

135. E. Hampe, *Kernenergie*, 1966, **9**, 100.

136. S. L. Forss, Ref. [45], Vol. II, p. 3.

137. T. Okamura, Y. Masuda, and S. Kikuta, *Sci. Rep. Research Inst. Tohoku Univ.*, 1949, **1**, 357.

138. W. Borchert and H. Carl, *Metall*, 1966, **20**, 103.

139. W. Borchert and E. Rieger, *ibid.*, 1964, **18**, 446.

140. M. H. Tikkanen, *Planseeber. Pulvermet.*, 1963, **11**, 70.

141. M. H. Tikkanen and S. Ylasaari, Ref. [45], p. 297.

142. M. H. Tikkanen and S. A. Mäkipirtti, *Internat. J. Powder Met.*, 1965, **1**, 15.

143. S. Mäkipirtti, Ref. [44], p. 97.

144. N. C. Kothari, *Powder Met.*, 1964, **7**, (14), 251.

145. N. C. Kothari, *J. Less-Common Metals*, 1963, **5**, 140.

146. N. C. Kothari and J. Waring, *Powder Met.*, 1964, **7**, (13), 13.

147. F. N. Rhines, R. T. de Hoff, and R. A. Rummel, 'Agglomeration' (edited by W. A. Knepper), p. 351. **1962:** New York and London (Interscience Publishers).

148. J. Amato, R. L. Colombo, and A. M. Protti, *J. Nuclear Mat.*, 1964, **11**, 278.

149. E. Kostic and M. M. Ristic, *Keram. Z.*, 1964, **16**, 351.

150. M. J. Bannister, *J. Nuclear Mat.*, 1964, **14**, 315.

151. E. A. Aitken, *J. Amer. Ceram. Soc.*, 1960, **43**, 627.

152. A. U. Daniels and M. E. Wadsworth, *U.S. Atomic Energy Commission Publ.*, (**TID 20150**), 1963.

153. C. A. Bruch, *Amer. Ceram. Soc. Bull.*, 1962, **41**, 799.

154. J. R. Keski and I. B. Cutler, *J. Amer. Ceram. Soc.* ,1965, **48**, 653.

155. P. J. Jorgensen, *ibid.*, 1965, **48**, 207.

156. H. U. Anderson, *ibid.*, 1965, **48**, 118.

157. H. Iwasaki, *Japanese J. Appl. Physics*, 1965, **4**, 190.

158. B. Cech and J. Bronkal, *Silikaty*, 1963, **7**, 193.

159. R. L. Coble, *J. Appl. Physics*, 1961, **32**, 787.
R. L. Coble and J. E. Burke, 'Reactivity of Solids', (edited by J. H. de Boer), p. 38. **1961:** Amsterdam (Elsevier).

160. H. H. Hausner, 'Symposium on Powder Metallurgy, London, 1954', (Special Rep. No. 58), p. 102. **1956:** London (Iron Steel Inst.).

161. N. A. L. Mansour and J. White, *Powder Met.*, 1963, (**12**), 108.

162. H. Stehle, *Ber. Deut. Keram. Ges.*, 1963, **40**, 129.

163. F. Thümmler and W. Thomma, Ref. [45], p. 361.
F. Thümmler and W. Thomma, Ref. [45b], p. 137.

164. W. D. Kingery and B. François, *J. Amer. Ceram. Soc.*, 1965, **48**, 546.

165. R. L. Coble and T. K. Gupta, *Proc. Amer. Ceram. Soc., 67th Annual Meeting* (Philadelphia, 1965), **17-B-65.**

166. R. L. Coble, *J. Appl. Physics*, 1965, **36**, 2327.

167. J. R. MacEwan, *J. Amer. Ceram. Soc.*, 1962, **45**, 37.

168. H. F. Fischmeister, Ref. [46], p. 115.

169. P. E. D. Morgan and A. J. E. Welch, 'Reactivity of Solids' (edited by J. H. de Boer), p. 105. **1961:** Amsterdam (Elsevier).

170. R. A. Brown, *Amer. Ceram. Soc. Bull*, 1965, **44**, 483.

171. R. A. Brown, *ibid.*, p. 693.

172. R. A. Brown, *J. Amer. Ceram. Soc.*, 1965, **48**, 627.

173. E. C. Duderstadt and J. F. White, *Amer. Ceram. Soc. Bull.*, 1965, **44**, 907.

174. P. Ram, H. S. Gadiyar, and P. K. Jena, *J. Less-Common Metals*, 1966, **10**, 185.

175. J. T. Smith, *J. Appl. Physics*, 1965, **36**, 595.

176. T. Vasilos and J. T. Smith, *ibid.*, 1964, **35**, 215.

177. I. M. Fedorchenko and N. V. Kostyrko, *Physics Metals Metallography*, 1960, **10**, 72.

178. W. Lange, A. Hässner, and W. Krug, *Physica Status Solidi*, 1965, **8**, K11.
179. M. Aucouturier, M. O. Pinheiro, R. de Castro, and P. Lacombe, *Acta Met.*, 1965, **13**, 125.
180. G. A. Geach, *Powder Met.*, 1959, (**3**), 125.
181. W. Friemel, O. Knacke, and I. N. Stranski, *Z. Metallkunde*, 1958, **49**, 404.
182. G. V. Samsonov and T. S. Verkhoglyadova, *Soviet Powder Met.*, **1963**, (2), 98.
183. V. A. Bron, *ibid.*, **1962**, (5), 339.
184. D. L. Greenaway and A. A. Woolf, *Assoc. Elect. Ind. Research Rep.*, (**A 689**), 1957.
185. G. A. Geach and A. A. Woolf, Ref. [44], p. 201.
186. K. Entress, *Silikattechnik*, 1964, **15**, 188.
187. F. Thümmler, *Freiberger Forschungshefte*, 1954, **35**, 40; *Die Technik*, 1954, **9**, 77.
188. A. R. Poster and H. H. Hausner, Ref. [45], Vol. II, p. 25.
189. G. Bockstiegel, *Arch. Eisenhüttenwesen*, 1957, **28**, 167.
190. E. Hampe, *Kernenergie*, 1965, **8**, 291.
191. Ref. [27], p. 157.
192. Ref. [17], p. 389.
193. P. Murray, 'Agglomeration' (edited by W. A. Knepper), p. 93. **1962:** New York and London (Interscience Publishers).
194. L. C. F. Blackman, *Indust. Chemist*, 1962, **38**, 620; 1963, **39**, 23.
195. K. Torkar and N. Perlhefter, Ref. [46], p. 155.
196. L. Harris, D. Jeffries, and B. M. Siegel, *J. Chem. Physics*, 1950, **18**, 261.
197. P. Royen, *Angew. Chem.*, 1954, **66**, 181.
198. V. N. Eremenko and V. J. Nizhenko, *Soviet Powder Met.*, **1963**, (3), 270.
199. J. Hinnüber and O. Rüdiger, *Arch Eisenhüttenwesen*, 1952, **23**, 475.
200. G. Zapf, *Powder Met.*, 1961, (**7**), 218.
201. Y. Harada, Y. Baskin, and J. H. Handwerk, *J. Amer. Ceram. Soc.*, 1962, **45**, 253.
202. V. V. Skorokhod and G. O. Ranneva, *Soviet Powder Met.*, **1963**, (3), 194.
203. A. R. Poster, *Internat. J. Powder Met.*, 1965, **1**, 23.
204. H. J. Oel, 'Agglomeration', p. 271. **1962:** New York and London (Interscience Publishers).
205. H. J. Oel, Ref. [45], p. 345; Ref. [46], p. 429.
206. H. J. Oel, 'Berichte über die II Internat. Pulvermet. Tagung' (Eisenach, 1961), p. 85. **1962:** Berlin (Akademie-Verlag).
207. V. K. Moorthy and S. V. K. Rao, *Plansee Proc.*, **1962**, 181.
208. T. Yamaguchi, *J. Amer. Ceram. Soc.*, 1964, **47**, 131.
209. G. Naeser and W. Scholz, *Ber. Deut. Keram. Ges.*, 1962, **39**, 106.
210. G. Naeser, W. Scholz, and A. Fiedler, *ibid.*, 1962, **39**, 280.
211. J. R. McLaren and P. W. M. Atkinson, *J. Nuclear Mat.*, 1965, **17**, 142.
212. V. A. Bron and N. V. Semkina, *Soviet Powder Met.*, **1962**, (5), 332.
213. C. Kooy, 'Science of Ceramics, (edited by G. H. Stewart), Vol. I, p. 21. **1963:** Oxford (Blackwell).
214. S. Z. Bokshtein, T. J. Gudkova, A. A. Zhukhovitsky, and S. T. Kishkin, 'Diffusion Processes, Structure, and Properties of Metals, (edited by S. Z. Bokshtein), p. 40. **1965:** New York (Consultants Bureau).
215. B. Ya Pines and Ya. E. Geguzin, *Zhur. Tekhn. Fiziki*, 1953, **23**, 2078.
216. Ya. E. Geguzin, *Physics Metals Metallography*, 1958, **6**, (5), 51.
217. Ya. E. Geguzin, *ibid.*, 1957, **5**, (3), 142; 1959, **7**, (5), 96.
218. B. Ya. Pines and A. F. Sirenko, *Fizika Tverdogo Tela*, 1965, **7**, 687.
219. P. Guiraldenq, *Compt. Rend.*, 1962, **254**, 99, 1994.
220. A. Hässner, *Physica Status Solidi*, 1965, **11**, K15.
221. J. Belle, *Proc. 2nd Internat. Conf. on Peaceful Uses of Atomic Energy*, 1958, **6**, 590.
222. N. Fuhrmann, L. D. Hower, and R. B. Holden, *J. Amer. Ceram. Soc.*, 1963, **46**, 114.
223. N. Müller, *Ber. Deut. Keram. Ges.*, 1963, **40**, 140.
224. J. Amato, R. L. Colombo, and A. M. Protti, *J. Amer. Ceram. Soc.*, 1963, **46**, 407.
225. H. J. Allsopp and J. P. Roberts, *Trans. Faraday Soc.*, 1959, **55**, 1386.
226. J. P. Roberts and J. Hutchins, *ibid.*, 1959, **55**, 1394.
227. V. J. Lee and G. Parravano, *J. Appl. Physics*, 1959, **30**, 1735.
228. G. C. Kuczynski, *Plansee Proc.*, **1962**, 166.
229. G. C. Kuczynski, Ref. [45], p. 332.
230. G. J. Dienes, 'Effects of Radiation on Materials', p. 1. **1958:** New York (Reinhold); London (Chapman and Hall).
231. W. K. Barney, *Proc. 2nd Internat. Conf. on Peaceful Uses of Atomic Energy*, 1958, **6**, 677.
232. J. P. McBride and S. D. Clinton, *U.S. Atomic Energy Commission Publ.* (**ORNL-3275**), 1962.
233. M. Clasing, *Z. Metallkunde*, 1958, **49**, 69.
234. M. Clasing and F. Sauerwald, *Z. anorg. Chem.*, 1952, **271**, 88.
235. H. Magdanz and F. Sauerwald, *Z. physikal. Chem.* 1957, **206**, 261.
236. K. Iwase and K. Ogawa, *Nippon Kinzoku Gakkai-Si*, 1955, **19**, 178.
237. P. Ramakrishnan and G. S. Tendolkar, *Trans. Indian Inst., Metals*, 1964, **17**, 115.
238. W. Rutkowski, *Neue Hütte*, 1961, **6**, 788.
239. W. Dienst and O. Werner, *Z. Metallkunde*, 1960, **51**, 45.
240. J. Williams, J. W. S. Jones, and K. H. Westmacott, *Powder Met.*, 1961, (**7**), 167.
241. J. T. Norton, *Trans. Amer. Inst. Min. Met. Eng.*, 1956, **206**, 49.
242. H. H. Hausner, *Precious Metal Molding*, 1957, **15**, (10), 44; (11), 91; (12), 44, 69.
243. F. G. Cox, *Metal Ind.*, 1960, **97**, 186, 207, 231.
244. M. Eudier, 'Symposium on Powder Metallurgy, 1954' (Special Rep. No. 58), p. 59. **1956:** London (Iron Steel Inst.).
245. Sh. Ya. Korovsky, *Doklady Akad. Nauk. U.S.S.R.*, 1954, **97**, 875.
246. R. A. Andrievsky and I. M. Fedorchenko, *Dopovidi Akad. Nauk Ukr. R.S.R.*, 1959, **4**, 392.
247. I. M. Fedorchenko, *Soviet Powder Met.*, **1962**, (2), 89; (3), 156.
248. R. A. Andrievsky and S. M. Solonin, *ibid.*, **1964**, (3), 198.
249. F. Eisenkolb, *Stahl u. Eisen*, 1958, **78**, 141.
250. G. H. Chalder, N. F. H. Bright, D. L. Paterson, and L. C. Watson, *Proc. 2nd Internat. Conf. Peaceful Uses Atomic Energy*, 1958, **6**, 590.
251. U. Runfors, N. Schönberg, and R. Kiessling, *ibid.*, 1958, **6**, 605.
252. A. H. Webster and N. F. H. Bright, *U.S. Atomic Energy Commission Publ.* (**NP-6667**), 1958.
253. W. E. Baily, J. C. Danko, and H. M. Ferrari, *Amer. Ceram. Soc. Bull.*, 1962, **41**, 768.
254. N. Fuhrmann, L. D. Hower, and R. B. Holden, *J. Amer. Ceram. Soc.*, 1963, **46**, 114.
255. A. J. Leonov, *Izvest. Akad. Nauk U.S.S.R.*, **1955**, 805.
256. P. P. Budnikov and S. G. Tresvyatsky, *Doklady Akad. Nauk U.S.S.R.*, 1954, **95**, 1041.
257. F. V. Lenel, H. H. Hausner, I. A. El Shanshouri, J. G. Early, and G. S. Ansell, *Powder Met.*, 1962, (**10**), 190.
258. G. Matsumura, *Planseeber. Pulvermet.*, 1961, **9**, 143.
259. M. G. Nicholas, *Trans. Met. Soc. A.I.M.E.*, 1963, **227**, 250.
260. B. Ya. Pines, A. F. Sirenko, and N. I. Sukhinin, *Zhur. Tekhn. Fiziki*, 1957, **27**, 1893.
261. H. H. Hausner, *Planseeber. Pulvermet.*, 1961, **9**, 26; *J. Metals*, 1961, **13**, 752.

262. H. H. Hausner, *Progress in Powder Metallurgy*, 1963, **19**, 67.
263. H. H. Hausner and O. V. Roman, *Soviet Powder Met.*, **1964**, (3), 180.
264. F. V. Lenel, H. H. Hausner, O. V. Roman, and G. S. Ansell, *ibid.*, **1963**, (5), 379.
265. T. R. Barrett, G. C. Ellis, and R. A. Knight, *Planseeber. Pulvermet.*, 1958, **6**, 34.
266. A. J. Martin and G. C. Ellis, *Powder Met.*, 1961, (**7**), 120.
267. B. Ya. Pines, *Zhur. Tekhn. Fiziki*, 1956, **26**, 2086.
    B. Ya. Pines and N. I. Sukhinin, *ibid.*, p. 2100.
268. J. Goodison and J. White, 'Agglomeration', p. 251. **1962:** New York and London (Interscience Publishers).
269. B. Ya. Pines and N. I. Sukhinin, *Zhur. Tekhn. Fiziki*, 1956, **26** 2076.
270. B. Ya. Pines, A. F. Sirenko, and N. I. Sukhinin, *ibid.*, 1957, **27** 1904.
271. B. Ya. Pines and A. F. Sirenko, *ibid.*, 1958, **28**, 150.
272. B. Ya. Pines and A. F. Sirenko, *Physics Metals Metallography*, 1958, **6**, 261.
273. J. Williams and J. W. S. Jones, *Powder Met.*, 1960, (**5**), 45.
274. E. M. Modl-Onitsch, *Plansee Proc.*, **1959**, 427.
275. B. R. L. Hodson and R. H. Read, *Armour Research Foundation Rep.*, (**ARF-2149-4**).
276. W. Schatt, *Planseeber. Pulvermet.*, 1960, **8**, 122. *Neue Hütte*, 1960, **5**, 287.
277. F. Thümmler, *Planseeber. Pulvermet.*, 1958, **6**, 2.
278. A. P. Mokrov, *Physics Metals Metallography*, 1964, **17**, 116.
279. R. E. Hoffman, D. Turnbull, and E. W. Hart, *Acta Met.*, 1955, **3**, 417.
280. K. May, *Arch. Metallkunde*, 1948, **2**, 154.
281. J. M. Butler and T. P. Hoar, *J. Inst. Metals*, 1951–52, **80**, 207.
282. C. Agte and J. Vacek, 'Neuere technische Richtlinien der Pulvermetallurgie. **1955:** Prague (SNTL).
283. J. Vacek, *Hutnicke Listy*, 1955, **10**, 469.
284. B. Fisher and P. S. Rudman, *Acta Met.*, 1962, **10**, 37.
285. A. M. Huntz, G. Ciceron, and P. Lacombe, Ref. [46], p. 141.
286. J. A. Lund, W. R. Irvine, and V. N. Mackiw, *Powder Met.*, 1962, (**10**), 218.
287. P. R. Rao, *Trans. Indian Inst. Metals*, 1964, **17**, 28.
288. K. Torkar and H. Götz, *Z. Metallkunde*, 1955, **46**, 371.
    K. Torkar and H. Mariacher, *Planseeber Pulvermet.*, 1955, **3**, 78; *Z. Metallkunde*, 1956, **47**, 260.
    G. F. Hüttig, K. Torkar, and H. H. Weitzer, *Powder Met. Bull.*, 1955, **7**, 48.
289. K. Torkar and H. Neuhold, *Z. Metallkunde*, 1961, **52**, 209.
290. A. I. Raichenko and I. M. Fedorchenko, *Voprosy Poroshkovoi Met. i Prochnosti Materialov* (Kiev), 1956, **6**, 3.
291. A. I. Raichenko, *Physics Metals Metallography*, 1961, **12**, 136.
292. G. C. Kuczynski and P. F. Stablein, 'Reactivity of Solids', p. 91. **1961:** Amsterdam (Elsevier).
293. P. F. Stablein and G. C. Kuczynski, *Acta Met.*, 1963, **11**, 1327.
294. R. C. Bradt, F. V. Lenel, and G. S. Ansell, *ibid.*, 1966, **14**, 553.
295. K.-I. Hirano, R. P. Agarwala, B. L. Averbach, and M. Cohen, *J. Appl. Physics*, 1962, **33**, 3049.
296. A. Hässner and W. Lange, *Physica Status Solidi*, 1965, **8**, 77.
297. S. Yu. Sharivker, *Soviet Powder Met.*, **1963**, (2), 108.
298. G. Ciceron, Ref. [45], p. 376.
299. J. Vacek, *Planseeber. Pulvermet.*, 1959, **7**, 6.
300. J. H. Brophy, K. G. Kreider, and J. Wulff, *Trans. Met. Soc. A.I.M.E.*, 1963, **227**, 598.
301. A. L. Prill, H. W. Hayden, and J. H. Brophy, *ibid.*, 1964, **230**, 769.
302. J. H. Brophy, H. W. Hayden, and J. Wulff, *ibid.*, 1962, **224**, 797.
303. H. Braun and K. Sedlatschek, *J. Less-Common Metals*, 1960, **2**, 277.
304. F. Eisenkolb and I. Kalning, *Planseeber. Pulvermet.*, 1957, **5**, 2.
305. E. Raub and W. Plate, *Z. Metallkunde*, 1951, **42**, 76.
306. P. Duwez, *Powder Met. Bull.*, 1949, **4**, 144, 168.
307. H. J. S. Kriek, W. F. Ford, and J. White, *Trans. Brit. Ceram. Soc.*, 1959, **58**, 1.
308. J. Dubuisson, A. Houyvet, E. le Boulbin, R. Lucas, and C. Morauville, *Proc. 2nd Internat. Conf. Peaceful Uses Atomic Energy*, 1958, **6**, 551.
309. A. Accary and R. Caillat, Ref. [44], p. 209.
310. S. Krapf, *Ber. Deut. Keram. Ges.*, 1954, **31**, 18.
311. E. Meyer-Hartwig, *ibid.*, 1956, **33**, 85.
312. W. A. Weyl, *Ceramic Age*, 1952, **60**, 28.
313. P. A. Marshall, D. P. Enright, and W. A. Weyl, *Proc. Internat. Symposium on Reactivity of Solids* (Gothenburg, 1952), **1954**, p. 272.
314. I. W. Nelson and I. B. Cutler, *J. Amer. Ceram. Soc.*, 1958, **41**, 406.
315. H. P. Cahoon and C. J. Christensen, *ibid.*, 1956, **39**, 337.
316. I. B. Cutler, 'Kinetics of High-Temperature Processes' (edited by W. D. Kingery), p. 120. **1959:** New York and London (John Wiley).
317. E. P. Hyatt, C. J. Christensen, and I. B. Cutler, *Amer. Ceram. Soc. Bull.*, 1957, **36**, 307.
318. J. T. Jones, P. K. Maitra, and I. B. Cutler, *J. Amer. Ceram. Soc.*, 1958, **41**, 353.
319. G. V. Kukolev and E. N. Leve, *Zhur. Priklad. Khim.*, 1955, **28**, 909.
320. R. Pampuch, *Bull. Soç. Franc. Céram.*, 1960, **46**, (Jan.–Mar.), 3.
321. P. J. Jorgensen and J. H. Westbrook, *J. Amer. Ceram. Soc.*, 1964, **47**, 332.
322. L. H. Sjodahl and J. H. Westbrook, *ibid.*, 1965, **48**, 478.
323. W. R. Bratschun, *ibid.*, 1962, **45**, 611.
324. E. J. Felten, *ibid.*, 1961, **44**, 251.
325. G. C. Nicholson, *ibid.*, 1965, **48**, 525.
326. H. J. Oel, *Ber. Deut. Keram. Ges.*, 1962, **39**, 78.
327. R. Ruh, N. M. Tallan, and H. A. Lipsitt, *J. Amer. Ceram. Soc.*, 1964, **47**, 632.
328. German Patent No. **1,189,001**, 1960.
329. L. M. Manojlović, R. M. Herak, S. S. Malčić, and M. M. Ristić, *Bull. Boris Kidrič Inst. Nuclear Sci.* 1965, **16**, 81.
330. F. V. Lenel, *Trans. Amer. Inst. Min. Met. Eng.*, 1948, **175**, 1051; 'The Physics of Powder Metallurgy' (edited by W. E. Kingston), p. 238. **1951:** New York and London (McGraw-Hill).
331. H. S. Cannon and F. V. Lenel, *Plansee Proc.*, **1953**, 106.
332. J. Gurland and J. T. Norton, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 1051.
333. W. D. Kingery, 'Kinetics of High-Temperature Processes', p. 187. **1959:** New York and London (John Wiley).
334. W. D. Kingery, *J. Appl. Physics*, 1959, **30**, 301.
    W. D. Kingery and M. D. Narasimhan, *ibid.*, 1959, **30**, 307.
335. W. D. Kingery, E. Niki, and M. D. Narasimhan, *J. Amer. Ceram. Soc.*, 1961, **44**, 29.
336. Yu. V. Naidich, I. A. Lavrinenko, and V. N. Eremenko, *Internat. J. Powder Met.*, 1965, **1**, 41.
337. Yu. V. Naidich, I. A. Lavrinenko, and V. Yu. Petrishshev, *Soviet Powder Met.*, **1965**, (2), 129.
338. V. N. Eremenko, Yu. V. Naidich, and I. A. Lavrinenko, *ibid.*, **1962**, (4), 282.
339. B. Cech, *ibid.*, **1963**, (1), 86.
340. N. M. Parikh and M. Humenik, *J. Amer. Ceram. Soc.*, 1957, **40**, 315.
341. J. Gurland, *Trans. Amer. Inst. Min. Met. Eng.* 1959, **215**, 601.
342. W. Dawihl, *Z. techn. Physik*, 1940, **21**, 336; *Z. Metallkunde*, 1953, **44**, 69.
343. W. Dawihl and G. Altmeyer, *Z. Metallkunde*, 1963, **54**, 645.
344. E. Pelzel, *Metall*, 1955, **9**, 565.

345. J. E. Elliot, *Metallurgia*, 1959, **59**, 17.
346. G. U. Gummeson and L. Forss, *Planseeber. Pulvermet.*, 1957, **5**, 94.
347. G. Bockstiegel, *Stahl u. Eisen*, 1959, **79**, 1187.
348. G. Matsumura, *Planseeber. Pulvermet.*, 1961, **9**, 33.
349. T. Nishijima, *J. Japan Soc. Powder Met.*, 1959, **6**, 91.
350. S. Scholz and B. Lersmacher, *Ber. Deut. Keram. Ges.*, 1964, **41**, 98.
351. R. C. Rossi and R. M. Fulrath, *J. Amer. Ceram. Soc.*, 1965, **48**, 558.
352. L. Ramqvist, *Powder Met.*, 1966, **9**, (17), 1.
353. P. Murray, E. P. Rodgers, and A. E. Williams, *Trans. Brit. Ceram. Soc.*, 1954, **53**, 474.
354. J. D. McClelland, Ref. [44], p. 157.
355. M. S. Kovalchenko and G. V. Samsonov, *Soviet Powder Met.*, **1961**, (2), 3.
356. G. E. Mangsen, W. A. Lambertson, and B. Best, *J. Amer. Ceram. Soc.*, 1960, **43**, 55.
357. T. Vasilos, *ibid.*, 1960, **43**, 517.
358. R. E. Jaeger and L. Egerton, *ibid.*, 1962, **45**, 209.
359. J. D. McClelland and E. H. Zehms, *ibid.*, 1963, **46**, 77.
360. B. Lersmacher, E. Roeder, and S. Scholz, *Naturwiss.*, 1962, **49**, 35.
361. F. E. Westermann and R. G. Carlson, *Trans. Met. Soc. A.I.M.E.*, 1961, **221**, 649.
362. R. G. Carlson and F. E. Westermann, *Planseeber. Pulvermet.*, 1962, **10**, 15.
363. J. D. McClelland and D. L. Whitney, *ibid.*, 1962, **10**, 131.
364. B. Lersmacher and S. Scholz, *Arch Eisenhüttenwesen*, 1961, **32**, 421.
365. M. Nacken, S. Scholz, and B. Lersmacher, *ibid.*, 1962, **33**, 635.
366. S. Scholz, 'Special Ceramics', p. 293. **1963:** London and New York (Academic Press); *Planseeber. Pulvermet.*, 1963, **11**, 82; *Soviet Powder Met.*, **1963**, (3), 170.
367. R. Chang and C. G. Rhodes, *J. Amer. Ceram. Soc.*, 1962, **45**, 379.
368. E. J. Felten, *ibid.*, 1961, **44**, 381.
369. Y. Hashimoto, *Univ. California Lawrence Radiation Lab. Rep.*, (**UCRL-11214**), 1964.
370. T. Vasilos and R. M. Spriggs, *J. Amer. Ceram. Soc.*, 1963, **46**, 493.
371. R. L. Coble and J. S. Ellis, *ibid.*, p. 438.
372. M. J. Salkind, F. V. Lenel, and G. S. Ansell, *Trans. Met. Soc. A.I.M.E.*, 1965, **233**, 39.
373. J. T. Smith and T. Vasilos, *ibid.*, 1965, **233**, 1431.
374. A. Accary and R. Caillat, *J. Amer. Ceram. Soc.*, 1962, **45**, 347.
375. W. D. Kingery, J. M. Woulbronn, and F. R. Charvat, *ibid.*, 1963, **46**, 391.
376. R. I. Garber and L. M. Polyakov, *Physics Metals Metallography*, 1961, **11**, 81.
377. Ref. [34], p. 354.
378. A. Rabenau, E. Roeder, and S. Scholz, *Rev. Hautes Temp. et Réfract.*, 1966, **3**, 85.
379. E. Roeder and M. Clerk, *Z. Metallkunde*, 1963, **54**, 462.
380. E. Roeder and M. Clerk, 'The Electron Microprobe' (edited by T. D. McKinley, K. F. I. Heinrich, and D. B. Wittry), p. 642. **1966:** New York and London (John Wiley).
381. C. S. Morgan, L. L. Hall, and C. S. Yust, *J. Amer. Ceram. Soc.*, 1963, **46**, 559.
382. A. A. Ammar and D. W. Budworth, *J. Brit. Ceram. Soc.*, 1965, **3**, 185.
383. G. Arthur, *J. Inst. Metals*, 1954–55, **83**, 329.
384. G. H. S. Price, C. J. Smithells, and S. V. Williams, *ibid.*, 1938, **62**, 289.
385. F. Thümmler, G. Ondracek, and V. Dalal, *Z. Metallkunde*, 1965, **56**, 535.