The Sintering of Uranium-Plutonium Carbonitrides

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Presented in partial requirement for the degree of Master of Philosophy in Materials Technology at the University of Surrey, April 1980
Abstract

The theory of solid-phase sintering and its experimental investigation are reviewed. Uranium-plutonium carbonitride powders were prepared by carbothermic reduction and their sintering kinetics studied by dilatometry using a constant-rate-of-heating and Dorn method. The influence of a presintering hydrogen treatment was investigated. The difference in the apparent activation energy of sintering determined by the two methods and the change in kinetics caused by the hydrogen treatment are explained with reference to the diffusion characteristics of carbonitrides.
# Table of Contents

## Chapter 1: Review of Theories of Sintering

1.1. Introduction 1  
1.2. Initial Sintering 3  
1.2.1. Evaporation - Condensation Mechanism 4  
1.2.2. Viscous and Plastic Flow 6  
1.2.3. Diffusion Mechanisms 7  
1.2.4. Simultaneously Operating Mechanisms 16  
1.2.5. Limitations of the two-particle model 22  
1.3. Intermediate and Final Stage Sintering 22  

## Chapter 2: Experimental Techniques

2.1. Powder Characterisation 29  
2.2. The Experimental Investigation of Sintering Kinetics 33  
2.2.1. Initial Stage 33  
2.2.2. Shrinkage Measurements 34  
2.2.3. Experimental Techniques 37  
2.2.4. Specific Surface Measurements 40  
2.2.5. Electrical Resistivity Measurements 42  
2.2.6. Intermediate and Final Stage 42  

## Chapter 3: Uranium-Plutonium Carbonitrides and Related Nuclear Fuels

3.1. General Characteristics 44  
3.2. Phase Relationships in the System U-Pu-C-N 46  
3.3. Preparation 50  
3.4. Sintering 54  
3.5. Diffusion 58  
3.6. Creep 61  

## Chapter 4: Experimental Procedures

4.1. Plan and Organisation of Experiments 65  
4.2. Preparation of Material 65  
4.3. Powder Characterisation 71  

Chapter 5: Results

5.1. Structural and Compositional Changes during Sintering 82
5.2. Shrinkage Behaviour under Isothermal Conditions 87
5.3. Shrinkage Behaviour under Constant Rate Conditions 91
5.4. Dorn Method 100

Chapter 6: Discussion and Conclusions

6.1. Without hydrogen treatment 102
6.1.1. Initial Stage 102
- Comparison of the results with Johnson's model and Ashby diagram
- Differing 'n' value determined in isothermal experiments
- Activation Energy determined by Dorn method
- Explanation of results considering anomalous diffusion behaviour
6.1.2. Intermediate Stage Behaviour 111
6.2. After hydrogen treatment 114
6.3. Summary and Conclusions 117
6.3.1. Initial Stage Sintering 117
6.3.2. Intermediate and Final Stage 117
6.3.3. Influence of hydrogen treatment 117

Appendix 1 Effect of Additional Mechanisms on the Value of Q Determined by the Dorn Method
Appendix 2 The Influence of Gas Pressure within Closed Pores on the Driving Force for Sintering
Appendix 3 The significance of the results for in-pile densification

Literature

Figures
1.1. Introduction

Modern work on sintering has been reviewed by Coble and Burke in 1963 /1/ and Thümmler and Thomma in 1967 /2/, the latter being a particularly comprehensive survey which considers not only mechanisms and models for solid phase sintering but also the influence of process and material variables on practical sintering. Ashby /3/ and Wilson and Shewmon /4/ discuss sintering models. The most recent survey of theories of sintering is contained in H.E. Exner's 'Habilitationsschrift' /5/ published in 1976. This review will be restricted to solid state sintering without the application of external pressure, with a particular emphasis upon the initial stages.

Sintering is defined by Thümmler and Thomma /2/ as "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 charged 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". The complexity of this definition illustrates the complexity of the phenomenon itself.

The driving force for sintering is supplied by the surface energy. As a system sinters the total surface area always reduces so that the free energy of the system is reduced. If \( E \) is the free energy of a system and \( A \) the total surface area then:

\[
\frac{dE}{dA} = \gamma \quad (1.1)
\]

If at a point on a curved surface with principal radii of curvature \( r_1 \) and \( r_2 \) a volume element \( dV \) is removed or replaced then it can be shown that /5/

\[
\frac{dE}{dV} = \gamma \frac{dA}{dV} = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1.2)
\]
the quantity \( \frac{dE}{dV} \) is equivalent to a stress so that 1.2 can be rewritten:

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

(1.3)

thus under concave surfaces a tensile stress, under convex surfaces a compressive stress exists. This results in a chemical potential \( \mu \) directly beneath the surface given by:

\[
\mu = \mu_0 - \sigma \Omega = \gamma \Omega \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

(1.4)

where \( \mu_0 \) is the chemical potential under a flat surface. Hence there will be a chemical potential gradient between concave and convex parts of a surface so that material transport will take place between the two.

The sintering of a powder compact is usually divided into several stages, typified by different structures. Thümmler and Thomma /2/ define three stages:

1) Initial stage sintering in which necks form and grow between the individual particles. Grain boundaries are located in most necks.

2) Intermediate stage sintering, where neck growth has proceeded beyond the stage where the particles can be considered separately. A continuous network of tubular pores exists which will in general follow the boundaries where three grains meet, as this is a minimum energy configuration. Generally pore coalescence occurs simultaneously with grain growth so that thus structural configuration is preserved.

3) Third stage sintering, where the amount of isolated porosity starts to increase. This occurs in nearly all materials /2/ at around 92% of theoretical density.

Ashby /3/ adds an extra stage, stage 0, in which a small neck is formed on the initial contact of the particles due to interatomic forces. This takes place practically instantaneously.
1.2. Initial Sintering

There are a number of mechanisms which could be responsible for the sintering process, the relative importance of which depends upon the properties of the material and the sintering conditions. They are:

1) Evaporation - condensation: material evaporating from the particle surface condenses in the region of interparticle contact
2) Viscous flow
3) Plastic flow
4) Diffusion mechanisms, which can be further classified following /3/, according to the type of diffusion and the source of the material (the sink being in every case the interparticle neck surface)
   a) surface diffusion from surface
   b) lattice or volume diffusion from surface
   c) grain boundary diffusion from interparticle grain boundary
   d) lattice diffusion from grain boundary
   e) lattice diffusion from dislocations

It is important that, among the diffusion mechanisms only those (c and d) which involve removal of material from the interparticle grain boundary can cause the particle centres to approach one another, resulting in densification.

The models discussed in this section are derived by considering two particles (usually spheres) in contact (Fig. 1). The rate of growth of the neck and the rate of approach of the centres of the particles are determined for the mechanism considered. The approach of particle centres relative to their original separation is usually taken to be equivalent to the fractional shrinkage of a compact of these particles. This is true for a regular array of regular particles. However, recent work by Exner /5, 6, 7/ has shown that this is not always the case in irregular compacts.
1.2.1. Evaporation - Condensation Mechanism

This mechanism, although in practice rarely found to contribute significantly to sintering, is a good illustration of the way in which rate equations can be derived for the two-particle model, as it is fairly straightforward to analyse. Referring to Fig. 1, the sharp concave curvature, radius $\rho$, of the neck surface results in a decrease in the chemical potential there according to equ. 1.4. This results in a corresponding decrease in vapour pressure over the neck surface given by:

$$\mu - \mu_0 = RT \ln \frac{P}{P_0}$$

($P$ is the vapour pressure, $P_0$ the vapour pressure over a flat surface) so that:

$$RT \ln \frac{P}{P_0} = \frac{\gamma \alpha \rho}{d} \left( \frac{1}{\rho} + \frac{1}{x} \right)$$

(Kelvin equation)

which for $P-P_0 \ll P_0$ and $x \gg \rho$, simplifies to:

$$\Delta P = \frac{\gamma \alpha P_0}{d \rho RT}$$

The rate of condensation per unit area of neck surface is proportional to this pressure difference and is given by the Langmuir equation:

$$m = \alpha \Delta P \left( \frac{\sigma}{2 \pi RT} \right)^{1/2} \text{kg m}^{-2} \text{s}^{-1}$$

($\alpha$ = accommodation coeff. $\approx 1$)

and the total volume rate of transfer

$$\frac{dV}{dt} = mA$$

(1.8)

where $A$ is the neck surface area.
Fig. 1: Two Particle Model
To form an equation for the rate of neck growth it is necessary to know the geometric relations between neck volume, neck width and neck surface area. As the exact expressions are unwieldy the following approximations are generally used, which are valid so long as $x \gg r$:

\[
\rho = \frac{x^2}{2r} \quad (1.9) \quad A = \frac{\pi^2 x^3}{2r} \quad (1.10) \quad V = \frac{\pi x^4}{2r} \quad (1.11)
\]

Combining equations 1.6 to 1.11 we obtain:

\[
\frac{dx}{dt} = \frac{2\pi \gamma \rho r}{3d^2 RT x^2} \left( \frac{\rho}{2RT} \right)^{1/2}
\]

which integrates to:

\[
\frac{x^3}{r} = \frac{2\pi \gamma \rho P_o}{3d^2 RT} \left( \frac{m}{2RT} \right)^{1/2} t
\]

The simplifications involved in this derivation are all of a geometric nature and such that the greater the neck growth the less accurate equation 1.13 becomes. Apart from this there is little to be brought against this treatment.

The growth law has been verified for spheres of NaCl \cite{8} and ZnO \cite{9}, but the vapour pressure of most materials is too low for this mechanism to be significant \cite{4}.

1.2.2. **Viscous and Plastic Flow**

Frenkel, in one of the earlier theories of sintering \cite{10}, proposed that sintering occurs by the Newtonian viscous flow of the material in the neck region under the forces of surface tension, the effective viscosity, $\eta$, being given by

\[
\frac{1}{\eta} = \frac{D_v a_e}{kT}.
\]

(1.14)
He arrived at a neck growth law of:

$$x^2 = \frac{3 \gamma \gamma_t}{2 \eta}$$  \hspace{1cm} (1.15)

This law has been found by many investigators (e.g. /11/) to be true for glass spheres. However, in view of modern understanding of the plastic flow of crystalline materials, it must be restricted to this case.

However, crystalline materials at high temperatures do not behave as Newtonian fluids, so that the solid state sintering of metals and ceromus cannot be explained by Frenkel's model.

On the other hand plastic flow (i.e. involving the movement of dislocations) is a feasible mechanism in crystalline materials which has been the subject of a lengthy controversy. Proponents of the theory point out that, in the earliest stages of neck growth, the stresses in the neck should greatly exceed the yield stress of the material. On the other hand investigations involving hot stage electron microscopy performed by Easterling and Tholen /59, 152/ failed to produce any evidence of dislocation movement even at the smallest neck widths. With the aid of a more thorough analyses of the stress distribution in the neck region they show that the necessary shear stress for generating dislocations is not in fact reached.

1.2.3. Diffusion Mechanisms

Diffusion-controlled sintering models have been for most materials the most successful in explaining experimental observations. They are, however, the most difficult to formulate due to the large selection of material sources and sinks and diffusion paths. The very likely possibility of the simultaneous operation and mutual interaction of several diffusion mechanisms increases the difficulty - it is advisable first to consider the various mechanisms, listed in Section 1.2.1, separately.
Surface diffusion from free particle surface

Kuczynski /12/ first derived the rate equation for this mechanism using the two-sphere model. He assumed a concentration gradient of adsorbed atoms on the surface of the neck of $\Delta N_{\text{tot}}/P$, where $\Delta N$ is the difference in equilibrium concentration between the neck and the rest of the particle surface. He obtained, following a similar method as has been described for the evaporation-condensation mechanism (Section 1.2.2.2):

$$x^7 = \frac{56 \gamma \sigma \rho^4}{kT} D_s t$$

(1.16)
Fig. 2: Concentration of adsorbed atoms as a function of position on particle surface for surface diffusion models

(a) Kuczynski

(b) Cabrera

N(0)  
\[ \frac{-\pi}{2} \quad 0 \quad \frac{\pi}{2} \]

\[ \eta - N(\infty) = \frac{2 \gamma q^2 N(\infty) e^x \exp(t/y_\eta)}{kT(0)} \]

(c) Schwed

(d) Rockland

\[ R_\perp \sim N(\infty) = \frac{(N(\infty) - N(0))}{(e^{\frac{t}{\gamma_\perp}} + e^{\frac{t}{\gamma_\parallel}})^2} \]

\[ \eta - N(\infty) = \frac{N(\infty) - N(0)}{1 - e^{\frac{\pi}{\gamma_\parallel}}} e^{-\frac{t}{\gamma_\perp}} \]

\[ \frac{-\pi}{2} \quad 0 \quad \frac{\pi}{2} \]

\[ N(0) \]

\[ \frac{d^2 N}{d \tau^2} = \frac{\partial N}{\partial \tau} = ml + c \]
Cabrera /13/ approached the problem differently. Whereas Kuczynski simply assumes a linear concentration gradient, which is not influenced by diffusion towards the neck, in Cobrera's model the process of re-establishment of equilibrium concentrations is considered to be rate-controlling (in Kuczynski's model this is tacitly assumed to be a much faster process than diffusion). The respective surface concentration gradients for the two models are shown in Fig. 2(a) and 2(b), where 1 is the distance from the centre of the neck surface. By considering the resulting flux at \( l = \frac{1}{2} \pi \rho \) (approximately the point of inflection of the neck surface), Cabrera obtains for the neck growth:

\[
X_5 = At
\]

\[
(A = [160 Y \alpha_0^6 / kT r^2] D_S N (\infty))
\]

However, Cabrera only considered diffusion over the convex part of the surface \((l > \frac{1}{2} \pi \rho)\). Consideration of Fig. 2(b) shows that there is no concentration gradient to distribute material over the concave part of the surface.

Schwed /14/ corrected this error by considering the concave part of the surface and arrived at the equation:

\[
X_3 = At
\]

He also considered the case where relaxation effects are not rate controlling. This depends upon the value of \( y_s \), the mean distance between sources and sinks for adsorbed atoms. If \( y_s \gg \frac{1}{2} \pi \rho \), then relaxation effects are rate controlling and eqn. 1.18 applies. If \( y_s \ll \frac{1}{2} \pi \rho \) then equilibrium concentrations prevail (see Fig. 2(c)). In this case Schwed found that:

\[
X_5 = At
\]

Rockland /10/ more recently showed that \( y_s \ll \frac{1}{2} \pi \rho \), at least on the concave part of the surface, because the curvature requires a large number of steps on the surface of a crystalline material, which will act as
sources and sinks. He does not, however, agree with equation 1.19, but considers 1.17 to be nearer the truth. His derivation is based upon the argument that to avoid the formation of a groove in the surface of the neck (which would mean an increase in surface energy), the area from which material is removed must be at least as great as that over which it is deposited. The time exponent results from the dependence of $\frac{dx}{dt}$ on $\rho$, in Rockland's case $\frac{dx}{dt}$ being proportional to $1/\rho^3$, this is because:

a) $\Delta n$ is proportional to $1/\rho$ from Thomson's equation;
b) the surface area over which material is deposited is proportional to $\rho$;
c) the mean distance over which material is transported is proportional to $\rho$.

In Schwed's model, for $y_s \ll \pi \rho$ the factor $1/\rho$ resulting from (c) is lost, and for $y_s \gg \pi \rho$ the $1/\rho$ resulting from (a) is lost, as $\Delta n$ is no longer rate controlling. In Cabrera's model the flux depends again on $\Delta n$ and the factor $1/\rho$ re-appears. Since $\rho \propto x^2$ this accounts for the differences in the time exponent for the three models.

**Volume diffusion from free particle surface**

Kuczynski /12/ derives an expression for neck growth by this mechanism using similar assumptions to this model for surface diffusion. Again a vacancy concentration gradient of $\Delta c/\rho$ is assumed. The significant difference is that the cross-sectional area available for the diffusion flux is taken as being equal to the neck surface area, and therefore increases proportional to $\rho$. Hence a further factor of $x^2$ appears in the expression for the rate of neck growth giving:

$$\frac{dx}{dt} = \frac{8 \gamma \omega D_v r^2}{kT} \cdot \frac{1}{x^4} \quad (1.20)$$

and

$$x^5 = \frac{40 \gamma \omega D_v r^2}{kT} t \quad (1.21)$$

These results have not been criticised by more recent authors, although similar objections to those levelled at the various surface diffusion models must apply.
Volume diffusion from the grain boundary

The availability of the grain boundary in the neck between particles as a source of material to fill the interparticle gap was not considered by earlier authors, although only mechanisms involving this source can result in the approach of particle centres and thus the densification of a compact. As densification is usually observed (and desired), this is an important mechanism which has received detailed treatment.

The difficulty in formulating a model for such a mechanism was in defining the diffusion flux. In the simplest solution /16/ the flux is taken to be proportional to $\Delta C$, the difference in vacancy concentration between the centre of the neck and directly beneath the neck surface. The concentration in the centre of the neck is assumed to be that under a free flat surface so the Kelvin equation (1.19) can be used for $\Delta C$. The diffusion flux is approximated by the solution for radial heat flow from the centre to the surface of an electrically heated cylinder, whose length is equal to the width of the neck, taken as $\rho$, and whose radius is the radius of the neck, $x$:

$$J = 4\pi D' \Delta C \rho \text{ vacancies/sec}$$

(1.22)

The volume flow of material is:

$$J a_0^3 = 4\pi D' \Delta C a_0^3 \rho = \frac{dV}{dt}$$

(1.23)

Geometrically, for the case where material is removed from between two spheres the following approximations are used:

$$\frac{dV}{dt} = \frac{\pi x^3}{2r} \frac{dx}{dt}$$

(1.24)

$$\rho = \frac{x^2}{4r}$$

(1.25)

therefore, substituting in equ. (1.23) for $\Delta C$ with equ. (1.19) and relating the vacancy diffusion coefficient to the volume diffusion coefficient by $D_v C a_0^3 = D'$ we have with equations 1.24 and 1.25:
\[
\frac{dx}{dt} = \frac{8 D_v a_0^3 r}{kT} \quad (1.26)
\]

Integrating:
\[
x^4 = \frac{32 D_v a_0^3 rt}{kT} \quad (1.27)
\]

The assumption that the vacancy concentration in the centre of the neck approximates that under a free flat surface is, however, not valid /2, 17/ and that the concentration varies linearly between the centre and surface of the neck is also an oversimplification. Berrin and Johnson /18/ and Johnson /19/ derive models which consider chemical potential gradients rather than vacancy concentration gradients as driving forces for the diffusion flux. This has the advantage of being valid where the activity coefficient of vacancies is not unity and that the chemical potential variation can be more easily determined by considering the variation of stress with position in the neck /20/.

The flux of atoms in the neck is thus described by
\[
J = -BaCa \nabla (\mu_a - \mu_v) \quad (1.28)
\]

assuming, as previously that a quasi-steady state exists, i.e. that the vacancy concentration at any point is determined by the local stress. This requires that the creation and annihilation of vacancies is a fast process compared with diffusion, then \( \nabla \mu_v \) is zero and the flux is given by
\[
J = -BaCa \nabla \mu_a \quad (1.29)
\]

The chemical potential \( \mu_a \) is related to the stress by
\[
\mu_a = \mu_a^0 + \sigma a_0^3
\]
\[
\nabla \mu_a = \nabla a_0^3 = a_0^3 \nabla \sigma
\]

if \( a_0^3 \) is assumed independent of stress and as \( Ca = 1/a_0^3 \) then
\[
J = -Ba \nabla \sigma \quad (1.30)
\]
If there is no plastic deformation, and no void formation at the grain boundary, then the vacancy annihilation rate must be uniform over the whole grain boundary. Therefore $\nabla J$ is constant and thus $\nabla^2 \mu$ is constant hence

$$\nabla^2 \sigma = K$$

or, for cylindrical coordinates $R, \phi$,

$$\frac{1}{R} \frac{\partial}{\partial R} (R \frac{\partial \sigma}{\partial R}) = K \tag{1.31}$$

It being tacitly assumed in /13/ that $\frac{\partial^2 \sigma}{\partial R} = 0$ (valid if the neck is cylindrically symmetrical) and $\frac{\partial^2 \sigma}{\partial z^2} = 0$.

Equation 1.31 is solved by taking $\sigma = \Upsilon (1/x - 1/\epsilon)$ at $R = x$ and by equating the integral of $\sigma$ over the cross-sectional area of the neck to $2\pi x \cos \alpha$. Thus the model takes the sophistication of a grain boundary groove angle of $\alpha$ into account. In /18/ the integral of $\sigma$ is erroneously equated to zero /19/. This gives an expression for the total flux arriving at the neck surface ($Ba = Dv/kT$)

$$J = \frac{4 \Upsilon DvA (x - \epsilon \cos \alpha)}{kT x^2 \epsilon} \tag{1.32}$$

The flux is readily related to the rate of interpenetration of particles by:

$$J = \frac{\pi x^2}{a_0^3} \frac{d\delta}{dt}$$

where $\delta$ is the distance of interpenetration. Thus giving

$$x^2 \frac{d\delta}{dt} = \frac{4 \Upsilon DvA (x - \epsilon \cos \alpha)}{kT} \tag{1.33}$$

This is quite a general equation for sintering by volume diffusion as no assumptions have been yet made about particle shape, except that the neck cross-section is circular. However, its applicability in practice is limited to model experiments where $x, \epsilon, \delta$ and $\alpha$ can be measured. To apply it to real powder compacts it is necessary to make assumptions concerning the particle shape, as previously. If one makes the same geometrical
assumptions as Coble (i.e. spherical particles, circular neck surface
tangential to the sphere surface) one obtains:

\[ \frac{\Delta l}{l} = y = \left( \frac{5.34 \gamma a D v}{kT r^3} \right)^{0.44} t^{0.49} \]  

(1.34)

for the shrinkage and

\[ x^{4.12} = \frac{75 \gamma a_o^3 D v r t}{kT} \]  

(1.35)

To obtain 1.34 and 1.35 the approximate geometric relationships relating
\( \phi \) and \( A \) to \( x \) (1.24 and 1.25), have not been used but the more exact
relationships published in /17/. However, since the geometry to which
they refer (the neck surface being tangential to the sphere surface, as
in Fig. 1) is impossible in practice due to the discontinuity in chemical
potential at the point of tangency, the advantage of using these relation-
ships must be considered minimal.

The similarity of equations 1.35 and 1.27 is notable, the difference in the
time exponents resulting from the different geometric relationships used.
Despite the more sophisticated approach the only difference is in the
numerical constant.

Grain boundary diffusion from the grain boundary

As with volume diffusion from the grain boundary this mechanism is important
as it causes shrinkage. An essential assumption in all derivations is that
material brought to the neck surface along the grain boundary can be
distributed by surface diffusion more rapidly than it arrives.

Coble /16/ derives a model in the same way as for volume diffusion. The
only difference is that in equation 1.23 the width of the neck (assumed to
be equal to \( p \)) is replaced by the grain boundary width, which is taken as
5 \( a_o \), i.e. five atomic diameters, giving:

\[ \frac{dV}{dt} = 4\pi D_b \Delta c a_o^4 \]  

(1.36)
The final equation for neck growth is:

\[ x^6 = \frac{96 D_b Y a_o^4 r^2}{kT} t \]  \hspace{1cm} (1.37)

and for shrinkage \[ y^3 = \frac{3 D_b Y a_o^4}{r^4 kT} t \]  \hspace{1cm} (1.38)

The exponents \( y \) and \( x \) differ from those for volume diffusion because the cross-sectional area for grain boundary diffusion does not change during the course of sintering.

The equations of Johnson for the diffusion flux can also be applied to grain boundary diffusion simply by substituting a fixed value of \( A \) in equation (1.32), corresponding to the grain boundary width, and of course substituting \( D_b \) for \( D_v \). The resulting equations are:

\[ x^{6.22} = \frac{114 Y a_o^3 b D_b r^2}{kT} t \]  \hspace{1cm} \text{for neck growth} \hspace{1cm} (1.39)

and \[ y^3 = \frac{2.14 Y a_o^3 b D_b}{r^4 kT} T \]  \hspace{1cm} (1.40)

### 1.2.4. Simultaneously Operating Mechanisms

All the sintering models so far described are derived assuming that a single mechanism operates. Clearly all feasible mechanisms will operate simultaneously - only in the case where one mechanism is very much faster can the others be ignored. The grain boundary diffusion mechanism can in fact only operate in conjunction with volume or surface diffusion to distribute the material from the grain boundary about the neck surface.

This point is considered by Gessinger /21/ who points out that, in order to distribute by surface diffusion the material arriving at the neck by grain boundary diffusion, a geometry as shown in Fig. 3a is necessary with a reduction in curvature from A to B. At B, however, the sign of the curvature has to change, which allows surface diffusion from the free, convex particle.
Fig. 3a

Fig. 3b
surface towards B. As the two fluxes, from the grain boundary and the free surface continuously tend to remove their driving force they will decrease, possibly becoming rate-controlling for shrinkage (by grain boundary diffusion).

Alternatively, as in Fig. 3b, volume diffusion may distribute material from the grain boundary, thus making volume diffusion rate-controlling if $D_v$ is low. Johnson /22/ shows that the relative importance of volume and surface diffusion is approximately given by

$$\frac{J_v}{J_S} = \frac{A_v D_v \nabla v \mu}{4 x a_o D_s \nabla s \mu}$$

and if $\nabla v \mu \approx \nabla s \mu$ it is clear that the dominant mechanism for distribution will depend on the ratio of the volume and surface diffusion coefficients (which will be temperature dependent), the particle size and the amount of shrinkage. If, as usually observed, $Q_s < Q_v$ then lower temperature, smaller particles and lower shrinkages favour surface diffusion.

The important point here is that, under certain conditions, although surface diffusion alone cannot cause densification, it may be rate-controlling.

Simultaneous volume and grain boundary diffusion from the grain boundary is straightforward to analyse. In general, expressions for the rate of neck growth by various mechanisms can be combined additively. Difficulties arise, however, in formulating integrated expression for shrinkage by several mechanisms, as only some of the mechanisms can cause shrinkage (the rates of shrinkage will, however, be affected by neck growth caused by other mechanisms). Even where combination is relatively easy, the resulting expressions are unwieldy: Johnson, for example /19/, combines his expressions for the rate of shrinkage by volume and grain boundary diffusion to give:

$$\frac{dy}{dt} = \frac{2.63 Y a_o D_v}{kT r^3 y} + \frac{0.7 Y a_o^3 b D_b}{kT r^4 y^2}$$

The result of integrating this expression is:
\[ \frac{\gamma^2}{2K^2 D v^2} - \frac{K'D}{K} \frac{D_6 y}{D v^2} + \frac{K'}{K} \frac{D_6^2}{D v^2} \ln (KD vy + K'D_b) + c = t \]  

(1.42)  

where \( K, K' \) contain the constants \( \gamma, a_0 \) etc.

This result is clearly of little use in analysing experimental data.

Useful analyses of the relative importance of simultaneously operating mechanisms can therefore only be achieved by the use of numerical methods. Here Ashby /3/ has made a considerable contribution by the development of "sintering diagrams" which constructed with the aid of rate expressions such as those discussed in this chapter, and material constants (such as diffusion coefficients, vapour pressures etc.) show the dominant sintering mechanisms under particular conditions.

Fig. 4 shows a hypothetical diagram for the purpose of illustration. The ordinate of the diagram is the logarithm of the ratio of interparticle neck radius to original particle radius and the abcissa is temperature or temperature/melting point. The diagram is divided into fields characterised by the dominant mechanism, i.e. that mechanism which, in the range of temperature and neck growth represented by the field, gives the fastest neck growth. The boundaries between the fields represent the conditions when two mechanisms are equally effective. Upon the fields are drawn contours of constant sintering rate or of constant sintering time.

In order to construct the diagrams it is necessary to have a set of expressions for the rate of neck growth as a function of neck size, original particle size, temperature and measurable or estimable physical constants of the material for all the mechanisms considered. Any conceivable mechanism may be included so long as such a rate expression can be constructed. Ashby considers surface diffusion, vapour transport, grain boundary and volume diffusion from the grain boundary and volume diffusion from the surface. Initial and later stage sintering are considered.

It is then necessary to determine which mechanism is the fastest for a given
FIG. 4. Hypothetical Ashby diagram

FIG. 5. Ashby diagram for UC

DATA USED:
- Surface diffn. coeff.: $0.56 \times 10^{-7} \exp(31400/RT)$ cm$^3$/sec
- Boundary diffn. coeff.: $1.8 \exp(74900/RT)$ cm$^3$/sec
- Volume diffn. coeff.: $4 \times 10^{-5} \exp(84000/RT)$ cm$^3$/sec
- Particle size: $10^{-6}$ mm
- Surface energy: 750 ergs/cm$^2$
neck growth-temperature combination. Boundaries between fields are
determined by equating the rates for two mechanisms and solving the result-
ing equation. Lines of constant growth rate are determined by summing the
growth rates for the various mechanisms (the different expressions for
initial and later stage sintering being considered as alternatives, the
faster rate being included in the sum). Isochronal lines are determined
by integrating this sum with respect to time.

The diagrams are clearly only as precise as the growth rate expressions
and the available data allow. This applies particularly to the constant
rate contours – the field boundaries are less sensitive to errors as these
frequently apply to all mechanisms equally. The use of neck growth as a
parameter for the degree of sintering limits the practical application of
the diagrams; furthermore, the concept of "neck size" in the later stages
of sintering is rather vague. However, since the degree of shrinkage cannot
be considered as parameter which represents the driving force for sintering
(the neck growth is closely related to the degree of surface curvature in
pore spaces), this is unavoidable. Another discrepancy is the failure to
account for the effects of grain growth in the later stages of sintering.

Notwithstanding these criticisms, the great value of Ashby's work lies in
the demonstration that the dominant mechanism of sintering is not a con-
stant for a particular material but can vary with particle size, temperature
and degree of sintering.

A diagram constructed by the author for UC using the diffusion data re-
commended by Routbort /23/ is shown in Fig. 5. It shows that, at tem-
peratures over 1400 °C an initial dominance of surface diffusion gives
way rapidly to grain boundary diffusion (at a neck radius of ≤ x/10).
Volume diffusion does not appear at all on the diagram.
1.2.5. Limitations of the two-particle model

As mentioned at the beginning of section 1.2 the equations obtained for the sintering of two particles can strictly only be extended to the shrinkage behaviour of particle compacts if they are perfectly regular. In practice it has been observed /5, 6, 7/ that in many cases not all the particles in a compact start sintering simultaneously. Many interparticle compacts will first form after a certain amount of shrinkage has occurred. Moreover the authors show that, in arrangements of three particles, interference between the two necks has been shown to cause a change in the angle formed by the lines joining particle centres. Similar effects in compacts cause random re-arrangements of the particle structure. Unfortunately the influence of heterogeneous nucleation and particle re-arrangement on compact shrinkage has not yet been quantified.

In defence of the two particle model it must be pointed out that in many cases (quoted in 1.2.1-1.2.4) actual compacts obey its predictions. It must be assumed that, at least in these cases, that the mean behaviour of interparticle contacts corresponds to that of the ideal case of two particles.

1.3. Intermediate and Final Stage Sintering

The initial stage of sintering is considered to end when sufficient neck growth has occurred to allow grain growth, although many of the initial stage models break down before this point is reached because the geometric approximations used are only valid for $x \ll r$. The intermediate stage lasts so long as the majority of the porosity is interconnected, that is to say, until about 90% of theoretical density is reached.
In contrast to the initial stage only two mechanisms are feasible: volume diffusion of material from the grain boundaries to the pores, and grain boundary diffusion between the same source and sink. Surface diffusion only plays a role insofar as the distribution of material arriving at the pore by grain boundary diffusion is concerned. It will also help maintain a low-energy pore cross-section.

The first model for intermediate stage sintering is due to Coble /24/. He considers an idealised geometry consisting of equal-sized tetrakaidecahedral grains with a continuous cylindrical pore of constant cross-section lying on the grain edges. He then proceeds in a similar manner as for initial stage sintering, using the expression for heat flow in an electrically-heated cylinder to represent the volume diffusion flux. This time the cylinder has a length equal to the pore diameter, $2 \varepsilon$ (the symbol $\varepsilon$ being taken due to its analogous role with the neck surface curvature), and the cross-section is, of course, hexagonal or square rather than circular.

Since the pore volume per grain can be expressed exactly in terms of the grain edge size $l$ and the pore radius an equation for the rate of decrease of porosity, $P$, is readily attained:

$$\frac{dP}{dt} = -\frac{10 \pi D_v \sqrt[3]{a_o}}{kT l^3}$$

(1.43)

To account for grain growth Coble makes use of the equation

$$G^3 - G_o^3 = At$$

(1.44)

where $G$ is the grain diameter (equivalent spherical diameter) and $G_o$ the grain size at $t = 0$. This is an empirical equation which is often observed for porous bodies /20, 25, 26, 27/ and has also been derived theoretically. Taking $l^3 = 0.0463 G^3$ and assuming $G \gg G_o$ equation 1.44 can be substituted into 1.43 and thus integrated to give:

$$P = P_o - \frac{720 D_v \sqrt[3]{a_o}}{AkT} \ln \frac{t}{t_o}$$

(1.45)

The predicted decrease in porosity with the logarithm of time is so
frequently observed in practice that it is sometimes referred to as the "logarithmic shrinkage law". The derivation has been criticised (e.g. /28/) on the grounds that the grain size cannot be zero at \( t = t_0 \), as results from the simplification of the grain growth law. However, so long as the grain size at \( t = t_0 \) is really small compared with \( G(t) \) there is no reason not to introduce this simplification. If this conditions is not fulfilled then equation 1.45 simply becomes:

\[
P - P_0 = -\frac{720 \, Dv \, \sqrt{2} \, \alpha^3}{AkT} \ln \frac{t + t'}{t_0 + t'}
\]  

(1.46)

where \( t' = G_0/A_0 \).

A further criticism /29/ of the choice of the tetrakaidecahedral grain shape, on the grounds that this can only arise from an unstable b.c.c. packing of particles in the compact, ignores the fact that grain growth is occurring during the intermediate stage, and that the grain shape is determined by the requirement for a minimal interfacial energy and not the initial particle packing.

The greatest weakness of the Coble model is the idealised regular pore and grain structure which continually grows. The real structural development in a sintering compact must be more complex, with individual grains growing sporadically as pores disappear. However, the frequent correlation with experimental data has encouraged its use in the interpretation of data.

Beeré /30/ has made some refinements to the Coble model. Rather than considering cylindrical pores on the grain boundaries he has calculated the equilibrium pore shape on the criterion of minimum surface energy. He has also taken the vacancy concentration near the grain boundary to be:

\[
C_b = C_0 \, \exp \left( -L \, Y \, a_0^3 \, \sin \, \Theta / ART \right)
\]  

(1.47)

where \( L \) (\( \approx 2 \pi x \)) is the grain boundary (or "neck") circumference and \( A \) its area (\( \approx \pi x^2 \)). This is in effect saying that the vacancy concentration will be a function of the mean stress - in fact the stress and therefore \( C_b \), will be a function of position but it is still a better approximation than \( C_b = C_0 \).
However, otherwise his approach is very similar to Coble's including the assumption of the cubic grain growth law, so that similar criticisms apply. His final equation for sintering by volume diffusion is:

\[ P = P_0 - \frac{12}{8\sqrt{2}} \cdot 145 \frac{DvB}{RTA} Y \frac{a_0^3}{ln \left( \frac{At + l_0^3}{l_0^3} \right)} \quad (1.48) \]

\( B \) being a geometrical constant equal to about 0.5, which is so similar to Coble's equation that one wonders if the extra effort was worth it.

Johnson /31/ has derived a model for intermediate stage sintering which he claims to be valid if a range of pore and grain shapes and sizes are present. The model is essentially a generalised form of his initial stage model, already described. The geometry is undefined except that an interconnected network of pores exists which are intersected by grain boundaries. The final sintering equation is:

\[ \frac{x}{HLv} \frac{dV}{dt} = \frac{8}{RT} \frac{Y a_0^3}{SV} + \frac{8}{RT} \frac{Y a_0^3 b D_b}{LV} \quad (1.49) \]

where:  
\( \bar{H} = \) "effective mean surface curvature"  
\( x = \) "mean diffusion distance"  
\( SV = \) pore surface area per unit volume  
\( LV = \) grain boundary-pore intersection length per unit volume

Johnson identifies, without proof, the quantity \( \bar{H} \) with the average mean surface curvature as defined by Cahn /32/ and de Hoff /33/. \( x \) is taken to be equal to \( \bar{G}/4 \) where \( \bar{G} \) is the mean grain diameter. The successful application of the model to the sintering of cobalt oxide /34/ is taken as justification of these assumptions.

The author believes that the introduction of the concepts "effective mean surface curvature" and "mean diffusion distance" are little improvement over Coble's idealised structure which could also be seen as a "mean grain size and pore shape". Furthermore, by leaving the equation in differential form, the problem of how to incorporate grain growth is simply avoided. The only real advance on Coble's model is the incorporation of both volume and grain boundary diffusion.
Rosolowski and Greskovitch /20/ derive a model for intermediate stage sintering which avoids the use of undefined parameters and also considers the effect of pore coalescence due to grain growth. It is based upon a calculation of the material flow into (or vacancy flow from) a single pore. In contrast to the models of Johnson and Coble it is not required that the vacancy annihilation rate everywhere on the grain boundary be equal, it being assumed that the vacancy mobility in the grain boundary is fast enough to avoid the build-up of stress. The flow is determined from the vacancy concentration distribution which is calculated by solving the differential equation:

$$\text{div } J = 0$$  \hspace{1cm} (1.50)$$

with the boundary conditions that the vacancy concentration near the grain boundaries is constant and equal to \(C_0\), and near the surface of the pore is given by the Kelvin equation. This is the three-dimensional equivalent of solving the equation \(\frac{dJ}{dx} = 0\) which was done by Rockland with similar boundary conditions for surface diffusion. From the solution to (1.49) an expression for the rate of disappearance of pore volume is obtained:

$$\frac{dV}{dt} = x a_o^3 \left( \frac{1}{p} \right) (3I + 11.4 \frac{bD_b}{P_{av}})$$  \hspace{1cm} (1.51)$$

where \(x\) is the number of pores per unit volume and \(I\) a structure-dependent numerical factor which is practically constant. In introducing \((T/P)\) and \(P\) the use of mean structural parameters has in this model also not been avoided, but they are better defined than Johnson's.

Equation 1.51 is integrated without assuming a particular grain growth law, arriving after the exchange of some structural parameters at:

$$\ln (1-P) = \frac{3I D_v}{k} \sum a_o^3 \left( \frac{f_{es}}{n} \right) \left[ \int_{t_0}^{t} \frac{f(t)dt}{(G^3)_{av}} \right]$$

$$+ \frac{bD_b}{3I D_v} \left[ \int_{t_0}^{t} \frac{(T/P)}{(G^3)_{av}} \frac{1}{dt} \right] + \ln (1-P_0)$$  \hspace{1cm} (1.52)$$
where: \( f = \) fraction of grain edges occupied by pores  
\( e = \) average number of edges per grain  
\( s = \) number of grains sharing one pore  
\( h = \) grain diameter-volume factor.

The derivation assures that \( \frac{1}{P} \) remains constant, it being argued that this has been observed experimentally during final stage sintering. The application to the intermediate stage is, however, not necessarily justified. In this form the first term in 1.52 (which concerns volume diffusion only) can be compared directly with Coble's model, simply by substituting his grain growth law in the integral and using the appropriate values of \( f, e, s \) and \( h \) for the tetrakaidecahedral structure. The result is:

\[
\ln (1-P) \approx P = \frac{54 D V_{2.0} \rho}{ART} \ \frac{1}{P} \ ln \frac{(t-t')}{(t_0-t')} + P_0
\]

The only significant difference between this and Coble's equation is the factor \( 1/P \), which, if it is constant, could be concluded in the numerical factor. In Coble's model, however, \( 1/P \) is porosity dependent, varying from a value of around 1.6 at \( P = 0.4 \) to 3.2 at \( P = 0.9 \). It is, however, arguable whether this variation by a factor 2 is significant.

In other respects Rosolowski and Greskovitch's model can be considered as a more generalised form of Coble's equation, as both volume and grain boundary diffusion are taken into account and no particular grain growth law is assumed. However, it does not contribute very greatly to sintering theory as the important question in intermediate stage sintering, the interrelation between densification and grain growth, is still not tackled; the theory predicts a certain densification rate for a given structure but does not consider the development of this structure.

An alternative approach to the intermediate and final stages of sintering which models more accurately the interdependence of shrinkage and grain growth has recently been made by Kuczynski /35, 36, 37/. He considers the change in pore diameter distribution by diffusion (both by vacancy annihilation at grain boundaries and by Ostwald ripening) in a system of
cylindrical or spherical pores of randomly varying diameter. The variance of the pore diameters is assumed to be constant. The mean grain size at any given time is determined by the pore structure and given by the Zener relation.

Kuczynski's resulting sintering equation is of the form:

\[ \frac{1}{P^n} - \frac{1}{P_0^n} = \alpha t \]  

(1.53)

where \( P_0 \) is the initial porosity and \( n \) a numerical constant greater than 3/2 for the intermediate stage and \( > 5/3 \) for the final stage. \( \alpha \) is a function of the initial structure of the specimen (\( P_0 \), total pore length, grain size) and the material constants (\( Y \), \( Dv \) etc.).

Unfortunately Kuczynski applies without comment the expression:

\[ \frac{dP}{dt} = \frac{K Y \Omega \cdot Dv}{\phi^2 \cdot R \cdot T} \]  

(1.54)

for the rate of change of pore diameter by volume diffusion. However, the vacancy concentration gradient, which is the driving force for diffusion, must be dependent on the pore to pore separation (cf. Johnson's model) but neither this, nor a related parameter appears in the expression. The effect of this omission on the final result is not known, but certainly casts doubts as to its validity.

Otherwise the approach seems very promising and may, on further development, provide more insight into the sintering process.
Chapter 2
Experimental Techniques

2.1. Powder Characterisation

For the purpose of determining the sintering behaviour of a powder, the important aspects of powder character are

- powder particle size and size distribution
- powder particle shape
- internal strain
- surface condition

Since the main driving force for sintering, particularly in materials which are not plastically deformable, results from the reduction in surface free energy caused by neck growth and the elimination of porosity, it is clear that the finer the mean particle size the more rapidly will a powder compact sinter. The particle size appears explicitly in all the initial sintering equations discussed in Chapter 1.

When dealing with particles of regular shape, spheres for example, the particle size is readily defined in terms of the volume surface area, or longest linear dimension of the particle. For particles of irregular shape the definition is more difficult, but a commonly used one is the diameter of a sphere of equivalent volume. However, many of the parameters measured by the various techniques to be described may not be readily related to the particle volume and it may be necessary to accept another size-related parameter, such as the specific surface of a powder.

In practice no powder is encountered with a single particle size - a size distribution is always present. The distribution plays an important role in determining the green density of a powder compact - a monodisperse powder of spherical particles cannot achieve a density of higher than 70% - for which a perfect close-packed structure is necessary. In practice much lower densities are achieved with monodisperse systems. A disperse system, however, allows smaller particles to get in the interstices between larger particles. Model experiments by McGeary /38/ demonstrated that by carefully
selecting proportions of several particle size, densities up to 95 % could be achieved by vibrational packing alone.

The particle shape of a powder consisting of irregular particles is difficult to define. For individual particles the 'elongation' or 'flakeness' may be difficult to determine for systems of more than a few particles. Particle shape may be important in determining the kinetics of initial stage sintering as these depend on the geometry of contacts between particles.

The role of internal strain in sintering is not yet well investigated as it is difficult to determine experimentally. With very fine particles the dislocation density may be determined by electron microscopy, and X-ray diffraction line broadening contains a component due to strain. It is, however, difficult to differentiate from size broadening.

The effects of powder surface irregularities and adsorbed surface layers and impurities on sintering may be of great significance. Clearly any lowering of the surface energy due to adsorbed layers will cause a reduction in the sintering rate, and irregular surfaces of high real surface area will encourage sintering. Apart from the surface area, which may be determined by gas adsorption methods, surface factors are difficult to quantify. Chemical analysis of surface layers is a complex task even on bulk samples and only a few techniques (e.g. auger electron spectroscopy) are capable of detecting low atomic number elements, such as oxygen which might have very significant effects.

The most common methods of powder characterisation, in particular particle size measurement are:

a) optical and electron microscopy
b) X-ray diffraction line broadening
c) specific surface by gas adsorption
d) permeametry
e) sedimentology
f) sensing zone methods
g) sieve analysis
h) elutriation
Microscopic methods are probably the most widely applicable and, given a representative sample, the most accurate. Optical microscopy can measure sizes down to about \( 1 \mu m \) diameter and transmission and scanning electron microscopy about \( 0.3 \text{ nm} \) and \( 0.1 \mu m \). Modern methods of automatic image analysis have greatly increased the ease of measuring the large number of particles which is necessary for statistically significant results. The greatest disadvantage is the difficulty in preparing specimens which are representative of the bulk /39-44/.

X-ray diffraction line broadening measures crystallite size, which is not necessarily the same as particle size. Corrections for 'instrumental' line broadening must be made by reference to the diffraction profile of a similar sample of large crystallite size, there being a number of methods of achieving this. Internal particle strain may also cause line broadening and the effects are only distinguishable by advanced techniques, using information from several diffraction peaks. The upper size limit is about \( 0.1 \mu m \); for crystallite sizes \( \geq 10 \mu m \) spot-size and spot-number on Laue back-reflection photographs may be used to determine crystallite sizes by reference to standard samples /45-50/.

The specific surface of a powder, as measured by gas adsorption methods, is a very commonly used method of determining its "sinterability". Nitrogen is most frequently used as adsorbate and the amount adsorbed as a function of pressure determined volumetrically. For low specific surfaces gases of low saturation vapour pressure such as krypton or ethylene are preferred, the former "labelled" with \( ^{85}\text{Kr} \) to facilitate pressure measurement. The adsorption equation developed by Brunauer, Emmett and Teller is used almost universally for interpreting the results, so that the methods is often referred to as the 'BET' method. For regular, smooth surfaced particles the mean particle size may be deduced from the specific surface, but the specific surface itself is a useful parameter for sintering behaviour, the driving force for sintering being reduction in surface area /113, 114/.

Permeametry is based upon the flow of a liquid or gas through a packed bed of powder. Using commercially available instruments a measure of particle size can be readily obtained for particles down to about \( 1 \mu m \) diameter. The method is, however, not absolute and may give unreliable results in the case of large particle size distributions.
Sedimentology utilises the variation in settling rate with size of particles in fluid suspension, results usually being interpreted with the aid of Stoke's law. A wide variety of experimental techniques are available to determine the settling rate of suspensions, either the concentration of the suspension as a function of time or depth being determined (by, e.g., sampling, light scattering or apparent density) or the amount of sediment (gravimetrically). The lower size limit of gravitational sedimentology of around 5 μm can be extended by using centrifugal methods down to 0.01 μm or lower. Particle size distributions are obtained but the inherent disadvantage is that the size measured is the diameter of a sphere with the same terminal velocity. Non-spherical particles may give quite erroneous results as may particle aggregates, so that for the purposes of sintering studies it is only useful as a comparative method /41, 53/.

Sensing zone methods involve the detection and sizing of individual particles in a suspension flowing through a small orifice. The detection may be optical, acoustic or electrical, the latter being most common and used in the commercial 'Coulter Counter'. The greatest advantage of the method is its speed in producing a particle size distribution based on particle volume. Accuracy is good but may be affected adversely by agglomeration, non-spherical particle shape and the simultaneous counting of two or more particles. The size range for a given orifice is also limited to a diameter ratio of 20:1; the lower limit of commercial instruments is at present 0.6 μm /54, 55/.

Sieve analysis is probably the most common form of particle size due to its simplicity. Accurate work, however, requires careful experimental techniques, as not all particles which could pass through a particular aperture do so. Conventional sieves are available with apertures as small as 50 μm diameter and electroformed micromesh sieves down to 5 μm.

In Elutriation, particles are classified by means of an upward-flowing fluid whose velocity is reduced by stages, so that particles remain in that stage of the apparatus where the fluid velocity is equal to their terminal velocity. As the principle is similar to sedimentology the same remarks concerning the significance of the sizes determined apply; the technique
is, however, useful for classifying fine powders between 10 μm and 100 μm diameter for further analysis.

2.2. The Experimental Investigation of Sintering Kinetics

2.2.1. Initial Stage

Since Kuczynski /12/ showed that equations could be derived showing different time dependencies of neck growth between spheres by different conceivable mechanisms, most investigations of sintering kinetics have been based on studies of the time dependence of neck growth and related parameters in powder compacts. Exceptions have usually been aimed at demonstrating the validity of a particular theory, for example the measurement of the concentration of one component of a solid solution in the interparticle neck to prove the contribution of diffusion /56/, or the observation of dislocation densities in necks by transmission electron microscopy to establish the contribution of plastic flow /57, 58, 59/. The principle of the method used by Kuczynski and other experimenters was to make metallographic measurements of the diameters between spherical particles and flat surfaces, sintered at different temperatures and for various times, thus obtaining a series of isothermal neck growth curves /60, 11/. Parallel wires have also been used to simplify experimental technique /4/. The mechanism controlling sintering was identified from the lime exponent of these isothermal curves. Unfortunately this method does not distinguish between those mechanisms having the grain boundary as the source of material for the neck and those with the particle surface as the material source, as with such an experimental arrangement it is not possible to make accurate measurements of the approach of particle centres. More recent investigators have favoured the study of compacts of spherical particles relating the approach of particle centres to the linear shrinkage of the compact and the neck widths by sectioning and metallography /17, 19; 9, 34, 61, 62; 122-125/. This is of course limited to those materials which can be sectioned and polished in a highly porous state. However, with the knowledge of both shrinkage and neck growth as a function of time, the
identification of the sintering mechanism can be made with a fair degree of certainty, so long as the theoretical models for the various possible mechanisms are correct /63/. Diffusion coefficients calculated from the results of such experiments have shown close correlation with values measured by other methods.

Such methods are limited to cases where the particle size is large enough for microscopic examination. Even the use of scanning electron microscopy only allows the examination of particles greater than 5 μm, due to the limitations imposed by polishing techniques. The application of conclusions drawn from experiments on larger particles to micron and sub-micron systems is questionable as the relative importance of different mechanisms may depend on both temperature and particle size /3, 4/. The use of larger particles demands higher temperatures for convenient rates of sintering to be measured. Hence it may be necessary to rely upon measurements of macroscopic properties of powder compacts which moreover are comprised of nonspherical particles with a large size distribution, dictated by the method of preparation. As the carbonitride powders studied in this investigation fall into this category, such methods will be discussed here in detail.

2.2.2. Shrinkage Measurements

For all thermally activated mechanisms which involve transport of material from the interparticle grain boundary to the neck, the rate of approach of particle centres can be expressed by an equation of the form:

\[
\left( \frac{\partial y}{\partial t} \right)_T = \frac{K}{T^2 y^n} \exp (-Q/RT)
\]  \hspace{1cm} (2.1)

where \( y \) = interpenetration of particles/particle radius, \( K \) is a constant related to the surface energy, molecular volume, particle diameter, and the pre-exponential of the activated process, \( Q \) is the actuation energy and \( n \) a numerical constant dependent on the mechanism. The equation applies to equisized, spherical particles and a single operative mechanism. It is usually assumed that the fractional shrinkage \( \Delta L/L \), of a compact of spherical particles is equal to \( y \), which is true for a regular array. Hence
so long as the conditions for the validity of equation (2.1) are fulfilled the initial sintering mechanism can be deduced from the values of n, K and Q determined by continuously measuring the shrinkage under isothermal conditions.

In practical powder compacts many of these conditions are not fulfilled so it is necessary to examine how well equation (2.1) can be applied to a real situation. The first problem arises from the fact that, even with equisized spherical particles $\Delta L/L$ does not always equal $y$. This has been observed experimentally /64, 65/ and is mainly attributed to the formation of new contacts and possibly the asymmetric sintering of some necks. The effect is greatest at the smallest values of shrinkage. Smaller particles are observed to exhibit behaviour closer to the ideal than large ones /65/.

Secondly, deviation of the particle shape from spherical will cause a variation in the observed value of $n$ for a particular mechanism. This is because the value of $n$ depends upon the interpenetration-neck volume and width continuity relations which will vary according to the exact contact geometry /66/. Bannister /67/ calculated the value of $n$ for volume and grain-boundary diffusion shrinkage mechanisms for a variety of contact geometries, and found values of $n$ between 0.99 and 2.02 for volume diffusion for example. Of greatest significance in determining $n$ is the exponent in the interpenetration-neck width relation, for all spherical geometries (including a sphere-plane geometry) the relationship may be approximated by:

$$y = K x^2$$

and for a pyramidal or conical contact:

$$y = K x.$$ 

The latter expression, which gives a higher value of $n$, will be valid for angular particles. Randomly shaped but non-re-rentrant particles are likely to have an average relationship similar to that for spheres. Hence a knowledge of the initial particle shape is a great aid in interpreting shrinkage data. Actual measurements of neck growth are, of course, even better, but difficult to obtain for the reasons just discussed.
The effect of a particle size distribution on initial stage sintering kinetics has been very much neglected in theoretical studies. Coble /68/ considered linear arrays of particles and concluded that the same behaviour should be observed for distribution of particle sizes as for a monodisperse system if the number average particle size is used. Johnson /69/ considers that a transient initial rapid shrinkage will occur, after which the behaviour will be the same as for equisized particles, although no theoretical grounds are given. Experimentally Coble's hypothesis is confirmed in /70/ for a binary mixture of alumina powder although Bacmann and Cizeron /71/ observed an increase in the value of $n$ for a broader size distribution for $\text{UO}_2$ powders.

Probably the greatest difficulty in the interpretation of shrinkage data lies in the possible contribution to neck growth by surface diffusion and other mechanisms which result in no shrinkage. In this case the assumed continuity relations will not apply and the measured value of $n$ will be altered. The problem is again removed if neck growth data are available. Failing this it may be possible to calculate the likely contribution of such competing mechanisms, although this requires accurate surface diffusion and vapour pressure data, which are not very often available. In the case of surface diffusion, which always has a lower activation energy than volume or grain boundary diffusion and is therefore relatively more important at low temperatures, a contribution may be detected if holding the compact at a temperature below that at which measurable shrinkage occurs has an effect on the subsequent sintering behaviour. The information from such an experiment is, of course, only qualitative.

Considerable support to conclusions drawn from the value of $n$ in equation (2.1) may be drawn from the activation energy $Q$ and the pre-exponential $K$. If volume diffusion, for example, is considered to be rate-controlling then $Q$ should correspond to the activation energy for volume diffusion of the material - in compounds that of the slower diffusing species. A much lower value would indicate a contribution from grain boundary diffusion. The value of $K$ should contain the pre-exponential factor $D_0$ for volume diffusion and so long as the particle size and surface energy are known or can be reasonably estimated it should be possible to calculate a value for the diffusion coefficient and compare it with that determined by other techniques.
2.2.3. Experimental Techniques

Conventionally, shrinkage measurements are carried out isothermally using a suitable dilatometer, a series of samples being used to cover a range of temperatures. The determination of the factors $K$, $n$ and $Q$ in equation (2.1) is then a straightforward matter. However, in practice a great deal of shrinkage occurs while the sample is being brought to temperature and thus much information is lost. The use of fast heating rates to overcome this problem is limited by the thermal conductivity of the sample and the rate at which the measuring instrument attains thermal equilibrium. A number of experiments /62, 72, 73, 74/ have therefore used a method in which shrinkage is measured while the sample is being heated at a controlled constant rate. This will be referred to as the CRH method.

Analysis of CRH experiments requires a way of relating sintering behaviour under isothermal conditions to that under CRH conditions. If the isothermal shrinkage rate be expressed by equation (2.1), and:

$$\frac{dT}{dt} = c$$

then

$$\frac{dy}{dT} = \frac{K}{cT} y^n \exp \left(-\frac{Q}{RT}\right)$$

hence

$$\int_0^y y^n dy = \frac{K}{c} \int_0^T \frac{1}{T} \exp \left(-\frac{Q}{RT}\right) dT$$

The right hand side of equation (2.2) cannot be integrated exactly but for $Q \gg RT$ an approximate solution exists giving:

$$\frac{y^{n+1}}{n+1} = \frac{KRT}{cQ} \exp \left(-\frac{Q}{RT}\right)$$

hence plotting $\ln \left(\frac{1}{y^{(n+1)}}\right)$ against $1/T$ gives a straight line with a slope of $-Q/(n+1)R$, the slope of the plot being insensitive to the value of $n$ which it is necessary to assume for the temperature exponent. If several experiments are performed at different heating rates then $n$ can be determined from a plot of $\log y$ against $\log c$ at constant temperature.
In the derivation of equation (2.3) it is assumed that the factors $K$, $n$ and $Q$ are independent of temperature over the range of integration. A change in the dominant mechanism with temperature may cause all of these factors to change. Any change in the value of $n$ will be seen as a curvature of the plot of $\log y$ v. $\log c$; the determination is independent of any change in the values of $K$ and $Q$. If the latter two factors are temperature dependent this will be seen as a curvature of the Arrhenius plot. Straight lines are, therefore, a very good indication of the dominance of a single mechanism over the range of temperature investigated.

Bengtsson et al. /78/ use a considerably simpler expression for the analysis of shrinkage data from WC power:

$$y = \left(\frac{K D}{T}\right)^n \left(\frac{T - T_0}{a}\right)^n$$

(2.3a)

This equation is, however, derived by substituting $T = T_0 + at$ in a sintering equation of the form:

$$y = \left(\frac{K D}{T}\right)^n t^n$$

(2.3b)

This is invalid since, because of the temperature dependence of $D$, equation 2.3b can only be valid for constant $T$. The more involved approach of Young and Culter is therefore necessary.

Another non-isothermal method, first used by Dorn/75/ has been applied to initial stage sintering studies on $UO_2$ /76, 73/ and copper /77/ to determine the activation energy, $Q$, from a single experiment. The rates of shrinkage of a powder compact immediately before and after a change in temperature $\Delta T$ from $T_1$ to $T_2$ are measured dilatometrically. For small $\Delta T$ the activation energy can be determined from the ratio of the two rates using the expression:

$$Q = \frac{R T_1 T_2}{\Delta T} \ln \left(\frac{y_1}{y_2}\right)$$

(2.4)

which is simply derived from equation (2.1), so long as the value of $y$ does not change significantly during the change in temperature.
The application of the method involves several problems. In order that \( y \) may not change significantly the heating rate must be rapid and the temperature change not too great. However, high heating rates may disturb thermal equilibrium in the dilatometer and thus introduce spurious length changes, and the sample itself must have time to come to thermal equilibrium at the new temperature. On the other hand, the temperature change must be sufficiently large for it, and the change in shrinkage rate, to be measured accurately. The need for a compromise in these conflicting requirements limits the accuracy of the method. Using a heating rate of 5 °C/min and a temperature change of about 20° (in the region 750–850°), Bacmann and Cizeron /76/ estimate the relative error in \( Q \) to be \( \pm 10 \% \). The greatest potential error in this type of experiment arises from the measurement of the shrinkage rate as this may be affected by transient expansions of the sample and apparatus due to the rapid change in temperature. The magnitude of these may be determined from "dummy runs" using non-shrinking samples. The error resulting from the change in \( y \) during heating or cooling may be reduced by taking the average values of \( Q \) determined from both positive and negative changes in temperature as in the one case the change results in an increase and in the other a decrease in the measured value of \( Q \). At low shrinkages where the shrinkage rates are fast and the relative change in \( y \) during the temperature change may be large, it is better to correct for the change in \( y \) by using the expression:

\[
Q = \frac{R T_1 T_2}{T} \ln \left( \frac{\dot{y}_1}{\dot{y}_2} \right) \frac{y_2}{y_1}^n
\]

if the value of \( n \) is known or can be reasonably estimated. For larger temperature changes the equation must be further modified by the term \( T_1/T_2 \) to account for the temperature dependence of the pre-exponential in (2.1):

\[
Q = \frac{R T_1 T_2}{T} \ln \left( \frac{\dot{y}_1}{\dot{y}_2} \right) \frac{y_2}{y_1}^n \frac{T_2}{T_1}
\]

The other source of potential error is of course the temperature measurement and this will depend on the instrumentation. If a thermocouple is used which is not, as in the ideal case, in contact with the specimen, then it will in general respond more rapidly to changes in the temperature of
its surroundings than the specimen. Hence after a rapid change in temperature the specimen temperature will lag behind the thermocouple temperature and therefore the actual value of $\Delta T$ will be lower than that recorded. The magnitude of this error is difficult to determine or estimate, whereas the errors in the measured values of $\Delta T$ and $T_1$, $T_2$ due to calibration uncertainties are straightforward to estimate.

The greatest advantage of the Dorn method compared with a series of isothermal shrinkage curves is that errors arising from slight differences in, for example, green density between specimens are eliminated. As the activation energy is obtained for a small temperature range then errors arising from a possible temperature dependence of activation energy are also eliminated. It can also be applied to later stages of sintering as it only requires that the shrinkage rate be an exponential function of temperature.

2.2.4. Specific Surface Measurements

Since the main driving force for sintering is the reduction of the total surface energy it is clear that the specific surface of a compact will decrease during the process and can therefore be used to study initial sintering kinetics. In particular the reduction in surface area can be related to neck growth which, as pointed out in the previous section, is a great aid in identifying the sintering mechanism in compacts of fine powder.

To a first approximation, valid for small necks relative to the particle diameter, the decrease in surface area is equal to twice the sum of the cross sectional areas of interparticle necks. In this case the average cross sectional area per neck is /79/:

$$ A = (S_0 - S_s) m N $$

(2.7)

where $S_0$ is the specific surface of the loose powder compact, $S_s$ the specific surface of the partly-sintered compact, $m$ the particle coordination number (number of contacts per particle) and $N$ the number of particles per gram.
In /79/ the actual value of $A$ is determined by calculating $N$ from the specific surface, assuming uniform spherical particles and $m$ from the shrinkage-specific surface relation. This method is not valid as it presupposes a particular neck growth-shrinkage continuity equation. In fact - it is not possible to determine $m$ from this data, but nevertheless the specific surface data are of use. If the continuity equation is of the form

$$A = ay^b$$  \hspace{1cm} (2.8)

then it is the value of $b$ which determines $n$ in equation (2.1) for a particular mechanism, and this can be found from a logarithmic plot of $(S_0-S_g)$ against $y$. The application of this method requires that $m$ remains constant, i.e. that no new particle contacts are formed, and as this can in no case be excluded results for low values of $y$ must be considered critically.

More precise relationships have been derived by German and Munir /80-83/ for the change in specific surface during the initial sintering of perfect spheres. A definite neck shape is defined of minimum surface area and the resulting surface area calculated as a function of neck diameter. Using Kuczynski's and other equations for the kinetics of neck growth they find that the surface area reduction can be expressed by equations of the form:

$$(\frac{S}{S_0})^\gamma = Kt$$  \hspace{1cm} (2.9)

where $\gamma$ varies from 1.1 for a viscous flow mechanism to 3.6 for a surface diffusion mechanism. In /83/ data for a variety of materials are analysed using this method and similar conclusions drawn as by other investigators using different methods. However, since the equations apply specifically to spherical particles then erroneous conclusions caused by other than spherical contacts may still be drawn so that the value of the increased precision afforded by an exact neck shape is questionable.

In all cases it is necessary to determine the specific surface with great accuracy, in particular that of the free powder as the results depend on the differences between these values. Results could also become confused by surface area reduction not associated with neck growth such as may arise
from the smoothing of irregular particle surfaces. The method should therefore only be used where precise measurements are possible and the particles are known to be smooth-surfaced.

2.2.5. Electrical Resistivity Measurements

The use of the electrical resistivity of a powder compact as a measure of neck growth is an attractive method which seems to have received little attention, probably due to uncertainties in interpreting the results. Zaverukha and Kislyi /84/, for example, found the method to be of great sensitivity, the resistivity of TiB$_2$ compacts changing by four orders of magnitude during sintering. However, no interpretation of the results is offered. Accary and Trouvé /85/ have applied the method to uranium carbide and copper, analysing the results on the assumption that the resistivity was directly proportional to neck cross-section. In the latter case the activation energy for volume diffusion deduced from these results was very close to the value determined from tracer measurements. The same method of interpretation was used by Lenel and co-workers in studies on silver powder /86/, where the effect of stress on the activation energy for sintering was studied. No proof of the validity of the method was given.

As an absolute measure of neck growth the technique does not appear to have been proved and potential sources of error such as the formation of new contacts, changes in the electrical resistivity of the material itself are legion. Furthermore, there is no conclusive way of relating resistivity to neck growth so that the method requires considerable further study for its potential to be realised /87/.

2.2.6. Intermediate and Final Stage

Studies of the later stages of sintering are almost exclusively confined to metallographic investigation of isothermally sintered compacts. The methods of preparation used depend upon the material and its density, the greatest difficulty being afforded by high porosity brittle ceramics.
The stereological parameters measured will depend upon the theoretical model being considered. Coble's model /24/ simply requires average grain diameters and total porosity whereas Johnson's /31/ requires the more complicated task of determining the average mean surface curvature.

The study of pores structures is feasible using other methods such as mercury porosimetry, but they seem to have received much less attention in the investigation of sintering.
Chapter 3
Uranium-Plutonium Carbonitrides and Related Nuclear Fuels

3.1. General Characteristics

Although the earliest power reactors have operated quite successfully using metallic uranium alloys as fuel, it was soon realised that ceramic fuels could offer improved reactor performance by operating at higher temperatures and possibly to higher burn-ups. For water-cooled reactors enriched uranium dioxide and uranium-plutonium dioxide are the only ceramic fuel materials to be considered due to the necessity for compatibility of the fuel with the reactor coolant in case of a fuel pin failure. In practice oxides have shown good in-reactor performance with a low degree of swelling, high fission gas retention, and compatibility with stainless steel and other cladding materials. For these reasons they have also been chosen for the first generation of fast breeder reactors. However, oxide fuels are limited in their potential power rating due to their poor thermal conductivity ($\sim 4 \text{ Wm}^{-1}\text{K}^{-1}$) and as in fast breeder reactors liquid metal (sodium or NaK) is used as the coolant, the necessity for compatibility with water becomes irrelevant, and alternative ceramic fuels with higher thermal conductivity become attractive /88/.

Uranium-plutonium monocarbide (U,Pu)C, mononitride (U,Pu)N and related compounds appear the most promising. For the sake of conciseness, these will be referred to as MX-type fuels where M is (U,Pu)$_{1-x}$ and X is (C,N)$_{1-y}$, x being between 0.8 and 0.85 for fuels of practical interest for fast breeders, although plutonium-free compositions (particularly UC) have been investigated for other types of reactor. All compounds of the MX type have the face-centered cubic NaCl structure and exhibit mutual solubility.

The thermal conductivities of MX compounds are considerably higher than for oxides ($20 \text{ Wm}^{-1}\text{K}^{-1}$) /88/ and they have the further advantage of a higher heavy atom density which allows a more compact reactor core with a lower inventory of fissile material. However, there are also a number of disadvantages with respect to oxides which are related to in-pile stability (swelling) fuel-cladding interaction and the relative complexity of
fabrication. The magnitudes of these problems depend on many factors and a detailed discussion is beyond the scope of this dissertation; however, a few points relevant to the fuel fabrication will be discussed.

Monocarbides have been the subject of the greater part of research into this family of compounds, complete reactor cores having already been loaded (e.g. the Hallam reactor in the USA). Fabrication on a large scale by means of carbothermic reduction of the oxides is reasonably straightforward, but due to the narrow range of stoichiometry the presence of second phases is almost impossible to avoid (see later discussion on phase relations). These may be detrimental to in-pile performance—e.g. the dicarbide, which is found as a Widmanstätten precipitate, accelerates carburization of the cladding in sodium-bonded pins by providing a fast diffusion path for carbon. In helium-bonded pins, swelling has been found to be very sensitive to temperature and temperature gradients making in-pile performance difficult to predict /89/. A further difficulty associated with the fabrication of carbides is the tendency of fine powders to oxidize—in air they are pyrophoric. This necessitates handling in very pure argon or nitrogen atmospheres with low oxygen and water vapour contents.

Mononitrides have a slightly lower thermal conductivity but a higher heavy atom density than carbides. They exhibit considerably better resistance to attack by water vapour, which facilitates handling and storage, together with better fuel-cladding compatibility and more predictable swelling behaviour /89/. However, nitrides produced by the economical carbothermic reduction process lose many of their advantageous properties due to carbon and oxygen impurities. A considerable disadvantage is the high cross-section for neutron capture in nitrogen-14 (the common isotope) which is detrimental to breeding characteristics /90/. The use of $^{15}\text{N}$ has been suggested but would be expensive to implement.

Carbonitrides with greater than 20% of MC substituted by MN are, for reasons discussed later, considerably easier to produce as single-phase material than carbides. Swelling behaviour is also more promising than carbides /89/ and the addition of nitride to carbide raises the melting point considerably, giving a maximum of 2910°C at a composition of about $\text{M(C}_{0.7}\text{N}_{0.3})$. This raises the maximum potential power rating of the fuel.
A carbonitride with the composition \( M(C_{0.8}N_{0.2}) \) has been the focal point of research into the swelling characteristics of MX fuels at the Transuranium Institute, and the fabrication of this compound is the subject of this dissertation. Since the amount of available data on matter transport and other relevant phenomena for this material is limited, this section will involve a discussion of all MX type materials.

3.2. Phase Relationships in the System U-Pu-C-N

Phase relations in this quaternary system are fairly complicated, so that it is only intended to discuss those aspects of the system which have a bearing on the fabrication of MX-type fuels. To this end the binary systems will first be described and more complicated compositions related to them.

The U-C phase diagram /91/ is shown in Fig. 3.1. It can be seen that up to fairly high temperatures the range of composition of UC is very limited. At typical sintering temperatures of around 1600°C the C/M atomic ratio may only vary between about 0.98 and 1.02 without precipitating uranium metal or higher carbides. Although below 1900°C the hyperstoichiometric carbide is in equilibrium with the sesquicarbide \( U_2C_3 \), the kinetics of formation of \( U_2C_3 \) are slow, so that the dicarbide is nearly always present at room temperature.

Plutonium similarly forms \( PuC \) and \( Pu_2C_3 \) of the same crystalline forms as UC and \( U_2C_3 \), although in this case PuC exists over a wider range of C/Pu ratios and is always hypostoichiometric with respect to carbon. PuC is mixible with UC in all ratio. At lower temperatures a further compound, \( Pu_3C_2 \) is formed but at sintering and reactor operating temperatures (above 634°C) the monocarbide is in equilibrium with the liquid metal. The U-Pu-C system is not well known in the temperature range 650-2000°C /92/, but the pseudo-binary \( (U_{0.85} Pu_{0.15})-C \) is very similar to the U-C system. An important difference is the stabilisation of the equiscarbide phase and a broadening of the range of stoichiometry of MC /93/ (Fig. 3.2).

With nitrogen uranium forms analogous compounds to those found in the U-C system (Fig. 3.4). \( UN_2 \) is not found in equilibrium with the mononitride,
Fig. 3.2: U-N Phase Diagram
however. No variation in stoichiometry of UN has been observed at room temperature and the compositional range remains narrow up to its melting point of 2830° /94/, varying at the most from N/U = 0.99 to N/U = 1.00 at 1500° to 200°C /95/. Plutonium only forms a mononitride with an uncertain range of composition. UN and PuN form a continuous series of solid solutions.

The form of the U-C-N ternary system in the temperature range 1400-1750°C is shown in Fig. 3.3 /96/. It can be seen that UC and UN form a continuous range of solid solutions which, on the hypostoichiometric side, are in equilibrium with liquid uranium and on the hyperstoichiometric side with uranium dicarbide, sesquicarbide and free carbon. As one of the components of the system is a gas, the equilibrium compositions will depend upon the nitrogen partial pressure. However, in the phase field U(C,N) + C the C/N ratio attained for a given nitrogen pressure depends on whether equilibrium is reached from the carbon or nitrogen rich side. This is because the carbon precipitated from the reaction UC + N → U(C,N) + C is in a higher state of activity than graphite /97, 98/.

The pseudo-ternary system given by the substitution of minor amounts of Pu for U differs from the U-C-N system mainly by the disappearance of the MC₂ phase field in the temperature range 1400-1650°C /103/ and the movement of point B to more nitrogen rich compositions. The partial diagram proposed by Potter /96/ is shown in Fig. 3.4.

The effect of the nitrogen pressure on equilibria in these systems is probably the most significant aspect from the point of view of fabrication technology. By use of sufficiently low N₂ pressures during preparation and fabrication the formation of higher carbides can be prevented. With nitrogen rich carbonitrides free carbon will be formed in any case. Equilibrium nitrogen pressures for the various phase fields have been determined by a number of experiments (e.g. /99, 100, 101/) and have also been calculated by Potter /96/.

Oxygen is substitutionally soluble in carbides and carbonitrides to a considerable extent, the maximum solubility in uranium carbide being 35 % "UO"
Fig. 3.3: U-C-N Ternary Phase Diagram 1400-1750 °C

Fig. 3.4: (U, Pu)-C-N Pseudo-Ternary System
and in plutonium carbide 65 % "PuO" /102/. Oxygen can therefore cause the appearance of higher carbides and carbon-rich carbonitrides whose M/C+N ratios are within the normal range of stoichiometry. Hence oxygen contents must be taken into account in the preparation of single-phased carbides. Oxygen solubility in mononitrides is considerably less, being a maximum of 7 % "UO" (1600-1900°C). Calculations /96/ show that the substitution of oxygen in carbonitrides in the presence of sesquicarbide result in an increase in the equilibrium nitrogen and CO pressures and a decrease in the Pu pressure.

3.3. Preparation

Carbides

The most frequently used methods for preparing uranium and uranium-plutonium carbides for use as nuclear fuels are based upon the following reactions:

a) \[ M + C \rightarrow MC \]
b) \[ M + CH_4 \rightarrow MC + 2 H_2 \]
c) \[ MO_2 + 3 C \rightarrow MC + 2 CO \]

Method (a) involves arc melting of the reactants in a skull furnace at around 2500°C under argon /104/. A product with low oxygen and nitrogen contamination can be produced, but the high vapour pressure of plutonium renders the method impractical for mixed carbides. The reduction of metal powder with hydrocarbon gases at 600-700°C results in a finely divided product that is suitable for subsequent fabrication by sintering without milling /105, 106/. The metal powder is initially prepared from the bulk metal by hydriding at around 200°C followed by dehydriding at 400°C under vacuum. A single phased product with < 1000 ppm oxygen and < 300 ppm nitrogen is obtainable.

However, since methods (a) and (b) require metallic uranium and plutonium as starting materials, these methods are at an economic disadvantage to method (c), as oxides are the normal end product of extraction and reprocessing procedures. The usual starting material will be either hyperstoichiometric
UO$_2$ or U$_3$O$_8$ which is first reduced to stoichiometric UO$_2$ by adding an appropriate excess of carbon to the reaction mixture. The reduction proceeds rapidly at 850°C as:

$$\text{U}_3\text{O}_8 + \text{C} \rightarrow 3 \text{UO}_2 + \text{CO}_2$$

The use of U$_3$O$_8$ has the advantage that its composition is well defined and therefore the correct amount of carbon can be readily determined /107/. For mixed (U, Pu) carbides the appropriate amount of PuO$_2$ is added.

The oxide and carbon are first mixed in the correct proportions and either pressed into pellets which are reacted at between 1300° and 1600°C under vacuum or in flowing argon, or alternatively formed into spheroids or a granulate and reacted in a fluidised bed. The progress of the reaction is routinely monitored by measuring the CO content of the exhaust gas stream.

The monocarbide is formed at the interface between oxide and carbon, and the reaction rate is controlled by the diffusion of carbon through this layer and by the carbon monoxide partial pressure /108/. Hence the reaction kinetics are favoured by finely divided and intimately mixed reactants and conditions where carbon monoxide removal is rapid. These requirements may be conflicting as in high density compacts of fine particles CO release may be retarded. It has been found that the CO partial pressure is only significant when greater than about two orders of magnitude below the equilibrium pressure /107, 108/. Where pressures are lower first order reaction kinetics have been observed with an activation energy of 92 kcal /109/.

The reaction product may be arc-cast into the final product or after ball-milling cold-pressed and sintered. Although with the former method it is easier to achieve low oxygen and nitrogen contaminations, and, of course, high density. However, in the case of plutonium-containing materials Pu losses may be too high in the case of arc-casting, and criticality requirements limit the size of the melt and hence the use of the method on a large scale. For these reasons sintering, which in view of the lower temperatures necessary is more economical, is the preferred method for large scale production.
A number of other techniques for producing carbides are reported in the literature. These include the reaction of uranium and carbon in solution in a liquid zinc-magnesium alloy at 700-800°C. Uranium carbide precipitates and the alloy is removed by vacuum distillation at 900°C. However, the products are hypostoichiometric in carbon (C/U = 1.05-1.10) and the process is not practicable for the production of mixed carbides as the metal solvent composition required for plutonium carbide precipitation has too low a solubility for uranium. The reduction of uranium halides with a reducing metal such as silicon or aluminium in the presence of carbon has been investigated with a view to producing carbides with a low oxygen content /110/ but the method has an unacceptably low yield of carbide (80%). Other investigators have tried to improve the production of intimate oxide-carbon mixtures with a view to increased continuity of production. Examples of this include spraying uranyl nitrate and sugar solution into a reaction vessel at around 700°C, where the reagents decompose to give an oxide-carbon mixture /111/. Alternatively carbon black may be incorporated into microspheres produced by the sol-gel method, which allows carboreduction and sintering at lower temperatures than usual, but in which the carbon content is difficult to control /112/.

**Nitrides**

On a laboratory scale the most common method of producing nitrides is the ex-metal route, in which hydriding at around 250°C is followed by reaction of the resulting fine powder with nitrogen at 400°C to 850°C /90, 113/. The product of this reaction is the sesquinitride (except in the case of plutonium, where the monocarbide is formed), which is decomposed to the mononitride by vacuum heat treatment between 800°C and 1500°C. The resulting reaction product can be sintered without subsequent treatment and has a low oxygen contamination. Uranium metal may also be directly nitrided but the resulting product must be milled before sintering and the method is not amenable to plutonium containing nitrides.

For preparation on a commercial scale, as with carbides, a cheaper raw material is required and hence carbothermic reduction of oxides in the presence of nitrogen is considered to have the greatest production potential. The reduction, which is performed in a similar manner to that described for
carbides, can be described by the following, much simplified, reaction:

\[
\text{UO}_2 + 2 \text{C} + \text{N} \rightarrow \text{UN} + 2 \text{CO}
\]

The kinetics of this reaction have been studied by Lindemer /114/. First an oxynitride, with the fluorite structure of \(\text{UO}_2\), is formed together with a carbonitride. Carbon transport is aided by HCN, which is present in traces. After the production of a continuous carbonitride interface the reaction is controlled by the solid-state diffusion of carbon. The reaction kinetics are dependent upon the amount of free carbon present and in practice with stoichiometric additions of carbon the reaction does not go to completion and traces of oxide (saturated with nitrogen) are found in the final product together with carbon in solid solution in the nitride /115/. Carbon and oxygen contents of < 2000 ppm are attainable /116/. By milling, cold pressing and sintering dense pellets of up to 95 % theoretical density can be fabricated from the reaction product.

Alternative routes for the production of nitrides have been investigated although none seems to be a serious competitor for carbothermic reduction. The chlorination of the oxide to form \(\text{UCl}_4\), followed by reaction with ammonia has been tried /106, 113/, as has reduction of the iodide with a solution of sodium in anhydrous ammonia at room temperature /117/. The iodide is produced from the oxide by chlorination with \(\text{CCl}_4\) at 900°C giving, for example \(\text{PuCl}_3\), followed by reaction and \(\text{NH}_4\text{I}\) at 400°C.

**Carbonitrides**

Carbonitrides may of course be prepared by arc melting uranium metal and carbon under a nitrogen atmosphere or by combining appropriate proportions of carbide and nitride powders and sintering the mixture. These methods are only of real interest on a laboratory scale except perhaps the co-sintering of \(\text{UC}\) and \(\text{PuN}\) powders to produce \((\text{U}_{0.8} \text{Pu}_{0.2})(\text{C}_{0.8} \text{N}_{0.2})\) which has the advantage that the uranium carbide may be prepared outside the plutonium facility /107/. However, high densities are difficult to achieve by this method.

More straightforward is the production of the carbonitride by the same
process described for nitrides by carbothermic reduction using an appropriate amount of carbon. For carbonitrides of a high nitrogen content there is no difficulty in obtaining a single phased product as carbonitrides with more than about 20% MN are in equilibrium with free carbon and nitrogen gas over a wide range of pressures in the temperature range used. In the case of carbon rich carbonitrides, however, the nitrogen pressure must be carefully controlled to avoid the formation of higher carbides. The problem extends in practice up to a C/N ratio of about 0.4/107/.

For these carbon-rich carbonitrides a variant of this procedure has been found to be of assistance/107/. Here carboreduction and nitriding are carried out in two stages, the product of the first stage being a single-phased oxycarbide. This is then nitried at 1600°C under a flowing nitrogen-argon mixture with a nitrogen partial pressure of around 1-10 Torr. Higher nitrogen pressures result in the formation of higher carbides, however it is the ability to control the formation of second phases via the nitrogen pressure which gives these low-nitrogen carbonitrides their advantage in fabrication over carbides.

3.4. Sintering

Although a number of investigators have concerned themselves with the fabrication of pellets of uranium carbide and related materials by sintering, the greater part of them have concerned themselves with the effects of various process parameters solely on the final density, composition and microstructure. Only one or two have studied the kinetics of the sintering process in order to determine the rate-controlling mechanisms.

Accary and Trouvé/85/ studied the sintering kinetics of uranium carbide powders by following the change in electrical resistance of power compacts during isothermal sintering. The powders were produced by an unusual method in which a uranium carbide-uranium cermet was first heat-treated to spheroidize the carbide phase, followed by removal of the uranium by reaction with hydrogen. The resulting particles were spherical and about 50 μm diameter. By assuming that the compact resistance was inversely proportional to the mean interparticle neck cross-section they found that, at sintering
temperatures between 700 and 1000°C, the results were consistent with a
neck growth law of the form

\[ x^7 = K t \]

and an activation energy for the process of 72 KCals. The neck growth law
would indicate a surface diffusion mechanism /12, 15/ but because the
activation energy is near that for volume diffusion in stoichiometric
carbides (see Section 3.5) the authors concluded that the rate controlling
mechanism was volume diffusion from the free particle surface through a
thin, constant cross-section near the surface. This result is somewhat
surprising as available diffusion data indicates that at 1000°C surface
diffusion should be about 10^8 times faster than volume diffusion. Even with
the greater available cross-section for volume diffusion of the order of
microns thick rather than angstroms, surface diffusion should still be
dominant. It must be concluded that either Accary and Trouvé's determina-
tion of the activation energy is inaccurate, due to the considerable
scatter in their results (although as the only available value of the
activation energy for surface diffusion is around half the measured value,
this seems unlikely), or that the volume and surface diffusion data avail-
able (which were obtained at considerably higher temperatures) are not
applicable.

It is in any case doubtful whether these results are relevant to the sinter-
ing of milled carbide powders for several reasons:

1) The spherical powder particles are considerably larger than those
found in practical sintering processes.

2) The sintering temperatures are very low - at these temperatures
shrinkage is not observed at all in "normal" carbide powders.
   It is not recorded in /85/ whether shrinkage of the compacts was
   observed.

3) The composition of the powder is not given except for 4.6 % carbon.
   From the production route the composition is almost certainly hypo-
   stoichiometric unless oxidation occurred between manufacture and
   sintering.
One important factor, however, is that, in this case at least, neck growth takes place at a temperature well below those temperatures at which shrinkage is observed.

McLaren et al. /118/ obtained isothermal shrinkage data at various temperatures for milled arc-melted uranium carbide powder compacts. They found that, at 1300°, 1600° and 1500°C the linear shrinkage was related to time by

\[
\left( \frac{\Delta L}{L} \right)^{3.5} = K t \quad \left[ \frac{dy}{dt} = \frac{K'}{y^{2.5}} \right]
\]

and that the apparent activation energy for shrinkage was 112 kcaI. The range of shrinkage involved (up to 10%) was too great to enable conclusions to be made to the mechanism of initial stage sintering from the value of the time exponent. However, so long as the material structure is only dependent upon the density the activation energy measured should represent that of the mass-transport mechanism for intermediate stage sintering. Caution should however, be excercised in analysing experiments of this type: in work on UO₂ an unexpectedly high apparent activation energy was found to be attributable to a difference in grain size between pellets of the same density sintered at different temperatures /119/. The value of 112 kcaI is considerably higher than the 84 kcaI /23/ determined for uranium volume diffusion in stoichiometric UC below 1800°C, but compares with values for plutonium diffusion (normally faster than U-diffusion) in hyperstoichiometric "technological" carbides /120/.

The data could not be fitted to Coble's /24/ intermediate stage sintering model for volume diffusion.

A number of other workers have investigated the influence of process parameters such as milling conditions, type of binder, composition of starting powder and sintering atmosphere on the final density of power compacts, without looking at the kinetics of the sintering process. A general discovery was that the purity of the atmosphere (with respect to oxygen and water contents) under which the powders were prepared and stored, is very significant, contents of these impurities of <100 ppm being necessary to achieve high sintered densities /118/. Potter /121/ studied systematically
the influence of oxygen contamination of the final density of uranium and
uranium-plutonium carbide powder compacts, and found in linear decrease in
density with increasing oxygen content, as measured after the sintering in
flowing argon. Other authors, for example /122/, have found that, whereas
oxygen remaining after carbothermic reduction has little influence on final
density, the effect of oxygen pick-up during powder processing in storage
is considerable, suggesting that a surface contamination with oxygen impedes
densification.

The observation that wet milling under xylene /118/, or with the addition
of stearic acid binder/lubricant /119/, increases sintered densities confirms
this view, as these additives could be expected to protect the powder sur­
face from oxidation.

A phenomenon encountered by all investigators is the reduction of carbon and
oxygen contents during sintering with the production of carbon monoxide
(except in the case of powders with minimal oxygen contents). A relationship
is found between the final sintered density and the compositional change
during sintering - high density pellets having higher carbon and oxygen
contents than low density pellets /116/. This is clearly due to the relative ease of escape of CO from more porous pellets, which lowers the CO
partial pressure inside the pellet and encourages the reaction. This in­
creases the difficulty in finding correlations between powder composition
and sinterability, as the oxygen content of the powder is difficult to
determine due to the likelihood of oxidation during handling.

Carbonitrides and nitrides have been the subject of relatively few in­
vestigations. Russian workers /124/ report the sintering of carbonitride
powders, produced by carbothermic reduction in a fluidised bed, to densities
of 93-95 % at high temperatures (3 hours at 1900°C), apparently without
milling. No mention of the influence of process variables is made. In
reference /113/ the co-sintering of ex-metal uranium carbide and nitride
powders to densities of 90-95 % is reported, with no influence of the
carbide/nitride ratio on the density of the final product being observed.
In studies on uranium nitride produced by the hydride-nitride route /125,
126/ it was found that the final density depended upon the nitrogen partial
pressure under which the sintering was carried out. Lower nitrogen pressures
gave higher final densities, which would not be expected from the known increase in diffusion rates with increasing nitrogen pressure. This effect is not explained by the authors.

At the Transuranium Institute carbonitrides (with 15-20 % Pu) have been produced on a more or less routine basis for several years. After ball-milling with stearic acid, pellets with high green densities (70-75 % theoretical) have been sintered to densities of > 95 % in 1 hr at 1620°C under vacuum. However, despite careful attention to the reproduction of all process variables the sintering behaviour is not always predictable. Occasional batches exhibited poor sinterability for no obvious reason. It is for this reason that it is considered that a quantitative investigation into the sintering kinetics of these materials is necessary.

3.5. Diffusion

Apart from the cases where plastic flow and vapour transport are responsible for sintering, it is controlled by solid state diffusion. Hence a knowledge of diffusion mechanisms and rates in the material of interest is essential for the interpretation of sintering experiments. Since the largest amount of experimental work on diffusion in MX-type materials has been performed on uranium carbide this will be discussed in detail, with a summary of the effects of substitution of plutonium, nitrogen and oxygen.

A process such as sintering will depend upon the effective molecular diffusivity, which will be a function of the self diffusion coefficients of the individual species in the material, given approximately by the expression:

$$D_{\text{eff}} = \frac{D_A D_B}{D_A + D_B}$$

for a two-component compound of type AB /127/. Hence, when one species is much slower than the other then the effective molecular diffusivity will be that of the slower moving species. This is the case in uranium carbide where the large uranium atom is very much less mobile than the small carbon atom. Only in the case where uranium transport by a faster mechanism (e.g.
through the vapour phase) is feasible could carbon diffusion be rate controlling, so that when considering shrinkage-producing mechanisms a discussion of metal atom diffusion is sufficient.

Studies of uranium diffusion in uranium carbide by different investigators show large discrepancies in values for the diffusion coefficient. According to a recent review /23/ these are due to the effects of variations in the carbon to uranium ratio and impurities in the materials studied, so that only results for well-characterised material are of use.

Diffusion data for polycrystalline uranium carbide show an apparent increase in activation enthalpy, $\Delta H$, with temperature, which is not observed in very pure single crystals which exhibit a constant, high value /128/. It is concluded that at high temperatures diffusion is dominated by an intrinsic, single vacancy mechanism with $\Delta H = 141$ kcaI, and at lower temperatures by an extrinsic, impurity controlled mechanism with $\Delta H = 84$ kcaI. In the high temperature intrinsic region (>1900°C) the effect of variations in metal to non-metal ratio (M/X ratio) has been studied /129/ showing a linear increase in $\Delta H$ from 87 kcaI at X/M = 0.93 to 175 kcaI at X/M = 1.07 or greater. The values of the diffusion coefficient fall and rise again with increasing carbon content, an as yet unexplained phenomenon. Impurities have been shown to enhance high temperature diffusion, but the exact nature of their effect, and that of the X/M ratio at temperatures in the sintering range (1500-1700°C) is not understood /23/.

Plutonium in (U, Pu)C diffuses somewhat faster than uranium in uranium carbide due to its smaller atomic radius and the larger lattice spacing (which may also increase uranium diffusion in (U, Pu)C although this is not known /23/). Since the same effects of impurities and X/M ratio are observed at high temperature then the mechanism of plutonium diffusion is probably the same as for uranium.

Substitution of nitrogen for carbon reduces metal atom diffusivities but the effect is not great for less than 50% substitution. Diffusion in pure nitrides is difficult to measure due to the effects of temperature and nitrogen pressure on composition (a variation with M/X ratio seems to exist /23/), but in general metal atom diffusion is slower than in corresponding
carbides, with an increase in diffusivity with increasing nitrogen pressure.

Some studies on plutonium diffusion in hyperstoichiometric (U,Pu)(C,N) similar to that investigated here have been performed in the temperature range 1300°-1800°C. Two materials were investigated which differed mainly in the amount of metallic impurities. Their diffusion coefficients were found to be given by /130/.

\[ D_1 = 0.15 \exp \left( -\frac{105,000}{RT} \right) \text{ cm}^2 \text{ sec}^{-1} \]

\[ D_2 = 0.11 \exp \left( -\frac{118,000}{RT} \right) \text{ cm}^2 \text{ sec}^{-1} \]

where \( D_1 \) is for the material with higher impurities. This also showed an unexplained discontinuity in the diffusion coefficient at about 1400°C, a phenomenon which was also observed, at temperatures between 1370° and 1630°C, in some, but not all, of a group of mixed carbides (with nitrogen and oxygen impurities) studied by the same investigators.

Grain boundary diffusion coefficients are difficult to measure and have not been extensively studied. For stoichiometric uranium carbide the grain boundary diffusion coefficient has been determined to be:

\[ D_{gb} = 0.18 \exp \left( -\frac{74,900}{RT} \right) \text{ cm}^2 \text{ sec}^{-1} \]

and for hypostoichiometric uranium carbide with \( X/M = 0.93 \):

\[ D_{gb} = 3.58 \exp \left( -\frac{68,700}{RT} \right) \text{ cm}^2 \text{ sec}^{-1} \]

by analysis of tracer data /131/, which show \( \Delta H_{gb} \) within the expected range of 0.5-0.8 times the volume diffusion activation enthalpy /132/.

The only value for the surface diffusion coefficient available is for hypostoichiometric uranium carbide by grain boundary grooving giving /133/

\[ D_s = 5.6 \times 10^{-8} \exp \left( -\frac{31,400}{RT} \right) \text{ cm}^2 \text{ sec}^{-1} \]

As previously stated, non-metal atom diffusion is unlikely to be rate-controlling in sintering, and in the case of nitrogen difficult to measure.
It is interesting to note, however, that the carbon diffusivity is also dependent on the X/M ratio and to impurities (O,N) on the non-metal lattice. Activation energies between 43 and 94 KCals have been determined and carbon diffusion is always slower than metal atom diffusion.

3.6. Creep

Creep is a phenomenon closely related to sintering and is likely to be controlled by similar mechanisms - for example volume diffusion controlled sintering may be regarded as a special case of Herring-Nabarro creep /134/ and plastic flow mechanisms are analogous to dislocation creep in the inter-particle neck. A review of creep in carbides and nitrides is therefore relevant to the interpretation of sintering experiments, particularly in view of the scarcity of data on sintering in these materials.

Primary creep is particularly relevant to sintering but has been the subject of few investigations. In a study by Matthews /135/ on slightly hyper-stoichiometric uranium carbide single crystals, that contained a small amount of dicarbide, two types of behaviour were observed. In the first case the dicarbide precipitate was retained and a power law dependence of strain rate on time was observed with $\dot{\varepsilon} \propto t^{-0.66}$, up to 2 % creep strain. In the other case the dicarbide disappeared during testing, where larger primary creep strains were observed. In stoichiometric polycrystalline samples /136/ a power law was also found with $\dot{\varepsilon} \propto t^{-0.4}$, where an activation energy of 80 KCals was observed, corresponding to carbon diffusion or uranium grain boundary diffusion.

Secondary, or steady-state creep, has received considerably more attention. Most studies have been performed on uranium carbide with much less attention having been paid to plutonium-containing materials, carbonitrides and nitrides. The studies are notable for the very wide variety of kinetics which have been observed by different investigators.

It is usual to fit steady state creep data to an empirical equation of the form:
\[ \dot{\varepsilon} = A\sigma^n \exp(-Q/RT) \]

where \( \dot{\varepsilon} \) is the strain rate, \( \sigma \) the stress, \( Q \) an activation energy and \( n \) a numerical constant. Theoretical models predict a variety of values for \( n \) and \( Q \) for different mechanisms; Routbort /23/ publishes a table giving values of \( n \) between 1 and 4.5, with \( Q \) being equal to the activation enthalpy for the appropriate diffusion mechanism. (It should be mentioned that creep models exist which predict other than a power law stress dependence, e.g. /137/.)

Published data for uranium carbide and uranium-plutonium carbide show values of \( n \) from 0.35 to 6 and \( Q \) from 38-240 \( \text{kcal/mol} \) so it is clear that a number of different mechanisms may operate depending on the exact state of the material and the conditions of the experiment, as discussed below. In particular stoichiometry, metallic impurities and temperature and stress ranges seem important in determining the rate-controlling mechanisms. With regard to stoichiometry, many investigators have used material in which higher carbides or a metallic phase must have been present in the temperature range which they investigated. The values of activation energy determined in these cases are suspect because the amounts of second phase may vary with temperature.

Three investigations on single crystals of uranium carbide, in which only dislocation mechanisms can be of importance due to the large diffusion distances involved, showed high values of \( n \) (6-12) and a wide range of activation energies - from 69 to 135 \( \text{kcal/mol} \) /138/. In each case a different stress range was involved, the highest activation energy being reported for the highest stress range. Thus even in this straightforward case a number of rate-controlling mechanisms must be involved, probably dislocation climb with diffusion in the dislocation core at lower stresses and climb controlled by bulk diffusion at higher stresses /139/.

In the case of polycrystalline samples, which have been the subject of most studies, the variety of results is even greater. The effect of varying stoichiometry has not been studied systematically /23/ but one can roughly distinguish between results on hypo- and hyper-stoichiometric material. Hypostoichiometric samples show creep rates which may be up to three or
four orders of magnitude higher than in carbon-rich material /23/. Low activation energies of around 45 KCal.s seem to be typical (e.g. /140/) together with low values of n (1.0 in /140/). Control of creep in these cases has been attributed to carbon monovacency diffusion, uranium transport being effected by dissolution of free uranium from the grain boundaries /141/.

Hyperstoichiometric polycrystalline carbides seem to show two types of kinetics. Two studies covering a fairly wide range of stress (13-54 MN/m²) and the temperature range 1100-1400°C gave n = 2.3 and 1.8, and Q = 44 and 49 kcal /142, 143/. However, other investigators /138, 144, 145/, although they found similar values of n (2-2.5) reported much higher activation energies, between 115 and 141 kcal and in one case /144/ a temperature dependent activation energy varying from 80 to 240 kcal. The former two investigators used arc-cast material and the latter three sintered samples but in all cases the carbon contents were such that they should have been single phased. The values of n suggest a grain boundary sliding mechanism as proposed by Langdon /146/, but the difference in activation energies has not been explained.

Other investigators have used material in which the carbon content was so high as to certainly have caused the presence of higher carbides in their samples. In one case /141/ a distinction could be made between a low temperature, low stress mechanism with Q = 69 kcal and n = 1.8, and a high temperature, high stress mechanism where Q = 142 kcal and n = 4.18. However, the variation in carbon content between samples used in this investigation makes the original analysis suspect /138/.

Investigations in slightly hyperstoichiometric plutonium-containing carbides /142, 145, 147/ all showed higher activation energies (100-126 kcal) and n = 1.4-2.4, where the activation energies compare well with the activation enthalpies for volume diffusion in mixed carbides measured by Matzke and Bradbury /130/. All experiments were performed on sintered materials. Strain rates for Pu-containing carbides are generally faster than for uranium carbide according to Routbort /23/ although Killey /140/ found no difference.

Studies on nitrides are difficult to interpret because of the dependence of
composition with temperature leading to doubts as to the deduced values of activation energies (values between 60 and 100 KCals are tabulated in /23/). In general, contrary to the indications of diffusion data, nitrides creep faster than carbides. A study on carbonitrides of various nitrogen content showed a rapid increase in creep rate going from UC to UC\textsubscript{0.78}N\textsubscript{0.22} with a minimum in creep rate for UC\textsubscript{0.28}N\textsubscript{0.72}. No activation energies were determined.

In both carbides and nitrides impurities have been found to influence creep, in particular Zr, Ni, and W. A detailed study of the effect of various concentrations of nickel was made by Hall /138/ who found that small additions of nickel up to 0.1 % by weight increased creep rates by a factor of up to $10^3$, depending on the amount added. Interesting results were also observed for larger additions (1 %) where very large and rapid primary strains were observed, attributed to a "soft" second phase at the grain boundaries. Subsequently, particularly high second stage activation energies were observed (up to 250 KCals) for which no explanation was offered.

Zirconium and tungsten, on the other hand, decrease creep rates, activation energies up to 155 KCals being measured /148/, although Ni, W, and Zr all have been observed to enhance diffusion. A possible explanation is the formation of a dispersed second phase which impedes dislocation motion.

To conclude: due to the lack of systematic study, particularly into the influence of stoichiometry it is not possible to present an overall description of the effects of the various significant parameters on the kinetics of creep. All that is certain is that no single mechanism controls creep except under very limited conditions.
Chapter 4
Experimental Procedures

4.1. Plan and Organisation of Experiments

During the course of the project the sintering kinetics of four batches of material were investigated. However the first three batches, with the numbers N45, C46, and C39 can be regarded as orientation experiments and only results for the last batch are reported and discussed fully. This batch had the number C63.

After preparation of the powders, investigations into their particle size distributions were made using a number of techniques. The shrinkage behaviour of compacts of these powders were then investigated under a variety of conditions, concentrating on the initial stages of sintering. In the case of batch C63 the influence of a heat-treatment under hydrogen on the subsequent sintering kinetics was also investigated. During the later stages of the project a scanning electron microscope in an $\alpha$-active facility was available and used to investigate structural development during the initial stages. Chemical analyses and X-ray diffractometry were also used to study compositional changes during sintering.

4.2. Preparation of Material

The carbonitride powders, of nominal composition $(U_{0.8}, Pu_{0.2})(C_{0.8}, N_{0.2})$, were made by the technique of carboreduction of a mixture of uranium and plutonium oxides. The raw materials used were:

- $U_3O_8$: (from USAEC) specific surface $9.6 \text{ m}^2\text{g}^{-1}$
- $PuO_2$: produced by decomposition of oxalate, $8-10 \text{ m}^2\text{g}^{-1}$
- carbon: Kropfmühle "AF Spezial" of 99.95% purity with $9.8 \text{ m}^2\text{g}^{-1}$. This was dried at $200^\circ\text{C}$ before use.

These were mixed in the following proportions by weight:
using a mechanical blender. Particular care was exercised during the weighting and mixing to ensure homogeneity of the mixture and to avoid loss of material. Total batch sizes were of the order of 0.5 kg.

The oxide-carbon mixture was then pressed into discs approximately 20 mm in diameter and 5 mm thick, using a force of 0.25-3 MN (2.5-3 tonnes). The densities of these discs were around 3.5 Mgm⁻³ (ca. 30 % dense). To ensure microhomogeneity of the mixture, they were crushed, passed through a 125 μm sieve, and re-pressed.

In the case of batch C39 the influence of varying the pressing force between 0.22 and 0.6 MN on the composition after carbothermic reduction was investigated, but no significant difference could be determined.

Carbothermic reduction was carried out in a dynamic vacuum of between 10⁻¹ and 10⁻² Torr in an induction furnace equipped with a CO gas analyser in the exhaust gas stream. The temperature programme used and the resulting CO evolution are shown in Fig. 4.1. Chemical analyses showed the reaction product to have the following composition:

\[
\begin{align*}
\text{U}_3\text{O}_8 & : 70.6 \% \\
\text{PuO}_2 & : 17.6 \% \\
\text{C} & : 11.8 \%
\end{align*}
\]

Nitriding was performed at 1600°C for 20 hours in a flowing nitrogen-argon mixture with a nitrogen partial pressure of 2 Torr. The gas flow rate was 120 l/h. Further CO-evolution occurred during this step as shown in Fig. 4.2. The nitriding was followed by a short vacuum (10⁻³ Torr) treatment at 1500°C. The composition of the resulting carbonitride was (again for C63):
using a mechanical blender. Particular care was exercised during the weight-
ing and mixing to ensure homogeneity of the mixture and to avoid loss of
material. Total batch sizes were of the order of 0.5 kg.

The oxide-carbon mixture was then pressed into discs approximately 20 mm in
diameter and 5 mm thick, using a force of 0.25-3 MN (2.5-3 tonnes). The
densities of these discs were around 3.5 Mg m\(^{-3}\) (ca. 30 % dense). To ensure
microhomogeneity of the mixture, they were crushed, passed through a 125 μm
sieve, and re-pressed.

In the case of batch C39 the influence of vary the pressing force between
0.22 and 0.6 MN on the composition after carbothermic reduction was in-
vestigated, but no significant difference could be determined.

Carbothermic reduction was carried out in a dynamic vacuum of between 10\(^{-1}\)
and 10\(^{-2}\) Torr in an induction furnace equipped with a CO gas analyser in
the exhaust gas stream. The temperature programme used and the resulting
CO evolution are shown in Fig. 4.1. Chemical analyses showed the reaction
product to have the following composition:

- U + Pu: 95.12 %
- Pu: 18.42 %
- C: 4.316/4.474 %
- N: 0.05 %
- O: 0.43 %

(in the case of the batch, C 63, used for the principle series of
experiments)

Nitriding was performed at 1600°C for 20 hours in a flowing nitrogen-argon
mixture with a nitrogen partial pressure of 2 Torr. The gas flow rate was
120 l/h. Further CO-evolution occurred during this step as shown in
Fig. 4.2. The nitriding was followed by a short vacuum (10\(^{-3}\) Torr) treatment
at 1500°C. The composition of the resulting carbonitride was (again for C63):
Temp. °C

CO

CO₂

Carrier gas
N₂ 125 cm³/h

time, hours

co/co₂
Vacuum

CO

carrier gas

N₂ 120 l/h

time, hours

0 5 10

0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600

Temp. °C

Temp.
After breaking-up the reaction products in a "coffee grinder", 1.00 % by weight of stearic acid was added and the mixture was milled in a rotary ball mill. At intervals the milling was interrupted, the powder allowed to cool for several hours (a temperature of 40-50°C was attained during milling), and sample pellets pressed. The densities of these compacts were determined by micrometer measurements and weighing.

With increasing milling time the densities of the compacts increased, reaching a maximum and then falling slightly, as shown in Fig. 4.3, which also shows the sintered density after a fixed sintering programme as a function of milling time. The basic form of this curve was the same for each batch, but the rate of milling varied considerably according to the amount of charge. A point was then reached in milling after which the powder was found to cling to the sides of the mill and balls, and no further change in powder properties could be determined. Larger batches of powder were removed from the mill and pressed into pellets before the maximum density was reached, at the maximum, and at the end of milling.

The pellets were cylindrical of approximately 6.5 mm diameter and 7 mm long. A double-ended hydraulic press was used with a pressing force of 0.5 MN (14 GNm⁻¹).

All powder handling operations after carbothermic reduction were carried out in nitrogen gloveboxes, in which the water vapour and oxygen contents were kept below 100 ppm. The pellets were stored in gas-tight containers in this glovebox chain.
Fig. 4.3: Change in green and fired density with ball-milling time

% Theoretical Density

Milling Time, hours

Fired density (6.5h at 1700°C)

Green density
4.3. Powder Characterisation

The determination of the powder particle size and size distribution, which was considered necessary for the evaluation of the shrinkage data, proved to be a difficult task. A number of methods were tried but the possibilities were limited, not only by the fact that the particle size proved to lie around one micrometer diameter, a particularly difficult size range, but also by the lack of apparatus in $\alpha$-active facilities. Realistic tests of new techniques could not be performed "inactive" as substitute carbides such as UC are pyrophoric and must be handled in inert atmospheres in any case.

The following techniques were evaluated:

- Optical microscopy
- X-ray diffraction line broadening
- Scanning electron microscopy

The procedure and results for each are discussed together.

Optical Microscopy

Samples from batch C39 after 23, 70 and 80 hours milling were analysed with the aid of this method. Small quantities of powder were dispersed in xylene and deposited on a microscope slide. Photomicrographs taken at a magnification of 160X were analysed with a Quantimet automatic image analyser, which measured more than 500 particles for each sample. The results are presented as a series of histograms in Fig. 4.5. The mean equivalent spherical diameters on a projected area basis were:

- 23 h: 3.75 $\mu$m
- 70 h: 2.74 $\mu$m
- 80 h: 1.94 $\mu$m

However, the shape of the histograms, showing a sharp cut-off at the limit of resolution of the microscope, indicates that a large number of particles may lie below this limit. The method was therefore not used for subsequent batches.
Fig. 4.6: Particle Size by Scanning Electron Microscopy

Total 296 particles

Particle diameter, μm

Frequency %

0  1  2  3  4  5  6  7  8  9  10  12
Scanning Electron Microscopy

Toward the end of the project a scanning electron microscope in an \(\alpha\)-active facility became available and was tried for particle size analysis on 100 h-milled powder from batch C63. It was found to be difficult to prepare the sample so that a low degree of agglomeration was present. The best results were obtained using a commercial non-aqueous medium "Sedisperse B", normally used for sedimentology, which was sprayed onto a transmission electron microscope sample grid. Photographs were taken of areas selected at random and the diameters of all the particles shown measured by hand. The results are presented in the form of a histogram in Fig. 4.6. Despite the higher resolution the results are similar to those obtained by optical microscopy for C39, so that the application of the latter method to all powders would have yielded useful information.

X-Ray Line Broadening

The method of X-ray line broadening was used to determine the crystallite size of batches C39 and C63. In the case of batch C39 Stoke's method of Fourier transforms was used to correct the line profiles for instrumental broadening. It was, however, found that the simpler method of using the integral breadth gave practically identical results. Hence the latter method was applied to the results from C63, which are given below:

<table>
<thead>
<tr>
<th>milling time</th>
<th>crystallite diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>45.6</td>
</tr>
<tr>
<td>20</td>
<td>52.4</td>
</tr>
<tr>
<td>35</td>
<td>48.5</td>
</tr>
<tr>
<td>50</td>
<td>24.4</td>
</tr>
<tr>
<td>70</td>
<td>19.6</td>
</tr>
<tr>
<td>90</td>
<td>17.0</td>
</tr>
<tr>
<td>100</td>
<td>12.2</td>
</tr>
</tbody>
</table>
These results apparently indicate that, although the mean crystallite size is more than an order of magnitude smaller than the mean particle size, that the crystallites are broken up during ball milling. This does not seem likely, so that the increase in line broadening is better attributed to an increase in defect concentration.
4.4. Shrinkage Measurements by Dilatometry

Apparatus

For the investigations on the first three batches a simple, horizontal push-rod dilatometer was used, with an alumina measuring system and heated by a rhodium wound muffle furnace, which gave a maximum temperature of around 1500°C. This was found to be inadequate, but extensive modifications, including a graphite-element furnace and tungsten measuring system, while giving satisfactory temperature performance, introduced thermal expansion problems which seriously affected the accuracy.

For the experiments on batch C63 a high temperature differential dilatometer was therefore obtained, and modified for use with active materials. With a differential dilatometer the problems arising from thermal expansion of the measuring system are considerably reduced. The test sample and a standard of known thermal expansion are positioned side by side in the hot zone of the furnace and length changes are transmitted by two identical push-rods to a transducer which produces an output proportional to the difference between the lengths of the samples.

The push-rods were of tungsten, only two millimeters in diameter to reduce weight and counterbalanced by a system of springs and pulleys. The load on the sample necessary to overcome friction in the push-rod bearings was around 0.25 N. The furnace was a tungsten resistance furnace with a cylindrical heating element surrounding the samples (see Fig. 4.4).

Temperature measurement was by means of a W/5% Re-W/26% Re thermocouple whose hot junction was between the sample and standard, about 3 mm away from their surfaces. A water-cooled part of the dilatometer served as a cold junction and the emf. was measured with a potentiometric chart recorder. In the case of the Dorn method a hand compensating potentiometer accurate to ± 0.005 mV was used. A proportional temperature controller, regulated by a 15-step programmer, utilised the output of the same thermocouple.

A vacuum of down to 10⁻³ Torr was provided by a two stage rotary pump rated
Fig. 4.4: Dilatometer Sample Holder

Side view

- Supporting rod
- Push rod
- Disc
- Sample
- Heating element

Plan view

- Heating element
- Electrode
- Push rod
- Sample
- Thermocouple
at 10 m$^3$h$^{-1}$ pumping through an absolute filter. Facilities were provided for operating under inert or reducing atmospheres.

Calibration of the instrument was performed by means of a set of length standards, made for the purpose, whose lengths were known to better than 1 μm. The transducer amplifier was then adjusted so that a relative length change of 1 μm was represented by 1 mm on the chart recorder. However, the transducer deviated from linearity over its range of 3 mm, so that the actual magnification of the system varied from X980 to X1020. Another cause of inaccuracy was the different thermal expansion of the two sides of the measuring system, presumably caused by an asymmetric temperature distribution. The magnitude of this error was determined by heating two identical tungsten samples. Although the deviation from a linear base line below 1000°C was found to be as much as 30 μm, above this temperature, where all the measurements were made, the maximum deviation was 10 μm. This was checked at periodic intervals.

Procedure

Shrinkage measurements were made on the pressed compacts using the constant-rate-of-heating (CRH), isothermal and Dorn techniques, the principals of which were described in the theoretical discussion. The experimental details for batch C63 are described here; the technique used with the simple dilatometer did not differ significantly.

The standards used were carbonitrides of similar composition to the batch being studied, which had been sintered at 1700°C for 18 hours before use. Thus the thermal expansion of the samples themselves did not have to be taken into account in the interpretation of the results. The standards themselves did not change their dimensions by more than a few micrometers over a series of a dozen or so runs. A number of different lengths were available, so that the lengths of test sample and standard did not differ too greatly, the standards being chosen to have about the average length of the sample during sintering.

For the CRH experiments a standard heating up programme was used in which the sample was first heated with 24°C/min to 400°C, at which temperature it
was held for 30 minutes. It was then heated further at 24°C/min to 1200°C, whereafter heating continued at a chosen constant rate between 1°C/min and 18°C/min to a maximum, in most cases, of 1685°C. This procedure was employed to ensure that, for each sample, elimination of the stearic acid binder occurred to the same degree, and to speed up runs at lower heating rates.

In the case of the isothermal measurements, after the pause at 400°C, the samples were heated at the fastest possible rate (ca. 33°C/min) to the desired temperature, in order to limit the amount of shrinkage occurring during heating up. Samples used for the CRH runs were also held at the maximum temperature attained in order to gain information on the intermediate and final stages of sintering.

For the Dorn method, the same procedure was followed as for the isothermal experiments, except that, after reaching temperature, at 6-minute intervals the temperature was alternately raised and lowered by about 50°C. As the value of $\Delta T$ is important in this type of experiment, the thermocouple em-f was measured by a hand compensating potentiometer, accurate to ± 0.005 mV (ca. ± 0.25°C), after each temperature change.

Hydrogen Treatment

A heat treatment under hydrogen on sintered carbide pellets is known to reduce the amount of higher carbides with the formation of hydrocarbons /149/. At the Transuranium Institute, pellets thus treated had been found to sinter to higher densities, and a dilatometric investigation in the early stages of this project showed that after the treatment shrinkage rates were considerably faster.

In order to investigate this phenomenon, a number of pellets from batch C63 were subjected to such a treatment prior to investigating their sintering behaviour in the same manner as for untreated pellets. The treatment was carried out in the dilatometer itself directly before sintering as the treated pellets were too friable to be handled. The temperature of the treatment was 950°C and the time 4 hours, at a hydrogen flow rate of 1.51/min and a pressure of 900-1000 Torr. Subsequent sintering was under vacuum, as for the untreated samples, using the CRH, Dorn and isothermal techniques.
4.5. **Investigation of Structural and Compositional Changes**

In order to help interpret the results of the dilatometric shrinkage experiments, it was decided to investigate the structural and compositional changes occurring during the initial and intermediate stages in both H₂-treated and untreated pellets. A number of samples were heated in the dilatometer at 2.3°C/min as for a CRH experiment, and rapidly cooled (by cutting the furnace power supply) as soon as a predetermined shrinkage was reached. The samples were weighed and measured before and after sintering (as were all pellets) so that a record of weight loss during sintering could be made. They were then subjected to the following investigations:

a) Chemical analysis  
b) X-ray diffractometry  
c) Scanning electron microscopy

As it was found that the equivalent carbon content could not be precisely determined by means of individual analyses of carbon, oxygen and nitrogen, due to the summation of the errors for each analysis, it was decided to determine the total metals content (U+Pu), and to deduce the non-metals content (C+N+O) by subtraction.

X-ray diffractometry was employed to determine the presence and quantity of phases other than monocarbonitride. The first series of results showed an unexpected scatter, so that fresh pellets were prepared, and samples taken after crushing and mixing each whole pellet, in order to avoid inconsistencies resulting from an inhomogeneous distribution of phases. The diffractometry was performed by the X-ray analysis department of the Transuranium Institute.

Scanning electron microscopy was performed by the electron microscopy department at the Transuranium Institute, in a newly created α-active facility. Examinations were made of freshly fractured surfaces on the specimens, and photographs taken of areas which were considered to be typical of the fracture surface as a whole. Energy dispersive analysis showed a homogeneous distribution of uranium and plutonium over the surfaces and could detect no trace of metallic impurities.
Specific surface measurements were performed on batch C46 using a commercial apparatus \textsuperscript{1).} This utilised argon as the adsorband gas and determined volumetrically the amount of gas adsorbed at a pressure of 60 Torr and 77.3°K, thus determining one point on the BET curve. The instrument is calibrated by means of standards.

It was intended to use the specific surface values obtained for partly sintered pellets to determine the rate of interparticle neck growth as described in Section 2.2.4. The results obtained were:

<table>
<thead>
<tr>
<th>% linear shrinkage</th>
<th>specific surface, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>unsintered powder</td>
<td>0.55</td>
</tr>
<tr>
<td>0.7 %</td>
<td>1.65</td>
</tr>
<tr>
<td>1.15 %</td>
<td>1.05</td>
</tr>
<tr>
<td>1.8 %</td>
<td>0.55</td>
</tr>
<tr>
<td>2.55 %</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Thus the compact which has already shrunk by 0.7 \% apparently exhibits a higher specific surface than the unsintered powder. This paradox would be explained by adsorption in microspores in the sintered compact resulting in failure to obey the BET-equation, which cannot be detected by the single-point method used.

The value of 0.55 m²/g for the powder corresponds to a particle diameter for equisized spherical particles of around 1 \(\mu\)m, about the same as the mean particle diameter measured on total C63 by scanning electron microscopy, thus supporting the view that the measurements of the partly sintered compacts cannot usefully be evaluated.

Therefore, no further measurements were made.

\textsuperscript{1) Leybold 'Areatron'}
Chapter 5

Results

5.1. Structural and Compositional Changes during Sintering

By heating 100-hour milled samples with a constant heating rate (2.4 C/min) to various limiting temperatures, samples were obtained with varying degrees of shrinkage and densification. Scanning electron micrographs of these samples are shown in Figs. 5.1 and 5.2.

The first sample, exhibiting only 0.25% linear shrinkage shows very little sign of contact growth between the particles (although some must exist, as the compact already had some strength). This amount of shrinkage is clearly due to the removal of the binder during heating up. At 0.5% shrinkage, although the density has remained much the same due to weight loss, a considerable amount of neck formation has taken place. This does not seem to be uniform; whereas a number of the particles form a continuous skeletal structure, giving rise to larger fracture surfaces, others appear to be only loosely attached. By 1% shrinkage (73.5% density) all the particles have formed a continuous network and by 3.25% (80% density) the structure is better described as a matrix of material interspersed with a network of tubular pores.

In the initial stages it is clear that neckgrowth does not progress uniformly between all neighbouring particles and that some particle rearrangement as described by Exner /6/ must be taking place. The transition to an intermediate stage structure clearly takes place between 1% and 3.25% shrinkage—although the initial stage models of Johnson and others (ch.1) are considered to be valid up to over 3% shrinkage. The reason for the early transition in this case is probably the high green densities.

Since the scanning electron micrographs are not of plane sections, and do not reveal grain boundaries, the grain sizes and pore diameters cannot be accurately quantified. However it is clear that between 74% and 84% density a coursening of the structure takes place. An estimate made assuming all the pores lie on grain boundaries is that the average grain diameter grows from 3 \( \mu \text{m} \) to 6 \( \mu \text{m} \) and the average pore diameter from 2/3 \( \mu \text{m} \)
to 1 \mu m. The higher grain size estimate is supported by the optical micrograph at 84.5 \%, which shows a grain size of 6 \mu m, and the lower by the initial powder particle size.

The appearance of the compact directly after the hydrogen treatment is very different to that of the untreated compact exhibiting the same amount of shrinkage. Here the larger particles seem interspersed with a considerably finer powder the form of which cannot be discerned owing to insufficient resolution. The structures at 74 \% and 78.5 \% density are, on the other hand much more closely related to the "untreated" structures. The difference between "untreated" and "treated" structures is at the lower density small, however at the higher densities the "treated" compact exhibits a finer structure with smaller pores. The grain size, so far as it can be estimated, has changed little between 74 \% and 78 \%.

The results of chemical and X-ray analysis of similar samples are given below.

### Wt.\% non-metallic elements (C + N + O)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Max. Temp.</th>
<th>Shrinkage %</th>
<th>Density %</th>
<th>C + N + O</th>
</tr>
</thead>
<tbody>
<tr>
<td>D79</td>
<td>1250</td>
<td>0.3</td>
<td>72.7</td>
<td>5.54</td>
</tr>
<tr>
<td>D80</td>
<td>1415</td>
<td>0.5</td>
<td>72.7</td>
<td>5.49</td>
</tr>
<tr>
<td>D76</td>
<td>1540</td>
<td>0.9</td>
<td>73.6</td>
<td>5.23</td>
</tr>
<tr>
<td>D78</td>
<td>1540</td>
<td>2.4</td>
<td>77.3</td>
<td>(4.99-5.56)</td>
</tr>
<tr>
<td>D81</td>
<td>1750</td>
<td>3.2</td>
<td>79.8</td>
<td>5.15</td>
</tr>
</tbody>
</table>

The results are the average of two analyses for each sample, which agreed within 0.05 \%, except for D78.

### X-ray diffraction

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Max. Temp.</th>
<th>Shrinkage %</th>
<th>Density %</th>
<th>% M_2C_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>D91</td>
<td>1410</td>
<td>0.5</td>
<td>72.8</td>
<td>18</td>
</tr>
<tr>
<td>D96</td>
<td>1550</td>
<td>0.9</td>
<td>73.7</td>
<td>5</td>
</tr>
<tr>
<td>D94</td>
<td>1650</td>
<td>1.8</td>
<td>74.5</td>
<td>4</td>
</tr>
<tr>
<td>D92</td>
<td>1750 (15 min.)</td>
<td>4.3</td>
<td>82.7</td>
<td>0</td>
</tr>
</tbody>
</table>
It can be seen that the initially present sesquicarbide disappears during the initial stages of sintering. This correlates with the chemical analysis above and the CO evolution which can be observed when sintering larger batches. Clearly a reaction of residual oxygen with excess carbon is responsible.
Fig. 5.1: Evolution of Microstructure during Initial Stage of Sintering Carbonitride Batch C63 100 h. No H₂-Treatment Nominal Magnification 5000X.

3175 L4-5 0.25 % shrinkage
3447 L4-7 0.5 % shrinkage
3364 L4-16 0.95 % shrinkage
3363 L4-9 3.25 % shrinkage
3446 L4-14 4.1 % shrinkage
Fig. 5.2: Evolution of Microstructure during Initial Stage of Sintering Carbonitride Batch C63-100 h. With H₂ Treatment. Nominal Magnification 5000 X
5.2. Shrinkage Behaviour under Isothermal Conditions

As the project concentrated on the use of the constant rate of heating (CRH) method only a few samples were sintered isothermally. The results are nevertheless significant. Fig. 5.3 shows the increase of relative density with time of samples not treated under hydrogen. The density was calculated from the shrinkage recorded on the dilatometer plot using the expression:

\[ d = \frac{d_0}{(1 - 3y)} \]

where \( d_0 \) is the starting density and \( y \) the fractional shrinkage. The expression ignores terms in \( y^2 \) and above and assumes isotropic shrinkage. In fact the diametrical shrinkage was always greater by a factor between 1.05 and 1.15. However the two approximations tend to cancel and the accuracy of the measurements did not, in any case, warrant greater precision. \( d_0 \) was calculated from the original dimensions and final weight of the sample as investigations of the weight loss during sintering (Section 5.1) show that the greater part occurs during the first few percent of densification. The theoretical density was taken as \( 1.37 \times 10^4 \text{ Kg m}^{-3} \) (13.7 gcm\(^{-3}\)).

Fig. 5.3 shows that initially the density increases at a steadily decreasing rate. This is followed by a period, between 75 % and 85 % density, in which the density increases linearly with time. Above 85 % the densification rate decreases again.

Fig. 5.4 shows the isothermal behaviour of a sample after the hydrogen treatment. In this case, after a slight initial acceleration, the densification rate is constant up to about 87 % density, after which the rate decreases rapidly. The rate of densification during the linear phase is considerably greater (5.8 \( \times 10^{-5}\text{s}^{-1} \)) than that of an untreated sample at the same temperature (3.0 \( \times 10^{-6}\text{s}^{-1} \)).

Fig. 5.5 shows the initial, non linear, behaviour of untreated samples as a log(shrinkage) against log (time) plot, the straight lines were drawn to give the best fit at higher shrinkages, as the error here is lowest. The slopes have an average value of 2.33, so that this stage of sintering can be represented by:

\[ y = K(T) t^{2.33} \]
Fig. 5.3: Isothermal Densification of Untreated Compacts

% theoretical density

D32 1695°C
D41 1695°C
D49 1675°C
D43 1600°C
D45 1650°C

Time, minutes
Fig. 5.4: Isothermal Densification after $H_2$-treatment

% theoretical density

$D53, 1695^\circ C$

$D54, 1605^\circ C$

0 100 200 300

time, minutes
Fractional linear shrinkage - %

Time in minutes

- 1695°C
- 1675°C
- 1650°C
- 1600°C

inv. slope = 2.28

- 2.38
- 2.48
- 2.68

Fig. 5.5: Log (shrinkage) vs. Log (time) for uncreased samples
or: \[ \frac{dy}{dt} = K' y^{1.33} \]

under isothermal conditions.

The results above 85% density (only available at 1695°C) are shown as a logarithmic plot of density against time in Fig. 5.6 and as a plot of \((1/P^n - 1/P_{0}^n)\) against time in Fig. 5.7 where \(P\) is the fractional porosity. The former plot is relevant to Coble's intermediate-stage sintering equation and the latter to Kuczynski's. These will be discussed in the following chapter.

5.3. Shrinkage Behaviour under Constant Rate of Heating

The data obtained under CRH conditions are shown as plots of \(\ln y/T\) against \(1/T\) for the 50-hour and 100-hour milled powders and for those treated under hydrogen in Figs. 5.8 to 5.10. Corresponding plots of \(\log y\) against \(\log\) (heating rate) are given in Figs. 5.11 to 5.13. From these plots the values of the constants in the equation:

\[ \frac{dy}{dt} = K \exp(-Q/RT) / Ty^n \]

can be determined (see previous discussion in Chapter 4).

50 hours milling
\[ n = 0.56 \]
\[ Q = 398 \text{ kJmol}^{-1} (95.4 \text{ kCalmol}^{-1}) \]
\[ K = 1.0 \times 10^5 \text{ s}^{-1} \]

100 hours milling
\[ n = 0.80 \]
\[ Q = 458 \text{ kJmol}^{-1} (109.6 \text{ kCalmol}^{-1}) \]
\[ K = 2.5 \times 10^8 \text{ s}^{-1} \]

After hydrogen treatment
\[ n = 0.04 \text{ to } -0.22 \]
\[ Q = 585 \text{ kJmol}^{-1} (140 \text{ kCalmol}^{-1}) \]
\[ K = 8.3 \times 10^{14} \text{ s}^{-1} \]
Fig. 5.6: Density v. log (time) for various $d_0$.
Fig. 5.7: 'Kuczynski' Plot for Isothermal Densification

\[
\frac{1}{p_{\text{th}} - p^{0.8}}
\]
Fig. 5.8: ln (y/\sqrt{T}) v. I/T for 50 hour milled powder at various heating rates

- 7 -
- 8 -
- 9 -
- 10 -
- 11 -

\( \ln \left( \frac{y}{\sqrt{T}} \right) \)

<table>
<thead>
<tr>
<th>Heating Rate</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 1.05 °/min</td>
<td>32.0 \times 10^3</td>
</tr>
<tr>
<td>O 1.0 °/min</td>
<td>25.2</td>
</tr>
<tr>
<td>x 2.2 °/min</td>
<td>33.6</td>
</tr>
<tr>
<td>△ 4.1 °/min</td>
<td>29.0</td>
</tr>
<tr>
<td>▽ 4.9 °/min</td>
<td>33.3</td>
</tr>
<tr>
<td>□ 6.6 °/min</td>
<td>31.6</td>
</tr>
</tbody>
</table>
Fig. 5.9: $\ln(y/\sqrt{T})$ v. $1/T$ for 100 hour milled powder at various heating rates

<table>
<thead>
<tr>
<th>Heating Rate</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 °/min</td>
<td>$28.0 \times 10^3$</td>
</tr>
<tr>
<td>3 °/min</td>
<td>$27.1 \times 10^3$</td>
</tr>
<tr>
<td>6 °/min</td>
<td>$27.8 \times 10^3$</td>
</tr>
<tr>
<td>12 °/min</td>
<td>$26.7 \times 10^3$</td>
</tr>
<tr>
<td>18 °/min</td>
<td>$28.8 \times 10^3$</td>
</tr>
</tbody>
</table>
Fig. 5.10: \( \ln \left( \frac{y}{\sqrt{T}} \right) \) v. \( \frac{1}{T} \) after \( H_2 \)-treatment

- \( x \) 0.95 °/min slope: \( 68.0 \times 10^3 \)
- \( \Delta \) 2.4 °/min slope: 54.2
- \( \bigcirc \) 4.0 °/min slope: 63.7
- \( \triangle \) 6.3 °/min slope: 70.6
- \( \square \) 9.3 °/min slope: 60.2

\( \frac{1}{T} \times 10^4 \text{ K}^{-1} \)
Fig. 5.11: log (shrinkage) v. log (heating rate) for 50 h milled powder
Fig. 5.12: log (shrinkage) v. log (heating rate) for 100-h powder
Fig. 5.13: log (shrinkage) v. log (heating rate) for H\textsubscript{2}-compacts
These values are averages of those obtained from the individual plots, which are shown on the figures themselves. In the case of the non-treated samples only values of the fractional shrinkage below 3% were used, for the hydrogen-treated samples below 5%.

In the case of the plots of log y v. log c there is a considerable amount of scatter, particularly at the lower temperatures. It is therefore not possible to say whether the relationship is truly linear or not. The best straight lines were determined by least-mean-squares analysis.

5.4. Dorn Method

The Dorn method of determining the activation energy of the sintering process was performed on compacts of 100-hour milled powder and hydrogen-treated compacts. The apparent activation energy, Q, was calculated from the shrinkage rates \( \dot{y}_1 \) and \( \dot{y}_2 \) before and after a change in temperature by means of the expression:

\[
Q = \frac{RT_1T_2}{\Delta T} \ln \frac{\dot{y}_1}{\dot{y}_2}
\]

The shrinkage rates were determined by drawing tangents to the length-time plot of the dilatometer output. The results are given in tabular form below.

Sample D48 - 100 h milled

\( T_1 = 1618^\circ C \) from potentiometric measurement of thermocouple emf.
\( T_2 = 1658^\circ C \)

<table>
<thead>
<tr>
<th>Shrinkage y at point of temp. change %</th>
<th>( \dot{y}_1 \times 10^6 ) sec(^{-1} )</th>
<th>( \dot{y}_2 \times 10^6 ) sec(^{-1} )</th>
<th>Q KJmol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.77</td>
<td>7.91</td>
<td>3.44</td>
<td>629</td>
</tr>
<tr>
<td>0.91</td>
<td>2.80</td>
<td>5.41</td>
<td>497</td>
</tr>
<tr>
<td>1.13</td>
<td>5.01</td>
<td>2.45</td>
<td>539</td>
</tr>
<tr>
<td>1.22</td>
<td>2.01</td>
<td>4.42</td>
<td>594</td>
</tr>
<tr>
<td>1.40</td>
<td>3.78</td>
<td>1.94</td>
<td>504</td>
</tr>
<tr>
<td>1.47</td>
<td>1.67</td>
<td>3.73</td>
<td>608</td>
</tr>
<tr>
<td>1.67</td>
<td>1.44</td>
<td>3.03</td>
<td>565</td>
</tr>
</tbody>
</table>
1.80  3.03  1.27  660
1.85  1.15  2.94  705
3.09  2.24  1.20  468
3.14  1.20  2.26  476
3.24  2.26  0.86  730
3.27  0.86  2.36  761
3.38  2.26  0.93  665
3.41  0.93  2.43  723
3.52  2.24  1.03  584
3.55  1.03  2.29  601
3.91  2.19  0.86  705
3.95  0.86  2.19  705
4.05  2.19  0.86  705
4.08  0.86  2.21  713

Average value of Q = 626 kJmol\(^{-1}\) (150 KCal mol\(^{-1}\))

**H\(_2\)-treated compacts**

Sample D67 \( T_1 = 1588°C; \quad T_2 = 1629°C \)

<table>
<thead>
<tr>
<th>Shrinkage %</th>
<th>( \dot{y}_1 \times 10^{-6} ) sec(^{-1} )</th>
<th>( \dot{y}_2 )</th>
<th>Q KJmol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>8.36</td>
<td>26.9</td>
<td>815</td>
</tr>
<tr>
<td>1.13</td>
<td>27.7</td>
<td>10.5</td>
<td>714</td>
</tr>
<tr>
<td>1.62</td>
<td>11.5</td>
<td>33.7</td>
<td>767</td>
</tr>
</tbody>
</table>

Average Q = 765 KJmol\(^{-1}\) (183 KCal mol\(^{-1}\))

Sample D68 \( T_1 = 1548°C; \quad T_2 = 1588°C \)

<table>
<thead>
<tr>
<th>Shrinkage %</th>
<th>( \dot{y}_1 \times 10^{-6} ) sec(^{-1} )</th>
<th>( \dot{y}_2 )</th>
<th>Q KJmol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.66</td>
<td>16.1</td>
<td>5.82</td>
<td>712</td>
</tr>
<tr>
<td>1.03</td>
<td>7.45</td>
<td>20.2</td>
<td>701</td>
</tr>
<tr>
<td>1.81</td>
<td>19.3</td>
<td>7.10</td>
<td>702</td>
</tr>
<tr>
<td>2.19</td>
<td>8.61</td>
<td>22.3</td>
<td>668</td>
</tr>
<tr>
<td>3.00</td>
<td>19.3</td>
<td>6.98</td>
<td>714</td>
</tr>
<tr>
<td>3.42</td>
<td>7.10</td>
<td>17.0</td>
<td>612</td>
</tr>
</tbody>
</table>

Average Q = 684 KJmol\(^{-1}\) (164 KCal mol\(^{-1}\))
6.1. Without hydrogen treatment

The isothermal shrinkage curves obtained for the 100 hour milled compacts show that the behaviour can be divided into three stages:

1) 70-75 % density: a period of reducing densification rate
2) 75-85 % density: a period of constant densification rate
3) 85 % density: a period of reducing densification rate.

The transition from stage 1 to stage 2 behaviour corresponds well with the transition from initial stage to intermediate stage structure described in 6.1. The change in behaviour at about 85 % density corresponds roughly with the disappearance of $M_2C_3$, reported in Ch. 5.1.

6.1.1. Initial Stage

Comparison of Results with Johnson's theory and Ashby diagram:

First the initial stage kinetics for the 100 hour milled compacts will be discussed; these formed the core of this investigation. The constant-rate-of-heating experiments indicate that the shrinkage rate up to 3 % shrinkage (extending slightly into the intermediate stage) can be described by:

$$\frac{dy}{dt} = \frac{2.5 \times 10^8 \exp(-458 \text{kJ/RT})}{T \cdot y^{0.88}}$$

(6.1.)

Johnson's model for the initial stage of sintering by a volume diffusion mechanism predicts that /14/

$$\frac{dy}{dt} = \frac{2.63 \gamma \rho \cdot \text{D} \cdot \gamma}{K T^3 \cdot y^{1.03}} \exp(-Q/RT)$$
Taking Matzke and Bradbury's values for the volume diffusion of plutonium in a mixed carbonitride /159/ above 1400°C of $1.5 \times 10^{-5} \exp(-439 \text{kJ/RT}) m^2 s^{-1}$ the mean value of the powder particle diameter as measured by scanning electron microscopy of 2.5 μm, and values of the other constants as given below* we find

$$\frac{dy}{dT} = \frac{3.2 \times 10^7}{T} \exp(-439 \text{kJ/RT})$$

Although the value of the pre-exponential constant here is a factor of 8 too small, considering the uncertainty in the values of $D_y$ and $\gamma$, and the importance of the exponential term (a difference of 30 kJ mol$^{-1}$ would give a similar error in $\frac{dy}{dT}$), this can be considered good agreement.

However, to a certain extent this agreement must be fortuitous as the Johnson model refers to a regular compact of equisized spheres. As Exner /5/, /6/ has shown, in irregular compacts, even of spherical particles, particle rearrangement hinders the formation of some interparticle necks whilst encouraging others. The SEM taken at 0.25% shrinkage shows that, while a few quite large necks have formed, most particles show no sign of neck formation, demonstrating that such a phenomenon occurs here. It must be assumed that the average behaviour of the interparticle necks approaches that of the "ideal" neck between two spherical particles on which the quoted theoretical model is based.

In view of this agreement it is surprising that in the Ashby diagram computed for UC (p16), no Volume diffusion field appears, densification by a grain boundary mechanism is predicted. This, however, would require an 'n' value of around 2 and an activation energy around 300 kJ (see Ch. 3.5) which cannot be correlated with any of the results reported here. It must be concluded that the grain boundary diffusion data used in constructing the diagram considerably over-estimates its significance.

* $k = 1.38 \times 10^{-23} \text{J.K}^{-1}$
  
  $= 0.725 \text{J.M}^{-2}$ (value for UC/204/)
  
  $= 0.30 \times 10^{-28} \text{m}^3$ (from lattice parameter)
Differing 'n' value determined in isothermal experiments:
The n-value determined from the isothermal experiments (1.33) is unfortunately in disagreement with the CRH results (0.88). This is unexpected since, so long as the sintering rate can be expressed as:

\[ \frac{dy}{dt} = \frac{K(T)}{y^n} \]  \hspace{1cm} (6.2)

the values determined from the two methods should be identical.

Equation 6.2. implies that the rate of shrinkage depends only upon the temperature and the instantaneous amount of shrinkage, and is independent of the thermal history of the sample. This will not be true if a mechanism such as surface diffusion, having a different temperature dependence to the shrinkage mechanism, contributes to neck growth without itself causing shrinkage, thus reducing the driving force for shrinkage. To quantify the influence of surface diffusion on the experimental "n" values determined by isothermal and CRH methods is difficult, because expressions for the rate of sintering by several mechanisms are not usually integrable. A qualitative discussion must therefore suffice.

Having a lower activation energy than volume or grain boundary diffusion, surface diffusion will be of greatest relative importance at lower temperatures. Hence the greatest reduction of observed shrinkage will be where low heating rates are employed. Thus the influence should be smallest for isothermal experiments, and a consideration of the plot of log y v. log c used to determine n in the CRH method, shows that the value of n determined in the CRH method should be higher - the opposite of that observed.

However surface diffusion has a higher time exponent than the shrinkage producing mechanisms, so that its influence should be greater at low shrinkage values i.e. at high heating rates. This should decrease the observed value of n. It is therefore clear that, without a precise quantitative model, it must be assumed that surface diffusion can either raise or lower the value of n determined by the CRH method.

If equation 6.2. applies, then the difference between the values of n determined by the two methods can only be explained by experimental error.
In the case of the isothermal method a fast heating rate is essential if the initial stage is to be studied. However, the use of high heating rates is likely to influence the accuracy of measurement, as the measuring system will take time to attain thermal equilibrium, resulting in spurious length changes.

This source of inaccuracy applies to a considerably smaller extent to the CRH method, where heating rates are lower. It must be concluded then, that the isothermal method is more susceptible to experimental error, which was the reason for the adoption of the CRH method.

Finally it should be noted that the experimental value measured is in both cases n+1, so that the discrepancy is between values of 1.88 and 2.33 rather than 0.88 and 1.33.

Activation energy determined by Dorn method:
A further discrepancy arises when the results of the Dorn experiments are considered, giving an average value of 200 KJ mol\(^{-1}\) higher than the CRH method for the phenomenological activation energy.

It is first necessary to consider the possibility of experimental error. The results depend on two measurements - that of the shrinkage rate and that of the temperature. The temperature was measured by means of a thermocouple close to the specimen. Since this has a lower thermal capacity than the specimen it will respond more rapidly to changes in the temperature of the furnace elements than the sample. Hence the change in temperature of the specimen will tend to be overestimated, which will result in values of the phenomenological activation energy which are too low. Clearly the explanation cannot lie here. The shrinkage rate is determinable with less precision due to the uncertainty of measuring the slope of the dilatation curve. This is reflected in the large scatter in the results. However, the errors in the slope measurement should be random; even if not, the fact that both upward and downward temperature changes were used should cause even systematic errors to cancel and, although the difference could just fall within the range of statistical variation of the results, the probability is low.
Ruling out, then, experimental error as the cause of the high values of the apparent activation energy it is necessary to consider other reasons for the observed temperature dependence of the sintering process to differ from that of the rate-controlling matter transport mechanism (it being assumed that there is no matter transport mechanism with a higher activation energy than volume diffusion). There are two possibilities:

1) Another rate-controlling factor is temperature-dependent
2) Processes other than volume diffusion influence the shrinkage rate.

Considering possibility (1), the rate of sintering will be controlled by the chemical potential gradients within the compact and the geometric factors relating the flow of atoms from grain boundary to pore (or neck surface) to the shrinkage of the compact. These factors will depend upon the interfacial energies and the compact microstructure (radius of curvature of pore surfaces, grain sizes etc). Unless phase changes occur the interfacial energies are unlikely to be strongly temperature dependent. Any changes in the microstructure will be irreversible and tend to reduce the chemical potential gradients and hence the rate of sintering. If, for example, the grain size increases during a positive temperature change, the sintering rate measured at the higher temperature will be reduced and hence the apparent activation energy will be lowered. The reverse will be true for a negative temperature change, so that the errors will tend to cancel. However grain growth is more likely to occur during a rise in temperature (being a thermally activated process) so that the net influence on a series of Dorn measurements will be a lowering of the observed value.

It is worth noting that, in the case of other methods of determining the activation energy of sintering which compare the sintering rates of a series of samples (CRH method, isothermal method) quite different structures may evolve during different thermal treatments, and that the activation energies determined may be higher or lower than that of the matter transport mechanism (e.g. Coleman and Beeré /119/ find a high activation energy for UO₂ sintering).

In Appendix 1 it is shown what effect the simultaneous operation of two or more processes influencing the shrinkage rate will have upon the apparent activation energy. So long as the processes work in the same direction (e.g. sintering by volume and grain boundary diffusion) the apparent activation energy
will lie between the values of the two mechanisms. The observed high Q value could possibly arise when a second mechanism operates which, acting alone, will cause swelling of the compact. One possibility is particle re-arrangement which reduces the expected shrinkage during the initial stages by reducing the number of interparticle necks which form. However this is not a particularly suitable candidate as, firstly, it can only operate at the beginning of sintering, whereas the high activation energy is observed beyond the initial stage; secondly, particle re-arrangement being due to the formation of asymmetric necks, and the interaction of neighbouring necks, it is unlikely to exhibit a different activation energy to the sintering process.

A second possibility is swelling due to gas pressure within the pores. However, not only is the majority of the porosity open during the initial and intermediate stages, but also, as shown in Appendix 2, the gas pressure required to influence the shrinkage rate significantly is much higher than the likely pressures of \( \text{N}_2, \text{CO} \) etc. within the sample.

Lastly, any such influence on the apparent activation energy determined by the Dorn method should also be observed in the CRH results. It must therefore be concluded that the observed temperature dependence of sintering occurs as a result of the temperature dependence of the matter transport mechanism itself, which is, considering the CRH results, highly likely to be volume diffusion.

Explanation of results considering anomalous diffusion behaviour:
To see how this can be possible, it is necessary to look more closely at diffusion phenomena in carbonitrides. The investigations of Matzke and Bradbury /130/ show in several cases a discontinuity in the Arrhenius plot of diffusion coefficient vs. inverse temperature as shown in fig. 6.1. The materials had nitride proportions between 12 and 24 mol% and the discontinuities were between 1420 °C and 1520 °C. Other similar materials showed no discontinuity but, where observed, it was reproducible. Such a discontinuity can only result from a change of structure on an atomic scale such as a phase change, but no change of phase in this range of temperature has been reported and the phenomenon has not yet been explained.
Fig. 6.1: Pu Diffusion in a hyperstoichiometric carbonitride
The data points available, however, permit two interpretations, as fig. 6.1 shows. The alternative form, exhibiting a peak has been observed in hyperstoichioimetric UC at higher temperatures and is attributed by the authors to the phase change between UC$_2$ and U$_2$C$_3$ occurring at around 1800°C. The phenomena was first noted and explained in the case of PbSiO$_3$ by R. Lindner /150/. Although the amounts of higher carbides in the UC were insufficient to have a significant influence on the observed rates of diffusion, while the phase change is taking place the rate of diffusion is considerably enhanced. Samples annealed very close to the temperature of the phase change may undergo repeated changes of structure caused by slight fluctuations in temperature.

A significant aspect of the phenomena is that it can cause a time dependence of diffusion rate as the phase change may not occur immediately. In the case of carbonitrides the observed rate of diffusion has been observed to accelerate and then decrease as a function of time, near the critical temperature.

Such a phenomenon is capable of explaining the difference between the activation energies measured by the CRH and Dorn methods. With the CRH method, on heating through the critical temperature, the effect on the sintering rate will not be noticed as a peak, because of the time-dependence of the effect. The enhanced diffusion will be noticeable as a somewhat higher sintering rate over a range of temperature. Hence the temperature dependence of sintering rate observed will follow the high temperature part of fig.6.1. and the apparent activation energy will correspond to that given by Matzke and Bradbury which again refers to fig.6.1.

However, once over the critical temperature, this enhancement of sintering rates will only occur once. Hence, when performing isothermal experiments it will be observed as an initial high sintering rate, decreasing faster than the geometry alone requires. This is equivalent to a higher value of "n". When cycling the temperature as in the Dorn experiments, the temperature dependence of sintering rate will be according to fig.6.2. When comparing the rates directly before and after a temperature charge, any enhancement
due to the unknown "structural change" will be the same for both temperatures and thus have little effect on the determined activation energy. Thus a higher activation energy will be measured.

As yet, no definite explanation has been found for the anomalous diffusion behaviour observed in this case. However, as the chemical analyses and X-ray diffractometry show, in the sintering experiments during the initial stages there is a certain amount of sesquicarbide present, at least at room temperature (the samples were cooled quite rapidly from the sintering temperature so it is likely that the phases present at temperature were quenched in). This is clearly formed at temperatures below those at which observable shrinkage occurs from the reaction of carbon remaining from the decomposition of the binder with the (initially single phased) carbonitride. During sintering the amount of $M_2C_3$ present decreases, together with the amount of oxygen, so that this is clearly due to a reaction of dissolved oxygen with carbon in the $M_2C_3$ evolving CO. (Large batches of carbides and nitrides evolve measurable quantities of CO at these temperatures). It is possible that the enhancement of diffusion is either connected with this reaction, or with the presence of $M_2C_3$ (crossing of the solubility limit of carbon in $M(C,N)$.

50-hour milled specimens

Here the number of experiments performed was considerably smaller. There were no Dorn experiments performed. The isothermal curve at 1740°C suggests similar behaviour to the 100 hour specimens with a period of reducing shrinkage rate. However the initial part of the shrinkage curve (as does an experiment at 1695°C) gives a value of "n" of around 2.

The CRH data also exhibit differences. Whereas the slopes of the $\ln(y/VT)$ plots are similar to those for 100 h specimens, the value of "n" determined is much lower, giving an apparent activation energy of 398 KJ mol$^{-1}$. The discrepancy between the values of "n" determined by the isothermal and CRH techniques is also much greater. This is probably due to the fact that the fractional shrinkages measured for the 50 h specimens are considerably lower than those for the 100 h specimens. In order to construct the plot
of log y v. log C it was necessary to use shrinkage data at the limit of accuracy of the dilatometer. In view of this it is considered that the possibility of experimental error is too great to justify further discussion of these results.

6.1.2. Intermediate Stage Behaviour

The linear increase of density with time which is observed in the range 75% to 85% density is unusual. The most commonly reported behaviour in the intermediate stage is a logarithmic increase in density with time, which is most simply described by Cobles semi-empirical model:

\[ P - P_0 = K \ln \left( \frac{t-t'}{t_0} \right) \]

which was discussed in the literature survey. Fig.5.2.3. shows clearly that, even with much larger values of \( t' \) than are justified to account for the initial grain size, the model is of no use in explaining these results.

In the derivation of 6.3. it is assumed that grain growth proceeds proportional to the cube root of time. If, instead, the grain size were to remain constant, it is readily shown that the observed linear density increase will be observed since, after Coble:

\[ \frac{dp}{dt} = \frac{-720 \gamma \Omega Dv}{kT g^3} \]

However the grain growth observed in the SEMs is too great for this to be plausible explanation, an 8-fold decrease in sintering rate would in fact be expected.
It is therefore necessary to consider, without the aid of a specific model, what factors will influence the rate of densification by diffusion mechanisms in the intermediate stage. These are:

a) the chemical potential gradients between pores and grain boundaries
b) the diffusion coefficients
c) the cross-sectional area available for diffusion per unit pore volume

As sintering proceeds the chemical potential gradients (determined by the grain size, pore surface curvature and surface energy) must decrease since the pore diameters and grain size are observed to increase. The cross-sectional area for diffusion per unit pore volume can only increase if the pores become smaller in diameter (i.e. there is no pore coalescence), which is the opposite to that observed. It must therefore be concluded that the effective diffusion coefficient of the material increases during densification in order to maintain a constant shrinkage rate.

This correlates well with the anomalous diffusion behaviour which accounted for the difference between Dorn and CRH activation energies in the initial stage. The reported time-dependence of diffusion rates should result in the reported sintering behaviour. A straightforward change in diffusion coefficients due to compositional changes seems unlikely as the Dorn activation energy remains constant throughout the sintering process.

A connection between the anomalous diffusion behaviour and the presence of $\text{M}_2\text{C}_3$ in the sample seems likely as the end of the linear densification behaviour corresponds approximately with the final disappearance of $\text{M}_2\text{C}_3$.

**Stage 3 behaviour**

The densification above 85% density still belongs to the intermediate stage ("final stage" sintering with mainly closed pores begins for nearly all materials at around 92%), but is treated here as a separate stage due to the different kinetics observed.
The amount of data obtained for this stage is limited, except at 1695°C, at which temperature a number of compacts were sintered for up to 17 hours following CRH investigations of the initial stage.

Fig. 5.6 shows that here again, the Coble equation cannot be applied to the shrinkage behaviour. This is to be expected if grain growth does not follow the common cubic law.

Kuczynski /37/ has recently developed a model for the intermediate and final stages of sintering, in which the cylindrical or spherical porosity is considered to have a statistical distribution of diameters. The grain size at any point is related to the pore size and distribution by the Zener relation. This avoids the assumption of the empirical grain growth law which effectively determines the result of Coble's calculations. Unlike Cobles' equation, Kuczynski's does not predict the shrinkage rate as a function of the material constants, but does predict a porosity time relationship of the form:

$$\frac{1}{p^n} - \frac{1}{Po^n} = K Po^{2-n} \frac{1}{t}$$

where $n$ depends upon the mechanisms of matter transport, $p$ is a function of the original porosity distribution and $K$ a constant containing the rate controlling physical parameters. Fig. 5.7 shows that the shrinkage behaviour at 1695°C is a good fit to this equation with $n=1.8$.

Only one sample was sintered at 1600°C to higher than 85% density. The data also fit well to Kuczynski's equation with $n=1.8$.

In order to determine the densification behaviour at considerably lower temperatures, a sample which had already been sintered to 84.5% at 1700°C was studied isothermally at 1455°C. After 60 hours an increase of density at 1.8% was noted. The dilatometer curve showed the unexpected behaviour of a shrinkage rate increasing with time. As the long-term stability of the dilatometer is not known, not too much weight should be put upon this result, however it is of significance that the high temperature behaviour is not necessarily reproduced.
6.2. After hydrogen treatment

The sintering kinetics of the samples treated with hydrogen differ from those of untreated samples as follows:

1) The initial stage of decreasing sintering rate is absent, the rate of shrinkage being practically constant up to 87% density (about 6% linear shrinkage).

2) The rates of shrinkage are considerably higher (at 1% shrinkage and 1600°C by a factor of about 20).

3) The apparent activation energy is higher, and the values determined by Dorn and CRH methods differ less.

The various analyses performed show the following significant differences:

1) Instead of $M_2C_3$ appearing during sintering, $MO_2$ is found.
2) The structural development revealed by SEM is different.
3) "Dense" samples show a higher oxygen content.

The absence of an initial decrease in sintering rate is probably connected with the unusual structure of the specimen directly after the hydrogen treatment, as shown by SEM (Fig.5.2). The surfaces of the particles are not at all smooth (as seen during the particle size analysis), although it is difficult to say whether the particle surfaces are themselves rough, or if finer particles (perhaps the oxide) are dispersed between the original ones. In either case this should encourage early growth of necks by surface diffusion, possibly before any shrinkage is observed. (Surface diffusion increases its relative importance as particle sizes become smaller /4/.)

If thus neck growth can proceed until an intermediate stage structure is formed, without shrinkage having taken place, then the subsequent constant shrinkage rate is explicable if one considers the structural development shown in the other electron micrographs. These show that, at least up to 2.4% linear shrinkage (78.4% density), no grain growth occurs. This is seen best in the 2100X micrographs. According to Coble /18/ the densification rate in the intermediate stage is given by:
\[ \frac{dP}{dt} = -720 D_v/kT G^3 \quad (G = \text{grain diameter}) \]

Rosolowski and Greskowitch /15/ give a similar expression.

It is clear that, if the grain size remains constant and the structure appropriate to the Coble model is retained, i.e. all the pores are situated on grain boundaries, that the rate of densification and of linear shrinkage will be constant.

The question remains: why do grain growth and pore coalescence not occur in this case? The answer must lie with the observed oxide. As this must first be formed on the particle surfaces it will, after neck formation, be found on the grain boundaries. It seems reasonable that the movement of the grain boundaries is hindered by the oxide thus preventing grain growth. The slowing down of the densification rate would then correspond with the disappearance of the oxide.

Since the oxide clearly plays an important role in determining the sintering kinetics, the question arises as to how it was formed, when not observed in the milled powder. The following explanation is therefore suggested.

During ballmilling a certain amount of oxygen pick-up always occurs so that the total oxygen content of the powder rises from around 0.1% to 0.3%. Since the temperature during ballmilling is only about 50°C diffusion into the particles must be very limited, so that it is probably that the oxygen is merely chemisorbed onto the powder surface without forming an oxycarbonitride or an oxide. Without the hydrogen treatment the carbon remaining from the decomposition of the stearic acid binder would, at sintering temperatures, react with this oxygen to form CO, as observed. However, the hydrogen treatment removes carbon by forming CH₄/149/, so that this reaction can no longer take place. An oxide can then be formed. The overall reaction taking place is:

\[ M(C_{0.8}N_{0.2}) + 2xH_2 + xO_2 \rightarrow xMO_2 + (1-x)M(C_{0.8}N_{0.2}) + 0.8xCH_4 + 0.1xN_2 \]

During sintering, when the hydrogen is no longer present, the oxide reacts with the carbonitride to form an oxycarbonitride:
Unanswered remains now the question of the high apparent activation energy. Since the CRH and Dorn methods both gave the same value, then the anomalous diffusion behaviour which explained the results for the untreated samples has clearly been changes. However, no diffusion data is available for carbonitrides in the presence of oxide - it being only certain that the diffusion coefficients for plutonium in hypostoichiometric oxides are about two orders of magnitude below those in carbonitrides /151/ at temperatures around 1600°C, and that diffusion through the oxide is therefore not likely to be important. This question is therefore left open pending more information on diffusion behaviour.
6.3. Summary and Conclusions

6.3.1. Initial Stage Sintering

Since the CRH measurements agree with Johnson's equation for a volume diffusion mechanism, it is concluded that this mechanism is dominant. A small deviation from the theoretical values for the constants could be explained by a contribution of surface diffusion to the earliest stages of neck growth, as predicted by the Ashby diagram. The higher activation energies determined by the Dorn method are possibly due to experimental error or the simultaneous operation of several mechanisms but are better explained by a peculiarity in the self-diffusion behaviour of carbonitrides reported by other workers.

6.3.2. Intermediate and Final Stage

The high apparent activation energies determined rule out all mechanisms other than volume diffusion. A period of constant isothermal sintering rate is explicable if the time-dependence of the anomalous diffusion behaviour is considered. Subsequent behaviour does not correlate with the much-used Coble equation for intermediate stage sintering, but is consistent with a statistical model recently developed by Kuczynski.

6.3.3. Influence of hydrogen treatment

A treatment of pressed compacts under hydrogen prior to sintering, which removes carbon, greatly accelerates the sintering process and alters the sintering kinetics. The observed activation energies are higher and the results of CRH and Dorn methods agree. It is suggested the presence of oxide on the particle surfaces encourages surface diffusion and hence the intermediate stage structure is reached without appreciable shrinkage. Subsequent intermediate stage sintering is rapid as grain growth is hindered by the presence of oxide in the grain boundaries, which later dissolves in the carbonitride. No completely satisfactory explanation for the high activation energies can be offered.
Appendix 1: Effect of Additional Mechanisms on the Value of Q Determined by the Dorn Method

If two thermally activated mechanisms, A and B, which, acting alone, give shrinkage rates $\dot{y}_A$ and $\dot{y}_B$, both contribute to the shrinkage process, then the ratio of the shrinkage rates at two temperatures, $T_1$ and $T_2$, will be:

$$\frac{\dot{y}_A + \dot{y}_B}{\dot{y}_A + \dot{y}_B}$$  \hspace{1cm} 7.1

Letting $T_1 > T_2$ and the activation energy for mechanism A higher than that for B it follows that

$$\frac{\dot{y}_A}{\dot{y}_B} > \frac{\dot{y}_B}{\dot{y}_A} \text{ (7.2) and } \dot{y}_A > \dot{y}_A, \dot{y}_B > \dot{y}_B$$  \hspace{1cm} 7.3

$$\dot{y}_A \dot{y}_B > \dot{y}_A \dot{y}_B$$  \hspace{1cm} 7.4

$$\dot{y}_A (\dot{y}_A + \dot{y}_B) > \dot{y}_A (\dot{y}_A + \dot{y}_B)$$  \hspace{1cm} 7.5

$$\frac{\dot{y}_A}{\dot{y}_A + \dot{y}_B} > \frac{\dot{y}_A}{\dot{y}_A + \dot{y}_B}$$  \hspace{1cm} 7.6

Similarly:

$$\frac{\dot{y}_A + \dot{y}_B}{\dot{y}_A + \dot{y}_B} > \frac{\dot{y}_B}{\dot{y}_B}$$  \hspace{1cm} 7.7

Since the higher the value of the ratio, the higher the apparent activation energy, it is clear that the apparent activation energy determined when two mechanisms operate simultaneously will lie between two true values.

Conversely, when mechanism B is a process causing swelling of the compact, then the ratio is given by:
From 7.3 we have:

\[
\frac{\dot{y}_{A1} - \dot{y}_{B1}}{\dot{y}_{A2} - \dot{y}_{B2}}
\]

\[
\dot{y}_{A1} \dot{y}_{A2} - \dot{y}_{A1} \dot{y}_{B2} < \dot{y}_{A1} \dot{y}_{A2} - \dot{y}_{B1} \dot{y}_{A2}
\]

hence

\[
\frac{\dot{y}_{A1}}{\dot{y}_{A2}} < \frac{\dot{y}_{A1} - \dot{y}_{B1}}{\dot{y}_{A2} - \dot{y}_{B2}}
\]

Hence the apparent activation energy is higher than that for mechanism A operating alone, so long as \( Q_A > Q_B \).
Appendix 2: The Influence of G as Pressure within Closed Pores on the Driving Force for Sintering

The effective negative pressure due to the surface tension in a cylindrical pore is given by the expression

\[-P = \frac{\gamma}{2r}\]

where \(\gamma\) is the surface tension and \(r\) the pore radius. The largest pores visible in the micrographs (5.1) are 1 \(\mu\)m diameter so that, taking the surface tension as 0.72 Nm\(^{-1}\) /133/ we have

\[-P = 0.36 \times 10^6 \text{ Nm}^{-2}\]

which is approximately 3.5 atmospheres or 2700 Torr.

The precise value of the internal gas pressure is difficult to estimate, in particular as equilibrium pressures will not necessarily prevail, however the CO pressure is not likely to exceed about 25 Torr (equilibrium pressure over UO\(_2\)-C mixture at 1560\(^\circ\)C) /107/ and the nitrogen pressure 10\(^{-2}\) atmospheres (equilibrium pressure over U (C\(_{0.8}\) N\(_{0.2}\)) /96/ at 1700\(^\circ\)C, which are two orders of magnitude lower than the pressure due to surface tension.
Appendix 3: Significance of the results to in-pile densification

Although the principal aim of this project was the quantitative description of the sintering process during carbonitride fuel fabrication and the influence of the hydrogen treatment on sintering, the results obtained at higher densities are interesting for the prediction of in-pile fuel behaviour.

A serious problem with helium-bonded carbide and nitride type fuels is the variation of the fuel-cladding gap during irradiation. Before swelling of the fuel due to the build-up of fission gas sets in, a certain amount of densification of the fuel occurs, a continuation of the sintering process, increasing the fuel-cladding gap. The temperature of the fuel is dependent upon this gap and as the swelling process is temperature dependent it can be seen that a knowledge of the densification process is essential to the prediction of fuel behaviour.

In-pile densification will be accelerated by the presence of radiation-induced defects, but, since in-pile experiments are difficult and costly, knowledge of the out-of-pile behaviour is also valuable, particularly if the mechanism of the process can be determined.

Apart from the one experiment performed at 1450°C, all the relevant densification data refers to considerably higher temperatures than are encountered in-pile. However, due to the aforementioned acceleration of the process in pile, these data are probably quite relevant.

From the ratio of the observed shrinkage rates (at 85% density) at 1695°C and 1455°C a phenomenological activation energy of 495 kJ mol$^{-1}$ (118 kCal mol$^{-1}$) can be calculated. Assuming that the time dependence of the densification process is the same over the whole of this temperature range, one obtains an empirical expression for isothermal densification above 85% density:

$$\frac{1}{p^{1.18}} - \frac{1}{p_0^{1.18}} = K \exp\left(-\frac{495 \text{ kJ}}{RT}\right)$$

where $K = 8.0 \times 10^{14}$. 
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