THE EFFECT OF IMPURITIES ON GRAIN GROWTH IN URANIUM DIOXIDE

A THESIS PRESENTED FOR THE DEGREE OF Ph.D. IN THE UNIVERSITY OF SURREY

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Grain growth has been investigated in high purity uranium dioxide and in uranium dioxide containing a number of additives.

High purity UO$_2$F$_2$ powder was chosen as the source material for the fine UO$_2$ powder needed to produce the specimens for this work. Ammonium diuranate was precipitated from a solution of UO$_2$F$_2$ using ammonia. Using a solution coating technique, quantities of ammonium diuranate were doped with various additives: Cr, Ni, La, Mo, and Al. The ADU was reduced to UO$_2$ by heating for two hours in dry hydrogen at 500°C. The resulting powder had a surface area of 18 - 20 m$^2$/g.

The UO$_2$ powder was cold pressed into pellets weighing 0.5g each and these were sintered at 1400°C in wet hydrogen. The water content of the hydrogen was not sufficient to cause deviation from stoichiometry. Completely pore free specimens were obtained.

The surfaces of the specimens were then ground and polished flat suitable for microscopic examination because thermal etching was relied on to reveal grain boundaries.

Grain growth experiments were performed at temperatures between 1400 and 1800°C, the majority however, were at 1500, 1600 or 1700°C. A multianneal technique on two specimens provided all the data for each experiment. Grain size measurements were made on photomicrographs of the specimen surfaces.
Spectrographic analysis was carried out on the specimens at the end of the runs. These revealed that excessive evaporation of the dopant compounds had occurred in most cases resulting in lower dopant concentrations than were intended and also in contamination of each batch of UO₂ with dopants used for the previous experiments.

The experimental results showed that the behaviour of the undoped UO₂ was controlled by the residual impurities of which iron and silicon were the most abundant. The molybdenum doped material showed results typical of a material containing inert second phase particles. The lanthanum doped material's behaviour indicated that solute drag was occurring. The activation energy for grain growth in this material was 40 kcal/mole.

The Cr, Ni, and Al doped specimens all showed different grain growth exponents at different temperatures indicating that the rate controlling process changed with temperature.

- Exaggerated grain growth occurred in Cr and La doped specimens.

It was concluded that impurity effects on grain growth are dependent on the concentration, the mobility and the energy of interaction of the impurity with the grain boundaries.
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CHAPTER 1  INTRODUCTION
1.1 THE AIMS OF THE PROJECT

The aim of the project is to investigate the grain growth behaviour of high purity uranium dioxide at a number of temperatures and then to compare this behaviour with that of uranium dioxide to which additions of various dopants have been made. Selection of the additives has been made in a way intended to enable identification of the properties of impurities which control grain growth behaviour. Knowledge of these properties would enable a greater degree of control to be exercised over the grain size in uranium dioxide bodies than is now possible. Since grain size affects such properties as mechanical strength, thermal shock resistance, creep behaviour and diffusion rates, such control is evidently desirable.
In investigating the effects of dopants on grain growth it is naturally highly desirable to compare the results with the behaviour of the pure material. Unfortunately it is impossible in practice to obtain completely pure materials and so comparison of results must be made with those of the purest material available. This means that there is a possibility that the residual impurities may affect the results obtained and that highly accurate quantitative results cannot be expected therefore. The effect of residual impurities should not be so great however as to prevent conclusions being drawn about the qualitative behaviour of various classes of additive. It should still therefore be possible to draw valuable conclusions about the parameters which control grain growth.

A requirement of grain growth specimens is that they should be fine grained so that as many orders of magnitude increase in grain size as possible can be covered in the minimum amount of time. In order to fulfill this requirement in the case of uranium dioxide it is necessary to produce specimens by powder fabrication methods. Cold pressing of the powders into green cylinders followed by sintering are the methods that have been used. If the sintering process does not go to completion, residual porosity remains in the material and this porosity would certainly obscure the effects of additives. It is necessary, therefore, to eliminate all porosity before beginning grain growth experiments if the effects of additives are to be properly investigated.

Since the rate of densification in a sintering body de-
creases exponentially as the theoretical density is approached it is not possible to determine the moment when full density is achieved. This means that measurement of \( t_0 \), the time at which grain growth begins, is impossible. Grain growth of an order of magnitude or more may occur during sintering and it is important to ensure that the grain growth occurring in the final stages of sintering is not used since this is porosity controlled. Only grain growth in fully dense bodies is considered in this work.

A method of analysing the results has been devised which eliminates the need for values of \( D_0 \) and \( t_0 \) and thereby reduces errors involved in attempting to obtain these values by extrapolation. It is believed this method has not been used previously.
2.1 INTRODUCTION

Much work has been carried out on the effects of impurities on grain boundary migration in materials and also on related topics such as impurity effects on grain boundary energies and diffusion rates.

A number of theories of grain growth, based on simple models of boundary migration, have been proposed. Although some of these take into account the effects due to porosity and second phase particles, experimental results usually differ from theoretical predictions. Progress in constructing an adequate theory has been hindered by the fact that the discrepancies between theoretical predictions and experimental results are not always uniform, suggesting that there are experimental variables which have not always been adequately controlled. This makes comparison between various pieces of experimental work and the drawing of conclusions rather difficult. It has been possible, however, to identify a number of parameters which appear to influence the way in which impurities affect boundary migration as well as the properties of impurities that determine their effect on boundary migration but it remains to be seen whether there are others as yet unrecognized. So that the experimental results can be viewed in perspective, the theories of grain growth will be reviewed first. They have been split into four groups: the first deals with pure systems, the second with porous systems, the third with systems containing solutes, and the fourth with those containing insoluble second phase particles. While it recognized that porosity can be treated as a second phase,
pores differ from other second phase particles in one important respect— they can very rapidly coalesce and thus their number and size change with time whereas other second phase particles are more accurately described as retaining constant size and number. This difference is important in the formulation of theories, therefore porosity is considered separately. The experimental work on grain growth has been split up into sections corresponding to those used for the theories.
2.2.1 Theory of grain growth in pure materials

2.2.1.1 The first kinetic theory to be developed was based on the following three assumptions.

1. Grain boundaries migrate towards their centre of curvature.
2. Migration rate is proportional to boundary curvature.
3. Average boundary curvature is inversely proportional to grain diameter.

From these assumptions the following equation may be written

\[ \frac{dD}{dt} = \frac{K}{D} \]  \hspace{1cm} (2.1)

which on integration yields

\[ D^2 - D_0^2 = kt. \]  \hspace{1cm} (2.2)

Since many experimental results fitted cubic kinetics more closely than squared kinetics attempts were made to modify this equation by including effects due to porosity.

2.2.1.2 Hillert\(^{(1)}\), however, developed a theory using only the assumption that boundary velocity is proportional to pressure difference across the boundary due to its curvature, this is essentially the same as the second assumption listed above.

From this assumption the following equation is derived

\[ V = M \Delta P \]  \hspace{1cm} (2.3)

The constant, \( M \), is called the boundary mobility. Substituting for \( \Delta P \) according to surface tension theory

\[ V = M \gamma \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) \]  \hspace{1cm} (2.4)

The rate of growth of a grain can be related to the boundary velocity by integrating \( V \) around the grain. By calling this integrated value \( V_{\text{average}} \) the growth rate can be written, \( \frac{dD}{dt} = g \cdot V_{\text{average}} \), where \( g \) is a constant depending on grain shape. It is greater than unity for all nonspherical grains. Thus equation 2.4 becomes
To ensure that this equation has the required characteristics, namely, it is positive for large \( R \) and negative for small \( R \), the following substitution is made

\[
g \left( \frac{1}{P_1} + \frac{1}{P_2} \right) = a \left( \frac{1}{D_{\text{crit}}} - \frac{1}{D} \right)
\]

Thus 2.5 becomes

\[
\frac{dD}{dt} = M \gamma \left( \frac{1}{D_{\text{crit}}} - \frac{1}{D} \right)
\]

\( D_{\text{crit}} \) is the critical grain diameter at which the rate of growth is zero.

Hillert noticed that this equation was similar to one obtained by Greenwood\(^{(2)}\) for the coalescence of particles. Using Greenwood's equation, Lifshitz and Slyozov\(^{(3)}\) were able to relate \( D_{\text{crit}} \) to \( D \) and calculate the distribution function of the particles. Hillert therefore applied this method to equation 2.7 and was able to evaluate \( a \) as \( \frac{1}{2} \) in two dimensional systems and as unity in three dimensional systems.

Substituting a factor \( U = \frac{D}{D_{\text{crit}}} \) into equation 2.7 and forming an expression for the relative growth of a grain gives

\[
N = 2aM\gamma \frac{dD}{dt} \frac{d^2}{D_{\text{crit}}}
\]

which when \( N \) is evaluated reduces to

\[
\frac{dD^2}{dt} = \frac{1}{8} a M \gamma
\]

which is the final growth rate equation for normal grain growth obtained in this analysis.

It is a consequence of the ability to determine the size distribution function of the grains that a prediction can be made that no grains larger than \( 2D_{\text{crit}} \) can exist during steady state grain growth. If such large grains do exist then exaggerated growth will occur until a size distribution sufficiently narrow to permit normal grain growth has been obtained.

The size distribution function is given by
\[ P(U) = \frac{2e^{-U}}{(2-U)^{2+\beta}} \exp \frac{2-U}{2-U} \]

\( \beta \) has the value 2 for 2 dimensions and 3 for 3 dimensions. From this function it follows that \( D = D_{\text{crit}} \) in 2 dimensions and \( \bar{D} = \frac{g}{9} D_{\text{crit}} \) in 3 dimensions. The maximum grain diameter, \( D_{\text{max}} = 1.8\bar{D} \) in 3 dimensions.

2.2.1.3 A third theory, also due to Hillert (1) based on a two dimensional pictorial model of the way in which grains of less than 6 sides are consumed, also arrives at a parabolic growth rate law. An ideal two dimensional array of hexagonal grains containing a pair of neighbouring grains, one 5 sided the other 7 sided, "a 5-7 pair", is considered. This 5-7 pair is termed a defect and observing the model as the 5 sided grain shrinks and disappears shows that another grain takes on the role of the consumed grain thus preserving the 5-7 pair defect. The rate of grain growth is thus assumed to depend on the number of defects present, \( c \), and the time, \( a \), needed for a newly formed 5 sided grain to disappear,

\[ - \frac{dN}{dt} = \frac{cN}{a} \quad 2.11 \]

The number of grains in the system, \( N \), is related to the size of the grains.

\[ N D^2 = \text{constant} \quad 2.12 \]

which is equivalent to

\[ 2 \frac{dD_{\text{crit}}}{D_{\text{crit}}} + \frac{dN}{N} = 0 \quad 2.13 \]

combining 2.11 and 2.13 gives

\[ \frac{dD_{\text{crit}}}{dt} = - \frac{D_{\text{crit}}}{2N} \cdot \frac{dN}{dt} = \frac{D_{\text{crit}}}{2} \cdot \frac{c}{a} \quad 2.14 \]

\[ \frac{dD_{\text{crit}}^2}{dt} = \frac{D_{\text{crit}}^2}{a} \cdot \frac{c}{a} \quad 2.15 \]

In view of possible interaction between defects at high concentrations equation 2.15 was modified slightly

\[ \frac{dD_{\text{crit}}^2}{dt} = D_{\text{crit}}^2 \sum \frac{c_p}{a_p} \quad 2.16 \]

where \( c_p \) is the concentration of grains with \( 6p \) neighbours and \( a_p \) is the time taken for such grains to disappear. By taking \( 6p = n \) and using
equation 2.4, \( a_p \) can be evaluated

\[
\frac{dD}{dt} = -\frac{P M Y}{6D} \tag{2.17}
\]

Integration from \( D_{\text{crit}} \) to zero gives

\[
a_p = -\frac{6}{p M Y} \int_{D_{\text{crit}}}^{D} D \cdot dD = \frac{3D_{\text{crit}}^2}{p M Y} \tag{2.18}
\]

This value of \( a \) is approximate and is larger than the true value since as the grain shrinks and loses another side the shrinkage rate will increase. This effect was judged sufficiently small to be neglected.

Therefore by combining equations 2.18 and 2.16 the parabolic growth rate equation 2.19 is obtained. This equation assumes that the number of defects remains constant which is equivalent to assuming a constant size distribution function and only applies to two dimensional systems.

An estimate of the defect concentration can be obtained by comparing equations 2.9 and 2.19

\[
\sum_{p} p \cdot c_p = \frac{3}{2} a = \frac{3}{4} \tag{2.20}
\]

Since this concentration is so high, interaction between defects seems highly likely, and it is postulated that when two defects meet they can annihilate each other and in this way maintain a constant defect concentration during grain growth. Should the concentration of defects be below that required for normal grain growth according to equation 2.20, thereby implying a narrow grain size distribution, then those grains with more than 6 sides will grow relative to the average size thus widen the range of grain sizes and thus produce more defects until a concentration sufficient for normal grain growth is obtained.
2.2.2.1 Kingery (6) modified the parabolic growth rate equations derived for non-porous systems to account for the effects of porosity by using two assumptions.

1. Pore diameter remains proportional to grain diameter as a result of pore coalescence which occurs when grains with more than one pore on their boundaries are annihilated through shrinkage.

2. The rate of pore migration is inversely proportional to pore diameter.

The first assumption has received some indirect support since it has been shown (3) that coalescing second phase particles retain a fixed size distribution.

\[
\frac{dD}{dt} = \frac{k_1}{D} \cdot \frac{k_2}{D_p} = \frac{k_1}{D} \cdot \frac{k_3}{D} = \frac{k_4}{D^2}
\]

or, on integrating

\[
D^3 - D_0^3 = kt
\]

2.2.2.2 Nichols (7) claimed that the second assumption is true only when migration occurs by the process of vapour transport with internal pore pressure of \(\gamma/r\). This conclusion was reached by considering the force, \(F\), exerted by a boundary on a pore, radius \(r\), located on the boundary.

\[
F = \pi r^2 \gamma \sin 2\theta
\]

where \(\theta\) is the half angle of a cone with its apex at the centre of the pore and its base at the intersection of the pore with the boundary.

This equation is independent of any specific mechanism of pore migration. Provided that \(\theta > 0\) the force, \(F\), is directly proportional to \(r\). Since \(\sin 2\theta\) increases as the boundary driving force, \(F_b\), increases, it is assumed that \(\sin 2\theta \propto F_b\) and it is also assumed that \(F_b \propto D^{-1}\). It therefore follows that:

\[
F = k_s r D^{-1}
\]

Let \(V\) = velocity of the pore and hence of the boundary, and \(M_p\) = pore mobility. It then follows that:
This is the final equation in Nichols analysis and to use it to predict the order of the kinetics the dependence of $M_p$ on $r$ must be known. A series of expressions of $M_p$ in terms of $r$ for various possible transport mechanisms has been derived using approximations \(^{(8)}\). All the expressions are of the form

$$M_p = K r^{-n} \exp \left(-\frac{Q}{RT}\right)$$

where the exponent $n$, the constant, $K$, and activation energy, $Q$, depend on the mechanism. The values of $n$ for various processes are listed below

1. Volume diffusion, $-3$,
2. Surface diffusion, $-4$,
3. Vapour transport ($P = \text{constant}$), $-3$,
4. Vapour transport ($P = 2\gamma/r$), $-2$.

By assuming boundary velocity directly proportional to $dD/dt$ and substituting the above results in to equation 2.26 it is apparent that vapour transport when $P = 2\gamma/r$ is the only mechanism which results in cubic grain growth kinetics. It is, of course, assumed that porosity is not reduced by gas diffusion along grain boundaries.

2.2.2.3 Another analysis of growth rate in porous systems was published by Nichols \(^{(9)}\). It uses as its starting point the fact that if pores remain on grain boundaries, the pore and boundary velocities are identical.

$$V = V_b = V_p \quad 2.27$$

thus

$$M_b F'_b = M_p F_p \quad 2.28$$

where

$$F'_b = F_b - n F_{\text{drag}} \quad 2.29$$

$b$ and $p$ subscripts denote boundary and pore respectively, $n$ is the number of pores per boundary.

$$F_p = \frac{V}{M_p} = F_{\text{drag}} \quad 2.30$$

therefore
In the limiting case where \( n = 0 \), \( V = \frac{M_b F_b}{M_p} \), and when \( n \gg 1 \), \( V = \frac{M_b F_b}{n} \).

The latter case is taken as representing real porous systems.

\[
\frac{dD}{dt} = \frac{k M_b F_b}{n} \quad 2.33
\]

This equation is now applied to the previously considered case of pore migration by vapour transport i.e. \( \frac{M_p}{\rho} \propto r^{-2} F_b \propto D^{-1}, r \propto D \), to give

\[
\frac{dD}{dt} \propto \frac{1}{n D^3} \quad 2.34
\]

The value of \( n \) cannot increase because of pore coalescence. If pores exist only at boundary intersections then \( n \) is constant and the rate equation is

\[
\frac{dD}{dt} = \frac{k}{D^3} \quad 2.35
\]

This may apply in later stages of grain growth but in early stages it seems likely that \( n > 1 \) and therefore \( n \) decreases as growth occurs i.e. \( n \propto \frac{1}{D} \) and therefore the rate equation is

\[
\frac{dD}{dt} = \frac{k}{D^2} \quad 2.36
\]

A transition between these two rates should be expected according to this theory.

2.2.2.4 However a basic assumption of this theory, namely \( F_b \propto \frac{1}{D} \), has been challenged by Brook who maintained that since

\[
F_b = \Delta P A \quad 2.37
\]

where \( A = \) boundary area, \( \Delta P = \) pressure drop due to curvature,

\[
F_b = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) A \quad 2.38
\]

\[
F_b \propto \frac{2\gamma}{D} \cdot D^2 \quad 2.39
\]
assuming boundary curvature is inversely proportional to D. This would make the kinetics of equations 2.35 and 2.36 squared and linear respectively.

2.2.2.5 It has been assumed in the theories presented above that all pores remain on the migrating boundaries and that all pores are equally effective in retarding boundary migration. However Speight and Greenwood\(^{(2)}\) in an analysis of the interaction between pores and boundaries, found that there was a critical pore radius, \( r_p \), at which pores would most easily become detached from a migrating boundary, although they would only become detached if the driving force was sufficiently high

\[
\frac{4 \pi}{kT} \exp \left( \frac{Q - Q_s}{kT} \right)
\]

where \( a = \) atomic volume, \( f = \) entropy factor for an atom crossing the boundary, \( l = \) interpore separation, \( Q = \) activation energy for boundary migration and \( Q_s = \) activation energy for surface diffusion, since it is assumed that surface diffusion of atoms of the solid across the pore surface is the mechanism by which pores migrate.

This equation assumes pores to be spherical, whereas they are more accurately represented by two sphere segments which join at the boundary\(^{(11)}\). Taking this more realistic pore shape into account has the effect of reducing the value of the critical pore radius in equation 2.40. The critical pore radius represents a minimum on a graph of pore radius versus probability of remaining on a boundary. It is concluded that pores smaller than \( r_p \), whilst not exerting very much retardation are sufficiently mobile to stay on the boundary and those above \( r_p \) although possessing low mobility exert sufficient retardation on the boundary to slow it down to the rate of migration of the pore. It should be noted that pores of radius equal to \( r_p \) will not necessarily become detached from boundary.
Lücke and Detert\textsuperscript{(12)} were first to propose the solute drag theory of grain growth. This theory predicted that there would be two extreme conditions under which boundaries could migrate with an unstable region between these two conditions. Under conditions of high impurity concentration or low driving force the boundary velocity is given as

\[ V = \frac{F \Gamma B}{k T \Gamma} \]  \textsuperscript{2.41}

\( \Gamma \) represents the number of adsorbed impurity atoms per unit area of grain boundary and \( B \) represents the bulk diffusion coefficient. This value is a function of the energy of interaction between an impurity atom and the boundary. The interaction energy was taken as positive in cases where adsorption occurred and where it was negative it was assumed that the impurity would have little effect on grain growth.

This assumption was challenged by Cahn\textsuperscript{(13)} who maintained that the sign of the interaction energy should be omitted. This modification was necessary if the theory was to explain experimental results obtained on the relative effects of silver, gold and tin in zone refined lead. It was justified by the results of detailed analysis of the shapes of concentration profiles of impurity concentrations around grain boundaries. Various interaction energy and velocity conditions were examined and it was discovered that a pile up of impurity atoms ahead of migrating boundaries occurred for impurity atom species which were not adsorbed by the grain boundaries under equilibrium conditions.

Again two possible conditions for grain growth were predicted with an unstable region in between. Under low boundary velocity conditions the velocity equation was

\[ V = \frac{P}{\lambda + a C_0} \]  \textsuperscript{2.42}

which implies that the impurity effect is independent of the sign of the interaction energy.

At high velocity the boundary migration rate is given by
Here, both $a$ and $a/p^2$ are functions of solute diffusion coefficient and solute boundary interaction energy. $\lambda$ is an intrinsic drag coefficient. This equation implies that impurity drag will decrease as the driving force, $F$, increases. This is equivalent to drag decreasing as boundary velocity increases. In addition, impurities with greater diffusivities should produce greater drag effects.

Work done on dilute lead alloys \(^\text{(14)}\) which shows a change in grain growth exponent, has been interpreted in terms of a change from the high velocity condition to the low velocity condition. However no decrease of drag effect was found in the high velocity region as velocity increased.

Grey and Higgins \(^\text{(15)}\) noted this fact and attempted to fit the same and other, data to their own grain growth equation. This is given below.

$$D^{-1} = \lambda D + \mu \quad \text{(2.44)}$$

Here $\lambda$ and $\mu$ are, respectively, velocity dependent and velocity independent drag coefficients. Expressed in terms of time this equation becomes,

$$t = \frac{\lambda}{\mu^2} \left( \ln \frac{1-\mu D}{1-\mu D_0} + \mu (D-D_0) \right) \quad \text{(2.45)}$$

In the case where $\mu$ is very small this equation reduces to a form identical to that for grain growth in pure materials.

$$t = \frac{\lambda}{2} (D^2 - D_0^2) \quad \text{(2.46)}$$

$\lambda$ and $\mu$ were obtained from equation (2.44) and these values used to represent the data graphically in terms of equation (2.45). An excellent fit of the data was obtained.

The similarity of equation (2.44) to one proposed by Burke \(^\text{(16)}\) to account for the limiting grain size phenomenon is obvious. This similarity provided a clue to the origin of the velocity independent drag coefficient, namely that the effect is similar to that produced by second phase particles. The only possible source of such particles is the mechanism by which clusters of impurity atoms are formed as proposed by Aust \(^\text{(17)}\) to explain grain boundary hardening (see section 2.3.4).
by Cahn's model for the low velocity boundary migration condition.

Grey and Higgins also made an additional point about Cahn's model concerning the high velocity condition. The impurity with the greatest diffusivity will not necessarily produce the greatest drag since drag effects also depend on the interaction energy of the impurity with the boundary and it is the relative changes in the two parameters which determines which solute produces the greatest drag effect.

2.2.4 Theory of grain growth in materials containing insoluble second phases

2.2.4.1 Zener derived a formula for the limiting grain size caused by second phase particles by equating the pressure which causes a boundary to migrate to the retarding force produced by the second phase particles and obtained the equation

$$r_c = \frac{4r}{3f}$$

where $r_c$ is the radius of curvature of the boundary when migration ceases, $r$ is the radius of the second phase particles (all assumed to be spherical and of equal size) and $f$ is the volume fraction of such particles. It has been found experimentally that the relationship between $r_c$ and grain diameter is $r_c = 9D^{\frac{18}{2}}$. Equation 2.47 thus becomes

$$D_1 = \frac{0.15r}{f}$$

2.2.4.2 Hillert\(^\dagger\) produced a theory based on similar lines to Zener's theory. The retarding force due to second phase particles, $S$, is defined as $S = \gamma Z$ where $Z$ is a function of the number and sizes of second phase particles. $Z$ is assumed to be independent of boundary curvature although it is recognized that this may not be entirely true. Equation 2.3 is then modified

$$V = M \Delta P_{\text{true}} = M (\Delta P + S)$$

$$= M \gamma \left[ \left( \frac{1}{P_1} + \frac{1}{P_2} \right) + Z \right]$$

Using this result equation 2.7 can be modified
The sign is chosen so that the force due to the second phase always opposes the boundary driving force. In addition the retarding force is never allowed to exceed the driving force and so \( \frac{dD}{dt} = 0 \) in this range of values.

This theory gives the limiting grain size \( D_1 = a/Z \) and it follows from equation 2.50 that no grains can grow when \( D_{\text{crit}} \) exceeds \( a/Z \).

2.2.4.3 Hillert \(^{(1)}\) also adapted his defect model of grain growth to cover the effect of second phase particles. By integrating equation 2.4 equation 2.51 can be derived

\[
\frac{dD}{dt} = \frac{M \gamma a}{D} \left( \frac{n}{6} - 1 \right) \tag{2.51}
\]

Comparison of this equation with equations 2.6 and 2.7 leads to equation 2.52

\[
n = 6 + 6a \left( \frac{D}{D_{\text{crit}}} - 1 \right) \tag{2.52}
\]

Equation 2.50 can now be transformed into equation 2.53

\[
\frac{dD}{dt} = \frac{M \gamma}{D} \left( \frac{n}{6} - 1 \pm 2D \right) \tag{2.53}
\]

Taking \( n = 6 - p \), as in the previous defect theory, and integrating, an expression for \( a_p \), the time taken for a 5 sided grain to disappear, is obtained. Combining this expression with equation 2.16 gives

\[
\frac{dD_{\text{crit}}}{dt} = \frac{1}{3} M \gamma \sum_p \frac{1 - 6Z}{p} \cdot D_{\text{crit}}^{2/3} \cdot C_p \tag{2.54}
\]

At low values of \( Z \cdot D_{\text{crit}} \), that is a low retardation due to second phase particles, this equation is equivalent to the equation obtained for systems not containing second phase particles.

At high values of \( Z \cdot D_{\text{crit}} \) a series of limiting grain sizes are predicted for \( D_{\text{crit}} \). The first of these occurs when all solitary defects are pinned, \( D_{11} = 1/6Z \), because 5 sided grains of average size \( D = D_{\text{crit}} = 1/6Z \) will not shrink according to equation 2.53. After this point growth can only occur through cooperating defects and another limit
of cooperating defects, become pinned. The result of this series of limits is a gradual reduction of growth rate up to the final limit $D_1 = 1/2Z$ which is the point at which groups of three cooperating defects cease to operate. Hillert however believes that grain growth should effectively cease at the limit $1/3Z$ since the number of groups of three cooperating defects is expected to be very small. It is possible that, if such groups did exist in small numbers and contained grains much larger than average, then these grains could grow at a rate given by equation 2.50 as

$$\frac{dD}{dt} = \frac{M \gamma}{6D_{\text{crit}}}$$

Once such growth has started the grain size distribution is altered and the upper limit of $1/2Z$ no longer applies.

2.2.4.4 It is not known whether the above conditions for abnormal grain growth will automatically result from normal grain growth but Hillert thinks it unlikely. An alternative explanation is that the second phase particles may coalesce eventually after a limiting grain size has been reached. As growth recommences $D_{\text{crit}}$ will remain equal to $1/3Z$, assuming this is the limit at which it stopped, but that grains at the maximum end of the size distribution which may have diameters above the $1/2Z$ limit could grow at a faster rate thus leading to abnormal grain growth. It has not been possible to describe this situation mathematically.

In the case where the second phase dissolves however, it is conceivable that $ZD_{\text{crit}}$ will remain constant as $D_{\text{crit}}$ increases according to a parabolic growth law. The consequence of this is that equation 2.23 can be rewritten in terms of the growth of a grain relative to $D_{\text{crit}}$ and a steady state expression obtained which indicates that under such conditions the maximum grain diameter in the size distribution can increase from $2D_{\text{crit}}$ during normal grain growth to a value that approached infinity as $D_{\text{crit}}$ approaches a limit of $a/Z$.

From this explanation it follows that abnormal grain growth would
2.2.5 Discussion of the Various Grain Growth Theories

Only the theoretical merits will be assessed here, how well they fit experimental data will be discussed in section 2.3.

All the theories make use of certain assumptions some of which need close examination. For example "Boundary curvature is inversely proportional to grain diameter" is not true of the absolute values of particular grains since a 30 µm grain, for example, may have a positive or negative curvature depending on whether it is set in a matrix of grains of average diameter of 100 µm or 10 µm.

Neither is this assumption true of \( \bar{D} \) as it increases with time in the case where \( \bar{D} = D_{\text{crit}} \) as in Hillert's two dimensional model, the average boundary curvature of all such grains is zero by definition. Thus the average boundary curvature will always be zero whatever the absolute value of \( \bar{D} \). In the case where \( \bar{D} \neq D_{\text{crit}} \) the boundary curvature depends both on the absolute value of \( D \) and of \( D_{\text{crit}} \) as described by equation 2.56

\[
\bar{r}_c = \frac{D_{\text{crit}} \cdot D}{D_{\text{crit}} - D} \quad 2.56
\]

The derivation of this equation is given in appendix 1 since it does not appear anywhere in the literature. If \( \bar{D} = kD_{\text{crit}} \) as \( t \) increases, in Hillert's three dimensional model \( \bar{D} = \frac{8}{9D_{\text{crit}}} \), then \( \bar{r}_c \propto \frac{1}{D} \) as assumed and \( \bar{r}_c = 9\bar{R} \). This value should be compared with one obtained experimentally \((18)\) when it was found that \( r_c = 9D \).

From this finding it can be seen that the first kinetic theory also makes the assumption that the grain size distribution function remains constant. In fact all of the theories make this assumption although only Hillert \((1)\) manages to show that a grain size distribution that remains fixed within quite narrow limits is possible, and indeed necessary, for normal grain growth. All of the theories of grain growth in non-porous bodies predict squared kinetics despite the number of different starting points these theories use and thus it seems that equations of the same form as equation 2.2 should accurately represent growth in pure non-porous
The theories of growth in porous bodies however do not show such agreement. Kingery's modification of the basic parabolic equation appears to be sound providing the two stated assumptions are correct. The second of these has been investigated by Nichols who concluded that, for the assumption to be true, the internal pore pressure must equal $2\gamma/r$. Although Nichols did not point out the fact, this finding is incompatible with the first assumption which requires pore volume to remain constant thus implying constant pore internal pressure. Maintaining a pore pressure of $2\gamma/r$ during the pore coalescence process requires an increase in the total pore volume. However, since pores remain on boundaries, they should tend to shrink due to gas diffusion along grain boundaries and if this process can under some conditions counterbalance the increase in pore volume then Kingery's 1st assumption will be true.

Nichols' assumption that $F_B \propto 1/D$ was challenged by Brook and his criticism appears to be correct and applying this modification leads to the conclusion that surface diffusion is the pore transport mechanism that fits Kingery's equation. Applying the above two modifications to Nichols' second analysis (section 2.2.2.3) leaves the resulting growth rate laws unchanged. Thus equations 2.35 and 2.36 may be regarded as holding for situations where pore diameter remains proportional to grain diameter. However in situations where pore volume increases with time the equations should be modified to

$$\frac{dD}{dt} = \frac{k}{D^4} \quad 2.57$$

for situations where $n$, the number of pores per boundary is constant and

$$\frac{dD}{dt} = \frac{k}{D^3} \quad 2.58$$

for situations where $n$ decreases with time.

The Zener formula, section 2.2.3.1, appears sound, bearing in mind the simplification that all second phase particles are spheres of equal diameter. Hillert's variation on this approach, section 2.2.3.2, does
Z, a function of the size and number of second phase particles, still remains, although the analysis of section 2.2.2.5 throws some light on the nature of this problem. The application of the Hillert equation of section 2.2.3.2 to his defect model is more fruitful however, since a number of limiting grain sizes is predicted thus predicting a gradual decrease in growth rate as a final limit is approached. Furthermore the conditions under which abnormal grain growth may occur are predicted. In conclusion it seems fairly certain that kinetics of grain growth in non-porous pure materials should be squared.

The presence of porosity in pure materials can lead to kinetics varying from squared to fourth power kinetics depending on the rate at which porosity is removed by grain boundary diffusion.

The presence of second phase particles which do not coalesce or dissolve to any great extent should lead to a limiting grain size phenomenon. In cases where the second phase is capable of slow dissolution exaggerated grain growth may occur later.

The findings of Speight and Greenwood (section 2.2.2.5) which show that one size of pores can be lost from a boundary makes porosity a possible second phase that could cause a limiting grain size effect due to the Zener mechanism. Such a limiting grain size effect however should only be a temporary limit since pores on boundaries will tend to disappear due to grain boundary diffusion. The various modifications made to the solute drag theory of grain growth have extended its scope to deal with a larger variety of solutes so that the theory of Grey and Higgins can be regarded as the best of them. One possible shortcoming of the theory concerns the assumptions made about the nature of solute clusters. These are taken to be insoluble second phase particles but since their formation is caused by boundary migration it seems probable that their concentration and possibly their size is a function of boundary velocity. They might certainly be expected to redissolve once a limiting grain size has been attained and thus, according to the Hillert theory, may be capable of
2.3.1 Introduction

Much of the work on grain growth has been carried out using metals and so the relevance of this work to grain growth in ceramics will be considered. From the standpoint of the theories discussed previously no differences should be expected between the two types of material. However, due to differences in the types of atomic bonding, the grain boundaries in ceramics are wider than those in metals and should therefore have a greater capacity for impurity atoms according to equilibrium segregation theories. However, in both metals and ceramics, it appears that a zone affected by the interaction of migrating boundaries with impurity atoms can extend far beyond the physical limits of the boundary so that differences in boundary structure between metals and ceramics may be less important than previously supposed.

Saturation limits for solute in grain boundaries definitely exist and as grain growth takes the boundary concentration above the limit rejection of impurity into the matrix can occur. From this it follows that initial doping levels should have no influence on boundary migration once the saturation limit has been reached.

This point is relevant when considering the way in which dopant has been added to a material. Dopant distributed uniformly throughout the material will accumulate progressively at boundaries until saturation is reached, whereas, dopants added directly to the boundaries (for example by solution coating of powder prior to pressing and sintering) will exert its full influence immediately that grain growth becomes possible. In the latter case the boundary initially is moving into a matrix free of dopant atoms whereas in the former case the boundary migrates into a matrix containing a large concentration of dopant.

2.3.2 Experiments on grain growth in pure materials

It is intended that in this section it should be shown that grain growth has never been studied in systems that are completely free from impurities.
aluminium. Total impurity levels in the three sets of specimens he used were 0.5, 2 and 4 ppm. It was nevertheless found that the same limiting grain boundary solute concentration was found for all specimens providing that the boundaries had swept through an adequate volume of material. This limiting value depended to a great extent on the velocity of boundary migration and was as much as 4 to 6 order of magnitude above theoretically predicted equilibrium values. It therefore follows that the retarding force on a boundary due to solute atoms increases with velocity. This has important implications for the growth rate law in such materials.

2.3.3 Experiments on Grain Growth in Porous Materials

Grain boundary migration in sintered bodies must always be considered in the light of the effects of residual porosity since the mobility of boundaries in pure systems or those in which impurities do not cause excessive drag should be higher than pore mobility. The presence of porosity in such systems will result in porosity controlled grain growth.

The experimental evidence on the effects of porosity on grain growth is fairly clear. It has been found in UO$_2$ and chromium carbide that, until the level of porosity is reduced to 2-3%, the relationship between porosity and grain size is independent of temperature, implying that grain growth only occurs to an extent that is controlled by reduction of porosity. This has been interpreted to mean that the open pore structure, which exists down to 6% porosity and which breaks down to a closed pore structure in the range 6-3% porosity, effectively prevents grain growth whereas closed porosity, while exerting a retarding force on migrating boundaries cannot prevent grain growth from occurring.

Recent work by Gordon on MgO has shown that small amounts of porosity, 0.1-0.8%, can have large effects on grain growth kinetics. By comparison with the work of Spriggs on fully dense MgO it was concluded that this porosity caused a limitation to the maximum grain size attainable of <100 µm. A similar limiting grain size effect has also been found by Gupta in MgO at temperatures above 1500°C. Porosity
of Spriggs was of similar purity and although it showed no limiting
grain size effect the grain growth rate was close to the initial grain
growth rate of Gordon's material \cite{28}. The limiting grain size found in
the latter's material was smaller for higher temperatures.

It was concluded that the limiting grain size was due to the
boundary breaking away from the porosity. At lower temperatures or when
Fe$_2$O$_3$ was added as a dopant the grain growth rate was reduced and higher
ultimate grain sizes achieved. The limiting grain size values agreed
well with those predicted for a Zener-type mechanism using the modified
equation of Haroun and Budworth \cite{18}.

2.3.4 Experiments on Grain Growth in Materials Containing Solutes

The most important point to emerge from work on this class of
materials is that solutes which segregate at grain boundaries, and also
those which do not, can both reduce boundary mobility by similar amounts.

Additions of Au, Ag and Sn to zone refined lead all reduced boundary
mobility \cite{31}. Au, Ag and Sn all segregate at grain boundaries in lead.
It was noted that effectiveness of the additive increased with concentra-
tion. A correlation was also found between the action of an impurity
in reducing boundary mobility and its effect in causing grain boundary
hardening. This is thought to reflect the different degrees of segrega-
tion characteristic of the different additives. The hardness profiles
across grain boundaries, however, indicated, by their great width (typically
several hundred μm), that the simple segregation model of McLean \cite{19} was
inaccurate. An alternative mechanism was proposed by Aust et al \cite{17}
which accounted for boundary hardening in terms of small clusters of
impurity atoms near the grain boundaries. These would certainly also
have a retarding effect on the boundaries.

Further evidence of the correlation between boundary hardening and
mobility was provided by Westbrook et al \cite{20,32}, this time for ceramic
materials. This data was for the effect of impurities on the densifica-
tion of powders, and, since it is widely accepted that additives which aid
preventing porosity from becoming detached from the boundaries \(^{(33)}\), it is reasonable to assume that it implies a correlation between boundary hardening and migration. Various metal oxide additions were made to both \(\text{Al}_2\text{O}_3\) and \(\text{BeO}\) and the results all fitted the predictions of the theory of Aust.

More recently however it has been discovered by Drolet and Galibois \(^{(14,34)}\) that the effect of antimony in tin is similar to the cases described above, i.e. the boundary migration rate is reduced. This result is of great interest since \(\text{Sb}\) does not segregate to the boundaries of tin and this behaviour can only be accounted for in terms of the Cahn theory of solute controlled grain growth \(^{(13)}\).

The effect of a solute in a porous material has been examined. Additions of \(\text{Fe}_2\text{O}_3\) in quantities of 0.1 to 0.48% by weight were made to slightly porous \(\text{MgO}\) \(^{(28)}\). It was found that kinetics were squared at 1300°C and cubic at 1400°C and 1500°C. It was concluded that at 1300°C the \(\text{Fe}_2\text{O}_3\) reduced boundary mobility and at the same time also reduced the rate of pore coalescence so that pores remained small and thereby retained a high mobility. This mobility was below that of the boundary with \(\text{Fe}_2\text{O}_3\) causing a drag effect. At 1400°C and 1500°C, however, pore coalescence occurs at a rate such that pore diameters increase sufficiently to cause their mobility to drop below that of the boundary thereby causing porosity controlled migration and, in consequence, cubic kinetics.

Previous work on \(\text{Fe}_2\text{O}_3\) in \(\text{MgO}\), however, had found a grain growth exponent of 4 rather than 2 or 3 \(^{(35)}\). This was found to hold over a temperature range of 1330°C - 1640°C and an activation energy for grain growth of 146 ± 25 kcal/mole was quoted.

Another instance of a solute reducing boundary mobility is the addition of \(\text{TiN}\) to niobium diboride \(^{(36)}\). Both a higher density was achieved during sintering and a finer grain structure obtained. The effects again increased as the amounts of additive used were increased up to a limit of 8.9%. This represents the limit of solid solubility of
High density, fine grain sized thoria has been produced by the use of additions of 0.5 - 8% CaO in the form of fine powder (0.1 \mu m)\(^{(37)}\). Since CaO can form a solid solution with ThO\(_2\) this result seems to indicate that solute restricted grain growth occurred enabling rapid elimination of porosity.

Additions of Y\(_2\)O\(_3\) to UO\(_2\)\(^{(38)}\) using a solution coating technique restricted grain growth in a manner typical of that produced by insoluble second phase particles. At the time of the experiment published phase diagrams of the Y\(_2\)O\(_3\) - UO\(_2\) system showed complete solid solubility and so the high degree of boundary retardation would not have been expected. However it has since been discovered that a compound YUO\(_4\) exists. This is an orthorhombic structure formed by heating up to 15% by weight of Y\(_2\)O\(_3\) with UO\(_2\) at 1800 - 2000\(^\circ\)C\(^{(39)}\). It is therefore possible that this compound was formed in the experiment in question\(^{(38)}\) and that it acted as an insoluble second phase rather than as a solute.

Experiments with additions of 0.77 mole% of CaO have shown that grain growth is reduced at temperatures up to as high as 2400\(^\circ\)C. Activation energy was also increased by 25%\(^{(40)}\). Extensive solubility of CaO in UO\(_2\) exists as well as a number of compounds\(^{(41,42)}\). These compounds however do not exist above about 1800\(^\circ\)C and so it was concluded that solute drag on the boundaries was the rate controlling process.

Additions of small quantities of TiO\(_2\) have frequently been made to UO\(_2\) to improve sintered density\(^{(43,44,45)}\). The optimum amount of TiO\(_2\) depends on sintering temperature. Up to 1550\(^\circ\)C as much as 2\(^{\text{W/o}}\) is beneficial, however at 1650 - 1750\(^\circ\) such large amounts cause bloating and only quantities up to 0.1\(^{\text{W/o}}\) are beneficial. This effect may be connected with variation of the slight solubility of TiO\(_2\) with temperature.

In grain growth experiments between 1450 and 1630\(^\circ\)C the higher rates observed compared with pure material was thought to be connected with the idea that TiO\(_2\) promotes non-stoichiometry in UO\(_2\)\(^{(44)}\). It is well known that increasing the O/U ratio from 2.00 to 2.23 while still
orders of magnitude and reduces the activation energy accordingly. It has been shown that the diffusion rate of the $U^{4+}$ ion in $UO_2$ increases when $TiO_2$ is added and that small amounts of $TiO_2$ are soluble in $UO_2$. The same effect is found in $ThO_2$ with $TiO_2$ additions.

A number of compounds exist in the $UO_2 - TiO_2$ system. One of these, $UTi_2O_6$, decomposes below $1300^\circ C$ and another, $UO_2.3TiO_2$, melts at $1450^\circ C$. It is possible therefore that a liquid phase may have been present in the experiments described above.

Niobium oxide, $Nb_2O_5$, has been used to aid sintering in $UO_2$. The general behaviour of this additive was similar to that of $TiO_2$ and when used at concentrations greater than $0.6\%$ at $1750^\circ C$ evidence of the presence of a liquid phase was found. Increasing the additive concentration at any given temperature resulted in a larger grain size. However, since densities greater than $98\%$ were not achieved no conclusions concerning the role of this additive on grain growth kinetics could be drawn due to the presence of porosity.

2.3.5 Experiments on Grain Growth in Materials Containing Insoluble Second Phases

All experimental work on this class of materials has shown decreased growth rates and, where heat treatment times have been long, evidence of a limiting grain size.

The main variables with these materials are the particle size of the additive and its distribution. Work on the effects of $MgO$, $NiO$, $ZnO$, $CoO$, $CaO$ and $Cr_2O_3$ on $Al_2O_3$ established that uniform distribution and insolubility of the additive were necessary to ensure high retardation of grain growth. (Co, Zn, Mg and Ni all form spinel type compounds with $Al_2O_3$).

More detailed work on the same system using additive concentrations of $0.25\%$ by weight showed that the particle size of the additive was important. A higher rate of growth was found in samples containing coarse additive particles. An abrupt step in the growth curves was also
with a slope of $3.7 - 25$ for the more normal parts of the curve. A large degree of non-uniformity also developed during this rapid growth stage at $1675^\circ C$ and from the published photomicrograph which showed a number of straight sided grains it appears that a liquid phase was present. Since the lowest melting point liquid that exists in this system, $\text{MgO - Al}_2\text{O}_3$, is $2030^\circ C$ it seems that some other impurity may have been present and affected the results.

Additions of an inert powder, $\text{SiC}$ or $\text{Si}_3\text{N}_4$, have been added to BeO to reduce grain growth \textsuperscript{(50)}. Increasingly smaller grain sizes were obtained as larger amounts of additive were used up to a limit of 10% above which no further benefit was obtained. At this level grain diameters of 10% of those in undoped material were obtained. It was found that greater effects were obtained with finer grades of the additive powder. It was not stated if a limiting grain size was obtained as would be expected from theory.

In $\text{UO}_2$ it seems to be well established that inert particles can pin grain boundaries and reduce grain growth. Both iridium \textsuperscript{(51)} and platinum have been found to be effective in this role. Solution coating with iridium was achieved by mixing $\text{UO}_2$ powder into an aqueous solution of ammonium chloro-iridite and drying the resulting slurry. The powder obtained was mixed with a binder and pressed, debonded and sintered at $1750^\circ C$ in hydrogen. At 5 micron grain size was obtained but the density of the specimens was only $10.54 \text{ g/cm}^2$. The specimens did not exhibit columnar grain growth when exposed to a temperature gradient of $17000^\circ C$/cm although equiaxed grain growth up to $25 \mu m$ occurred after $25 \text{ h}$ in parts of the specimen heated to $1800^\circ C$. This much less than would be expected in undoped material. Experiments with platinum showed very similar effects.

Vanadium pentoxide has been found to reduce grain growth in $\text{UO}_2$ \textsuperscript{(52)}. The effectiveness of this additive increased with concentration and the mechanism by which it acts is thought to be by the pinning of boundaries by insoluble particles of $\text{V}_2\text{O}_3$ formed by the reduction of $\text{V}_2\text{O}_5$. 
2.3.6.1 High-Purity Materials

Work on high-purity, non-porous systems has demonstrated that the amount of solute impurity that interacts with migrating boundaries is 4-6 orders of magnitude greater than predicted by equilibrium models. The fact that the interaction increases with increasing boundary velocity implies that the retarding force per unit area of boundary will be higher for small grain sizes assuming that the boundaries are initially saturated with impurity. High purity materials will not exhibit this characteristic however and retarding pressure across the boundary should at first increase until the dynamic equilibrium concentration of impurity has been reached and will then decrease as boundary velocity decreases as explained above.

2.3.6.2 Porous Materials

The work on the effects of porosity on MgO seems to demonstrate that porosity can cause limiting grain size effects. The finding that lower temperatures result in a larger limiting grain size might be expected since at low temperatures most of the porosity remains on the boundaries and therefore is reduced in volume by grain boundary diffusion. At higher temperatures however a higher proportion of porosity is detached from the boundary and thus cannot shrink further until it is swept up by another boundary later on. Thus for equivalent average grain diameters a material treated at high temperatures should have a greater volume of porosity than one treated at a lower temperature and this could cause the observed differences in limiting grain size values.

However it is conceivable that solute impurities could produce the same effect providing two conditions are fulfilled. The first is that diffusion rate of the solute across the boundary should be low, the second is that the diffusion rate of the solute in the solvent is also low. These conditions correspond to those for the low velocity condition in the solute-drag theory.

These conditions should result in an increasing concentration of solute
tration of solvent in contact with the boundary, the rate of solvent transfer across the boundary will decrease, and hence the boundary migration rate will also decrease.

Some slight evidence for asymmetrical distribution of solute about grain boundaries comes from microhardness, and thermoelectric probe analysis, profiles of grain boundaries\(^{(17,53,54)}\). However since the specimens used in these experiments had very large grains it is possible that a limiting grain size condition had been reached and that diffusion had reduced some of the expected asymmetry of solute distribution.

In any case it is difficult to visualize any mechanism by which a migrating boundary can gain an increased solute concentration without developing an asymmetric concentration profile since there is no reason why solute atoms behind a migrating boundary, once they are separated from it by a few atom diameters, should migrate with the boundary. The converse should be true since they would then be diffusing against a concentration gradient.

If it is then accepted that the solute concentration ahead of the boundary increases, the boundary migration rate will be reduced until it is limited by the diffusion rate of solute atoms away from the boundary. If this rate is much lower than the initial growth rate then the observed effects will appear very much like a limiting grain size effect.

Such a solute induced limiting grain size effect could equally well explain the results on MgO which were ascribed by their author to porosity since at high temperatures solute will be concentrated ahead of boundaries more rapidly than at low temperatures, (this follows provided the activation energies for boundary migration and solute atom diffusion do not change with temperature), resulting in the observed lower limiting grain size in the higher temperature specimens. The fact that the material used in this work was similar in purity to that used in work that showed no limiting grain size is meaningless in light of the results of Kasen\(^{(23)}\) who showed that as little as 0.5 ppm of an impurity can saturate boundaries.
limiting grain size effect would the comparison be completely valid.

It is therefore concluded that it has not yet been demonstrated beyond doubt that porosity can cause a limiting grain size effect.

2.3.6.3 Materials Containing Additives

The experimental work on systems containing impurities shows that both solute atoms which segregate and those which do not segregate at grain boundaries can reduce boundary velocity. It has also been shown that the degree of segregation depends on the rate of boundary migration and evidence exists for both metallic and ceramic systems to show that solute atoms from clusters. The properties of such clusters as well as those of their constituent atoms will control boundary migration and the existence of a limiting grain size effect, similar to that observed in materials containing insoluble second phase particles, could be expected.

All the results of work on systems containing second phase particles has shown reduced grain growth rates. It has been established that finer particles are more effective than coarse ones and increased volume fraction of second phase particles results in lower growth rates. A limit of 10% addition has been found to be the maximum effective concentration although this figure is probably dependent on particle size. In the few cases where increased growth rates have been observed it seems probable that a liquid phase has been present. The presence in the boundary of a phase with a higher diffusion coefficient than that of the matrix could also cause such an effect, but no definite evidence exists to show this occurs.

2.3.6.4 The Interaction of Several Impurities

In cases where deliberate additions of an impurity have been made to a material it has been usual to conclude that the additive alone was responsible for the resulting grain growth behaviour, unless, of course, some other known grain growth modifying phenomenon, such as porosity, has been observed. The justification of this view is that the relatively large concentration of the additive will swamp out any effects due to
assumption that the affinity of the additive for grain boundaries is
greater or equal to that of the other impurities thereby assuming that
the composition in the region of the boundaries remains constant. The
situation in which a minor impurity has a greater affinity for grain
boundaries than the additive could be expected to produce a much different
result and such systems probably represent the majority of situations
encountered in practice. In such systems it can be envisaged that the
deliberately added impurity would influence grain growth in the initial
stages since this would be the first to attain the dynamic equilibrium
concentration at the boundaries. As the boundaries sweep through
progressively larger volumes of the material, however, the concentration
of the minor impurity with a greater affinity for the boundaries would
increase there, thus changing the chemical composition of the boundary.
Providing that these minor impurity atoms have higher diffusion coefficients
than those of the main impurity then no great change in behaviour would
be expected. If the reverse is true then they will eventually become the
rate controlling species. It is possible to envisage this process
happening a number of times in succession with different minor impurity
species. It is extremely unlikely that such behaviour would result in
perfect squared or cubic kinetics since the overall growth curve would
be composed of a series of other curves each representing the behaviour
of a single impurity.

If such behaviour does in fact occur then it would readily explain
why such a wide variety of grain growth exponents is found in practice.

The model described above is a rather simple one and in practice the
effect of any particular minor impurity will of course be very depen­
dent on the chemical nature of the boundary. For example systems such
as $\text{Al}_2\text{O}_3$ containing additions of the oxides of Co, Zn, Mg or Ni, all of
which form spinel type compounds, may well be able to absorb minor
impurity atoms with high boundary affinity into the relatively open spinel
lattice and thus prevent them exerting any influence on the boundary.
In this chapter the apparatus that was used is described in section 3.2 and the various methods and techniques in the subsequent sections. This section deals with a number of general considerations.

The first of these is the atmosphere used for sintering and grain growth. It was discovered during preliminary work that alumina from the furnace tube vaporized and recondensed on the specimens. This obviously undesirable behaviour was very marked at 1700°C and above, and alumina crystals up to 1 mm in diameter were found. The vaporization could be suppressed by using wet instead of dry hydrogen. The method used to wet the hydrogen was to bubble the hydrogen through a bottle of water at room temperature using a sintered glass plate to ensure good mixing. It was assumed that the hydrogen became fully saturated. The maximum $\frac{H_2}{H_2O}$ ratio obtainable would have been 42:1. This is equivalent to a $\Delta G_2^O$ value of $-365$ k.J/mole at 1800°C. Since $UO_2$ does not deviate from stoichiometry at values of $\Delta G_2^O$ of less than $-340$ k.J/mole\textsuperscript{(58)}, which corresponds to a water temperature of $44^\circ C$, it was concluded that the specimens did not deviate from stoichiometry under any of the conditions used.

A second point concerns the use of inert (argon) atmospheres in the glove boxes in which the $UO_2$ powders were handled. Although the oxygen content of the argon was kept at a fairly low level (10-20 v.p.p.m) the freshly prepared $UO_2$, which was a rich golden brown when taken from the reduction furnace, nevertheless oxidized rapidly to a dull dark brown in less than one hour. The as-pressed pellets that were loaded into the furnace for sintering were therefore non-stoichiometric and the sintering atmosphere was relied upon to restore stoichiometry. The hydrogen used as the sintering atmosphere was high purity $H_2$ and this was treated with a catalytic converter to remove oxygen prior to wetting. In a non-inert atmosphere the fine $UO_2$ powder would rapidly be converted to $U_3O_8$.

It had originally been planned to carry out runs at temperatures
up to 1000°C. The furnace oven was to permit a thermal shock to permit the specimens to be lowered rapidly into the hot zone at that temperature so 1700°C was chosen as the maximum temperature.
A. APPARATUS USED IN PREPARING SPECIMENS

CHEMICAL PREPARATION OF AMMONIUM DIURANATE (A.D.U.)

In order to reduce risks of accidental contamination all chemical reactions were carried out inside an air filled glove-box. Reaction vessels were all made of polythene to prevent the risk of silicates being leached out of glass vessels by the solutions.

The apparatus was very simple and consisted of only 2 polythene bottles and some polythene tubing. The first bottle contained ammonia solution and the second UO$_2$F$_2$ solution. Nitrogen gas was introduced into the first bottle through a polythene tube which reached to the bottom of the bottle so that the nitrogen became saturated with ammonia.

This gas mixture was led to the second bottle through another polythene tube and the gas mixture was bubbled through the UO$_2$F$_2$ solution to precipitate A.D.U. Suck-back from the second bottle due to reaction of the ammonia was easily prevented by choosing an adequate nitrogen flow rate.

After all the A.D.U. has been precipitated the bottle containing it was transferred to a vacuum desiccator, which was situated in the same glove box, and the contents evaporated to dryness.

DOPING OF ADU

Polythene bottles were again used to hold the A.D.U. + dopant + solvent mixture (see section 3.3.3). The slurry was agitated using a roller mill until the agglomerates of A.D.U. broke up. The mill consisted of two horizontal parallel rollers, one of which was driven by an electric motor so that the bottle was rotated when laid horizontally on the rollers. The slurry was dried out by the same process as in the previous section.

REDUCTION OF A.D.U. TO UO$_2$

This process was carried out in a second glove-box, this time argon filled to prevent oxidation of the UO$_2$. This glove-box contained only the reduction furnace shown in fig. 2. This furnace was used only
tube, 5.6 cm internal diameter, and open at both ends, on which a molybdenum furnace winding was wound. The argon atmosphere of the glove-box prevented oxidation of the winding. The hot zone was 20 cm at \( \pm 5^\circ C \) at the operating temperature of 500°C. The gas supply for the furnace atmosphere came through a control panel that enabled argon or hydrogen to be selected. The hydrogen was used for the reduction process and the argon to flush out the hydrogen at the end of each run before opening the furnace to the glove box atmosphere.

**POWDER COMPACTION**

This operation was performed in another glove-box under an argon atmosphere. This box contained a 250,000N Research and Industrial Instruments Company ring press and a balance. 0.5g quantities of \( \text{UO}_2 \) powder were weighed out and pressed at a pressure of \( 1.5 \times 10^8 \) Pascals (10 t.s.i.) in a 6.35 mm diameter (\( \frac{\text{in}}{2} \)) die. The die was a cylindrical tungsten carbide lined die with a slight relief taper at one end to expedite the removal of pressed pellets. The die plungers were also tungsten carbide tipped. The die walls were lubricated before each pellet was pressed by wiping the die walls with a small brush moistened with a 1% solution of stearic acid in alcohol. After each pellet had been extracted from the die the die was cleaned with a fine cut round steel file to remove the loose particles of \( \text{UO}_2 \) adhering to the die walls.

**SINTERING**

Sintering was performed in a fourth argon filled glove-box which had 3 Metals Research type PCA10 furnaces built into its base and which extended vertically below it so that they could be loaded from inside the glove-box. One of these furnaces was used for sintering. This arrangement is shown in figure 3 which also shows the 'cake-stand' type sintering stand on which the pellets were supported during sintering. The collar which joined the furnace to the underside of the box was originally made of steel but it was found that this had a tendency to
collar. This collar contained the gas inlet to the furnace, the gas outlet was situated in the top of the sintering stand.

To ensure that the gas would circulate properly inside the furnace it had to pass through an alumina tube incorporated into the centre of the stand which reached down almost to the level of the specimens. This tube also protected the thermocouple (W5Re/W26Re) from accidental damage. This feature was importance since tungsten/rhenium thermocouples become very brittle after they have been in use for some time.

As can be seen from fig. 3 the thermocouple junction was situated inside the hollow shaft which supported the specimen holders. The junction therefore should have monitored the specimen temperatures accurately.

Molybdenum was the material chosen for the sintering stand since it was compatible with both Al2O3 and UO2 under the conditions used. The sintering stand could accommodate 10 pellets, five on each level.

The furnace itself had a 2.5 cm internal diameter alumina furnace tube closed at the lower end. The winding was of molybdenum wire and since Mo oxidizes readily in air, even at moderate temperatures, the winding had to be supplied with a protective atmosphere of 5% H2/95% Ar.

**SAFETY**

In view of the damage that could be caused to the furnace in the event of failure of the cooling water or of the gas supply to the winding, a number of safety devices were built into the furnace control circuit.

The furnace was controlled by a Eurotherm controller which "failed safe" in the event of a thermocouple breakage. A relay switch was therefore incorporated into the thermocouple circuit, this switch broke the circuit when power to the relay coil was cut off. The safety devices were all connected in series with the relay coil. These devices were:

1. A Rotameter, a magnetically operated water flow switch connected into the water cooling circuit on the outlet side of
2. A thermally operated switch attached to the furnace case. This provided additional security in the event of a failure of the Rotameter.

3. A pressure operated switch connected into the gas supply to the furnace windings.

Besides breaking the thermocouple circuit the relay also operated an electromagnetic valve, to shut off the hydrogen supply to the interior of the furnace. Therefore, in the event of the furnace burning out and fracturing the furnace tube there was no danger of hydrogen escaping in large quantities.

**GRAIN GROWTH**

The grain growth experiments were carried out in the three Metals Research furnaces described in the previous section. The type of specimen holders used to support the specimens is shown in fig. 1. The main requirement of the specimen holder was that it should enable the specimens to be moved into and out of the hot zone rapidly in order to minimize errors in the measured heat treatment times. As in the case of the sintering stand it was constructed out of molybdenum. It was basically a 0.95 cm diameter rod which was drilled to a depth of 5 cm along its axis at the lower end with a 6.4 mm drill to provide a cavity in which the specimens could sit. The specimens were prevented from falling too far down inside the cavity by a pin located 12 mm below the loading slit. The end of the tube was sealed with a plug to prevent gas escaping from the furnace into the glove-box during loading and unloading. The hollowed rod also served to lessen the thermal mass of the specimen holder and, in order to reduce heat conduction up the rod, a number of 4 mm holes were drilled through it along its length. The rod was held in place by an 'O' ring seal in the furnace head. This also prevented gas leaks from the furnace. Raising and lowering the rod was accomplished simply by loosening the vacuum coupling securing the rod, sliding the rod to the required position, and
Circulation of the furnace atmosphere was ensured by means of an alumina tube alongside the specimen holder.

Because of the small bore of the furnace tube (2.5 cm) it was not possible to incorporate a recording thermocouple into the furnace. Because of the wet hydrogen atmosphere in the furnace, such a thermocouple would have needed a special protective gas supply.

The desired temperatures were maintained by using a constant power input after the initial calibration. The calibration was checked after each run to see whether any drift had occurred. This did in fact occur on two occasions and the experiments had to be repeated after replacement of the control thermocouple in one case and after replacement of the furnace element in the other.

To measure grain size the specimens were mounted in Plasticine and examined on a Vickers 55 metallurgical microscope. Photographs were taken of the microstructures and intercept counts were made from them. To facilitate counting of the intercepts a sheet of Perspex 11 cm x 7 cm with 9 parallel lines, each 10 cm long scribed on it, was placed over the photographs. This method was quicker, more accurate and easier to use than drawing lines on the photographs or counting directly from the specimen surface.

After examination the specimens were cleaned in alcohol in an ultrasonic bath to remove traces of oil left on them by the Plasticine.
Fig 1

SPECIMEN HOLDER FOR GRAIN GROWTH EXPERIMENTS.

'O' RING SEALS

GAS IN

GAS OUT

GLOVE BOX FLOOR

FURNACE WALL

SPECIMENS
Fig 3
SINTERING STAND
3.3 PREPARATION OF UO₂ POWDER

3.3.1 CHEMICAL PREPARATION OF AMMONIUM DIURANATE (A.D.U.)

In order to study the effect of dopants on grain growth in UO₂ it was obviously desirable to know the behaviour of the pure material. In this context "pure" must be taken to mean the lowest impurity content that is at present obtainable. At the start of this project, however, only commercial grade UO₂ was available and the impurity content of this material was too high for the purposes of the planned work. There were two main options open for obtaining more suitable material. The first was to purify the commercial UO₂ and the second was to convert a high purity compound of uranium (zone refined uranium carbide, for example) to UO₂. The second alternative was pursued as this seemed to offer the best chance of success.

The only high purity uranium compound that was available initially was zone refined uranium carbide in the form of bars 10cm long with a cross-sectional area of less than 1cm². The impurity content of this material varied from bar to bar so if they were converted to UO₂ one at a time it was probable that the starting material for the grain growth experiments would have a non-uniform impurity content.

The most direct way of converting the carbide bars to UO₂, and hence the way that offered the best chance of minimizing pick-up of impurities, was to dissolve them in nitric acid to form a uranyl nitrate solution and then add ammonia to precipitate ammonium diuranate (ADU). The subsequent reduction of ADU to UO₂ in hydrogen at 500°C is a well-known technique which presented no difficulties.
The first step of dissolving the carbide in nitric acid was the most difficult and the problems which were encountered were to lead to the eventual abandoning of this method of preparation. The shortcoming of the method was that organic compounds were formed during the reaction of UC with nitric acid; these turned the solution brown. Since these compounds later precipitated out with the ADU and were not burnt out during the reduction of ADU to UO$_2$, they caused a high level of carbon contamination in the product. An attempt was made to burn off the carbon by heating the UO$_2$ in air and then reducing the resulting U$_3$O$_8$ back to UO$_2$ in hydrogen but the oxidation step resulted in an unacceptable sintering of the powder into lumps.

It was discovered that the amount of organic compounds increased with increasing reaction temperature so the reaction temperature was lowered to try to suppress formation of these compounds. At room temperature the reaction was so slow that 1-2 weeks were required to dissolve one of the carbide bars but unacceptably large amounts of carbon contamination still occurred. No way could be found to overcome this difficulty so when another high purity uranium compound, UO$_2$F$_2$, later became available, the use of carbide as a source material was abandoned.

The UO$_2$F$_2$ was depleted in U-235 and contained about 25 ppm of Fe as the main impurity. Other impurities were present at lower levels than in the zone refined carbide. Although no information could be found in the literature on how to convert UO$_2$F$_2$ to UO$_2$, it was discovered that simply the addition of ammonia to an aqueous solution of UO$_2$F$_2$ at
room temperature caused ADU to precipitate. The reduction of ADU to UO$_2$ is not difficult as mentioned earlier. It seemed, therefore, that the reaction chemistry would present few problems. The main effort was therefore directed against contamination by impurities during the reaction.

It was decided at the outset to use an all polythene apparatus to minimise the risk of contamination by silicon which might arise by leaching out of Si if glassware was used. In addition the apparatus was installed in an air filled glove box to reduce contamination by airborne dust and to control the problem of liberation of HF during the reaction. The design of the apparatus was modified a number of times as a result of experimental experience and it became apparent that the simpler the design the better. Therefore the final design was very simple and consisted of only two polythene screw top bottles and polythene tubing. One bottle contained ammonia solution and the other UO$_2$F$_2$ solution. Nitrogen gas from a cylinder was introduced into the bottle containing ammonia through a polythene tube which reached to the bottom of the bottle so that the nitrogen became saturated with ammonia.

This gas mixture was led to the second bottle through another polythene tube and the gas mixture was bubbled through the UO$_2$F$_2$ solution to precipitate the ADU. Suck-back from the second bottle due to reaction of the ammonia was easily prevented by choosing an adequate nitrogen flow rate.

The use of ammonia vapour in this way had several advantages compared with the use of aqueous ammonia solution. First, the amount of Si introduced into the product was
reduced; ammonia solution which is stored in glass bottles contains large amounts of dissolved silicon impurity. Second, the gas bubbling through the $\text{UO}_2\text{F}_2$ solution agitated it and thus eliminated the need for a mechanical stirrer. Third, the rate and amount of ammonia added could be controlled precisely and easily. The rate at which the ammonia was added was important since the reaction was strongly exothermic. The total amount of ammonia used was important because it was desired to add the minimum amount of ammonia necessary to precipitate all the uranium; if excess ammonia is present it is necessary to remove it from the product by washing with demineralized water. After all the ADU had been precipitated, the bottle containing the yellow product was transferred to a vacuum desiccator in the same glove box and the contents were evaporated to dryness.

The ADU prepared by this method was as fine as that obtained from uranyl nitrate solutions. The specific surface areas of powder samples were measured on a B.E.T. gas adsorption apparatus. Surface areas of about $20\text{m}^2/\text{g}$ were obtained. ADU from the $\text{UO}_2\text{F}_2$ was used in all grain growth experiments.

### 3.3.2 SELECTION OF ADDITIVES

The properties of additive elements which have been investigated and which were expected, on the basis of work reported in the literature, to affect grain growth are:

1. the size of the impurity atom or ion
2. the melting point of the impurity element
3. the state of the impurity at the grain boundary, i.e. solid solution or insoluble particles.
In addition to these properties the way in which the additive is introduced into the UO\textsubscript{2} will affect its behaviour. Blending of powders presents difficulties which are mentioned in the next section. Co-precipitation of an impurity species with ADU during the preparation of ADU would ensure mixing on an atomic scale but could introduce many other variables such as changes in the morphology of the precipitated ADU particles and the process of migration of the impurity to the grain boundaries could affect the initial stages of grain growth.

Solution coating, however, ensures uniform distribution and places the impurity in the grain boundaries where it is required; this is the technique that was used in all experiments.

Concentration of the additive has been expressed in atomic percent rather than weight percent and a dopant level of 1000 parts per million was aimed for in each case. This level was rather arbitrary but was a level which could be expected to produce a measurable effect if the additive was capable of influencing grain growth. In the case of soluble impurities, the fact that an equilibrium concentration is predicted for the impurity at grain boundaries implies that the average bulk concentration is not of great importance.

From the considerations discussed above the following additives were selected for investigation.

**GROUP 1**

Dopants in this group were chosen to investigate the effects due to variation in the melting points and atomic (or ionic) diameter of the additive species. Three elements in this
group Mo, Cr, and Ni, are all stable in the metallic state in UO₂ under the conditions of the grain growth experiments (57). Since the self-diffusion coefficients increase as the melting point of the element is approached, the additives were expected to show increasing effectiveness in reducing grain growth rates in the order Ni < Cr < Mo as a result of their melting points. Atoms of these three species all have approximately the same diameter as shown below. The diameter of the U⁴⁺ ion is 0.97 Å.

<table>
<thead>
<tr>
<th>Species</th>
<th>Mo</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point</td>
<td>2617°C</td>
<td>1830°C</td>
<td>1455°C</td>
</tr>
<tr>
<td>Atomic Diameter</td>
<td>1.36Å</td>
<td>1.35Å</td>
<td>1.32Å</td>
</tr>
<tr>
<td>Structure</td>
<td>HCP</td>
<td>HCP</td>
<td>HCP</td>
</tr>
</tbody>
</table>

**GROUP 2**

This group consists of Mo, Al and La and was selected to investigate the third of the variables listed at the beginning of this section, namely the state of the impurity at the boundary. Lanthanum forms a solid solution with UO₂ whereas Al should be present as Al₂O₃ which is insoluble. However, the vapour pressure of Al₂O₃ at temperatures of 1700°C and above is large and so it should act as a highly mobile species. Molybdenum should have a very low mobility due to its high melting point and insolubility. This group, therefore, contains low, medium and high mobility species.

Lanthanum does not cause deviation from stoichiometry in UO₂ under the experimental conditions used in this work (57).

**3.3.3 DOPING TECHNIQUE**

Two possible doping techniques were possible. The first
was dry mixing of the additive in the form of a fine powder with UO$_2$ powder and the second was solution coating. The first of these methods had the disadvantages of difficulty in obtaining uniform mixing and of obtaining sufficiently fine powders(48). This problem was discussed in section 2.3.5. The solution coating technique had neither of these disadvantages and the only problem lay in finding a suitable solvent-dopant combination.

Naturally the solvent used must not react with the UO$_2$ and a suitable compound of the dopant required the following properties.

1. Solubility in the solvent.
2. Decomposes to the required dopant.
3. Low vapour pressure so that evaporation would not occur before decomposition.
4. The products of decomposition other than the required dopant should be either volatile or gaseous so that they would not remain in the UO$_2$.

It was considered that organometallic compounds would best meet the fourth requirement as the minor decomposition products are all volatile or gaseous.

The procedure followed in performing the solution coating was as follows. Two polythene bottles were carefully cleaned. Into one was weighed out sufficient of the selected dopant compound to provide 2000 atomic parts per million of the dopant element. To this was added a quantity of solvent and the dopant compound was dissolved. This solution was added to the bottle containing the A.D.U. The amount of solvent was chosen so that a thin slurry resulted. The bottle containing the
slurry was agitated on a roller mill until the agglomerates of A.D.U. broke down. The contents of the bottle were then evaporated to dryness leaving a loosely agglomerated powder.

A list of the dopant compounds used is given below. The solvent in all cases was demineralized water.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>chromium acetate</td>
</tr>
<tr>
<td>Ni</td>
<td>nickel oxalate</td>
</tr>
<tr>
<td>Mo\textsubscript{I}</td>
<td>molybdic acid</td>
</tr>
<tr>
<td>Mo\textsubscript{II}</td>
<td>molybdenum trioxide</td>
</tr>
<tr>
<td>Al</td>
<td>aluminium chloride</td>
</tr>
<tr>
<td>La</td>
<td>lanthanum acetate</td>
</tr>
</tbody>
</table>

3.3.4. REDUCTION OF ADU TO UO\textsubscript{2}

This operation was performed in the reduction furnace shown in fig. 2. The process is a well established one and simply requires heating the ADU powder to 500°C for two hours in a stream of hydrogen.

Charges of approximately 15g of A.D.U. were spread out in the bottom of a molybdenum boat to a depth of about 3 mm. The boat was placed in the furnace and heated to 500°C at a rate of 250°C/hr. After holding at this temperature for two hours it was cooled at the same rate.

The reduction temperature is very critical, 480°C is inadequate and 520°C causes sintering of the powder and a reduction of its surface area. Under the conditions used a reduction of surface area of 2 m\textsuperscript{2}/g was encountered.
3.4 SPECIMEN PREPARATION

3.4.1 POWDER COMPACTION

In the argon atmosphere of a glove box, as protection against oxidation, UO₂ powder was weighed out into 0.5 ± 0.01g amounts for specimen preparation. This quantity was chosen to minimise the amount of powder consumed and to provide pellets with a low thermal mass compatible with the requirement that the pellets should not be so small that the specimen surfaces restrict grain growth.

A standard 0.25" (0.635 cm) diameter, tungsten carbide lined, cylindrical die was used to cold press the powder. A 1% solution of stearic acid in alcohol was used to lubricate the die walls. The die was cleaned with a file and relubricated for each pellet. Double ended pressing was used on all pellets and a pressure of 150 M.Pa was found to be satisfactory for all powders. Higher pressures generally resulted in pressing faults and lower pressures in excessively fragile green pellets. The green pellets thus produced were right cylinders 0.635 cm in diameter and 0.4 cm high.

3.4.2 SINTERING

The green pellets were supported in a vertically mounted furnace (type Metals Research PCA 10) on the sintering stand illustrated in fig. 3. The stand was constructed of molybdenum since this material is compatible with UO₂ in hydrogen to temperatures in excess of 1800°C, the maximum of which the furnace was capable. The capacity of the stand was ten pellets which were positioned within 1 cm of a recording thermocouple (W5Re/W26Re). The sintering atmosphere was wet hydro-
gen with a $\text{H}_2/\text{H}_2\text{O}$ ratio always greater than 42:1. A gas flow rate of 150 - 250 ml/min was used, this represented a complete change of furnace atmosphere each 1 - 2 minutes. The sintering temperature was 1400°C and this was held for 2 hours. The heating rate was restricted to 150°C/hour in order to prevent cracking of pellets of doped UO$_2$ due to gas evolution during decomposition and volatilization of the dopant compounds. Undoped UO$_2$ could be heated much more rapidly (500°C/hour) without adverse effect.

3.4.3 DENSITY MEASUREMENT

Specimens intended for grain growth experiments had their densities measured by immersion in Xylene. Xylene is inert with respect to UO$_2$ and due to its high volatility is easily removed from the specimen afterwards. The following procedure was used to obtain density values.

1. The pellet was weighed in air.
2. A fine copper wire was tied around the specimen to enable it to be weighed while suspended in liquid Xylene.
3. The pellet + attached wire were immersed in a beaker of Xylene which was then placed in a vacuum desiccator and subjected to a vacuum to displace air trapped in open porosity or pressing faults.
4. The pellet in the Xylene was then removed from the desiccator and left to re-equilibrate with the surrounding atmosphere.
5. The specific gravity of the Xylene was measured.
6. The pellet was suspended by its wire from the beam of a balance and weighed while the specimen was immersed
7. The pellet was removed from the Xylene and the excess liquid removed from the pellet surface by wiping with a tissue dampened with Xylene. The pellet + wire was then reweighed while suspended above a beaker of Xylene i.e. in air saturated with Xylene vapour.

8. The pellet was removed from the wire and the wire was weighed.

9. The wire was immersed in Xylene to the same depth as when it carried the pellet and was then reweighed.

From the above procedure 6 measurements were obtained:

a. The weight of the pellet in air
b. The weight of the pellet + wire in Xylene liquid.
c. The weight of the pellet + wire in Xylene vapour.
d. The weight of the wire in air.
e. The weight of the wire in Xylene liquid.
f. The specific gravity of Xylene.

Two density values, the bulk mean density (B.M.D.) and the apparent solid density (A.S.D) were then calculated.

\[
\text{B.M.D.} = \frac{a \cdot f}{c - d - b - e} , \quad \text{A.S.D.} = \frac{a \cdot f}{a - b - e}
\]

Repeated measurements showed that the values obtained were reproducible to within 1.5% for B.M.D. and 1.1% for A.S.D. taking the theoretical value for UO\textsubscript{2}, 10.97 g/cm\textsuperscript{3}, as the base value.

The absolute accuracy of the density values measured in this way was not known; metallographic examination was relied
upon to reveal any residual porocity.

3.4.4 SURFACE PREPARATION

Chemical etching with 10% \( \text{H}_2\text{O}_2 \) in \( \text{H}_2\text{SO}_4 \), the standard etchant for \( \text{UO}_2 \), does not show up grain boundaries satisfactorily, particularly when grain diameters are below 10 microns, due to etch pits, and in any case low angle boundaries were never adequately attacked and their existence had to be inferred from the shape of the surrounding grains. Because of these limitations in revealing grain boundaries, thermal etching was employed.

The pellets, after density measurements had been performed, had one face ground flat and polished suitable for microscopic examination. During the grain growth heat treatments boundary etching took place and since this became deeper with time it was necessary to regrind and repolish the surface when the etching became too deep. At very long treatment times it was necessary to remove the specimens for regrinding and polishing and reinsert it for a short period to give a light etch prior to grain size measurement. In this way it is reasonably certain that the grain size observed was representative of the bulk material since, if the same surface was observed without repolishing, it is possible that the heavy thermal grooving which eventually formed was sufficient to retard boundary migration and thus give a value not representative of the bulk material.

For the initial grinding and polishing it was necessary to set the specimens in a cold setting plastic. Afterwards
they were physically broken out of the mounts. Dissolving the plastic in chloroform was tried but this was a lengthy and messy process. For subsequent repolishing the specimens were hand held. An attempt was made to make a mount that held the specimens mechanically so that they could be easily removed but this did not hold them rigidly enough or support the specimen edges and these became chipped.
In order to use the furnace time as economically as possible and to avoid the need for corrections to heat treatment times to allow for heating and cooling of the specimens, it was decided to run the furnaces at operating temperature continuously and to move the specimens into and out of the hot zone rather than switch the furnace off every time a specimen change had to be made. Since the bore of the furnace tube was only 2.5 cm it was not possible to accommodate simultaneously in the furnace sufficient pellets to provide one pellet for each point on a grain growth plot. It was therefore decided to use the average values from two pellets treated simultaneously to provide the data for all the points on each grain size versus time plot. The pellets were supported in the specimen holder shown in figure 1. This holder, which was basically a hollowed-out molybdenum rod, could, by virtue of the "O" ring seals used, be lowered into or raised out of the hot zone in seconds, thereby eliminating corrections to the heat treatment times. The relatively low thermal mass of the pellets and specimen holder enabled the pellets to cool from 1800°C (the highest temperature used) to room temperature in 10 minutes. Such rapid heating and cooling, however, was capable of cracking the furnace tube by thermal shock and so it was customary to cool slightly more slowly.

A further 20 minutes were needed to photograph the microstructure so that the time lost on examination of the specimens was quite low. Photographs of the specimens were taken both for ease of grain size measurement and to minimize the
length of time for which the specimens were kept out of the furnace.

3.5.2 GRAIN SIZE MEASUREMENT

The parameter that was measured was the average intercept length. No attempt was made to convert this parameter to grain diameter because information about grain shape and grain size distribution would be needed. This conversion is made by multiplying the intercept length by a constant, the size of which can vary considerably depending on the assumptions made about grain shape etc.

The method of measuring the average intercept from the photographs was the following. A perspex sheet scribed with a grid of parallel lines was placed over the photograph and a count was made along each line of points where the scribed line intersected grain boundaries. See figure 4 below.

![Figure 4: Determination of Average Intercept Length, I=18.08μm. Pure UO₂, 14h at 1700°C, Magnification x300.](image-url)
The average intercept length was obtained by dividing the length of the grid line by the product of the total number of intercepts and the magnification of the photograph. In the example given here the value was:

\[
\frac{1.15 \times 10^6}{212 \times 300} = 18.08 \text{ microns}
\]

The usual practice was to take 2 or 3 photographs of each specimen and take the average of all of them so that approximately 1000 grain boundaries were counted for each data point.
INTRODUCTION

The various doped samples of $\text{UO}_2$ were sent for analysis after the grain growth runs had been completed in order that the level of additive would be known. The analysis was a general spectrographic analysis and was capable of determining the concentration of all the chosen additives to an adequate degree of accuracy. The reproducibility of the analysis procedure was checked by submitting identical samples of undoped $\text{UO}_2$ powder for analysis, the results were sufficiently reproducible.

The detection levels for different elements varies quite a lot with spectrographic analysis and in the tables below those elements which were present in quantities above 10 parts per million or were above the detection level, whichever is the larger, have been shown.

A UNDOPED $\text{UO}_2$

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>12</td>
</tr>
<tr>
<td>Cr</td>
<td>10</td>
</tr>
<tr>
<td>Fe</td>
<td>26</td>
</tr>
<tr>
<td>Si</td>
<td>30</td>
</tr>
</tbody>
</table>

The nickel and chromium are thought to have been introduced during the grain growth treatments since they were present at only about half this level in the ADU from which the $\text{UO}_2$ was prepared.

B NICKEL DOPED $\text{UO}_2$

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>270</td>
</tr>
<tr>
<td>Fe</td>
<td>45</td>
</tr>
<tr>
<td>Cr</td>
<td>35</td>
</tr>
<tr>
<td>Si</td>
<td>50</td>
</tr>
</tbody>
</table>

The nickel content in the as reduced $\text{UO}_2$ powder was 300 ppm and so only 30 ppm of nickel were lost during the grain growth runs. The
level of 300 ppm was lower than intended, but it was sufficiently above the levels of the other impurities to make it reasonable to assume that nickel was the rate controlling species.

C CHROMIUM DOPED UO₂

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>230</td>
</tr>
<tr>
<td>Ni</td>
<td>240</td>
</tr>
<tr>
<td>Fe</td>
<td>85</td>
</tr>
<tr>
<td>Si</td>
<td>25</td>
</tr>
</tbody>
</table>

The level of chromium doping turned out to be about the same of that of nickel in the nickel doped sample but heavy contamination with nickel has obviously occurred. The most likely explanation for this is that in reducing the ADU to UO₂ some of the nickel dopant evaporated and recondensed without decomposing and that when the chromium doped material was reduced some of the nickel decomposed on to this UO₂ resulting in equal levels of Cr and Ni.

The results for the chromium doped material should therefore be compared with the nickel doped material and any differences can be attributed to the presence of the chromium.

D MOLYBDENUM(D)-DOPED UO₂

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>100</td>
</tr>
<tr>
<td>Fe</td>
<td>140</td>
</tr>
<tr>
<td>Cr</td>
<td>100</td>
</tr>
<tr>
<td>Ni</td>
<td>150</td>
</tr>
<tr>
<td>Si</td>
<td>25</td>
</tr>
</tbody>
</table>

As can be seen from this table the resulting level of molybdenum was lower than the other major impurities. The table shows that the chromium dopant has acted in the same way as the nickel did before it.
The steady increase in iron concentration is now believed to be due to rust formation on the steel collars which joined the grain growth furnaces to the glove box.

Because of the low level of molybdenum it was decided to produce another batch using a different dopant which it was hoped would not volatilize so readily.

**E Lanthanum Doped UO₂**

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>1600</td>
</tr>
<tr>
<td>Fe</td>
<td>140</td>
</tr>
<tr>
<td>Ni</td>
<td>230</td>
</tr>
<tr>
<td>Cr</td>
<td>20</td>
</tr>
<tr>
<td>Mo</td>
<td>15</td>
</tr>
<tr>
<td>Si</td>
<td>35</td>
</tr>
</tbody>
</table>

The lanthanum doping was successful, since it had been intended to introduce 2000 ppm. It can be seen that very little was lost. Contamination from the previously used dopants is again evident.

**F Aluminium Doped UO₂**

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>160</td>
</tr>
<tr>
<td>Ni</td>
<td>300</td>
</tr>
<tr>
<td>Fe</td>
<td>150</td>
</tr>
<tr>
<td>Cr</td>
<td>80</td>
</tr>
<tr>
<td>Cu</td>
<td>25</td>
</tr>
</tbody>
</table>

The resulting level of aluminium is low but this was to be expected to some extent since it was known that Al₂O₃ could be volatile at high temperatures. The Al level of the freshly prepared UO₂ powder was 460 ppm. The presence of the Cu could perhaps have been due to the change from steel collars to brass collars. Since the collars never
got hot the only possible way they could cause contamination is if the wet hydrogen atmosphere caused corrosion of the brass surfaces to produce loose corrosion products which could fall into the hot zone of the furnace. It was noted that the brass collars did become blackened internally.

\[ \text{Element} \quad \text{Concentration (ppm)} \\
\text{Mo} \quad 50 \\
\text{Ni} \quad 270 \\
\text{Cr} \quad 90 \\
\text{Fe} \quad 130 \\
\text{Si} \quad 95 \\
\text{Cu} \quad 18 \]

This attempt to improve the molybdenum concentration compared with the first attempt obviously failed since the resulting level is exactly half that of the previous level.

The other impurities are again present including copper.

Unfortunately, due to the length of time taken for the analysis, the results were not known until after the grain growth runs had been performed.
4.2 THE ANALYSIS OF GRAIN GROWTH DATA

The analysis of grain growth data, as distinct from the graphical presentation of the data which will be discussed later, has been the subject of comments in the literature as it is not an entirely straightforward matter. It has been stressed that equation 4.1 should be used rather than equation 4.2 which assumes that $I_0$ and $t_0$ are negligibly small.

\[ I^n - I^n_0 = k(t - t_0) \]  
\[ I^n = kt \]

In practice, however, equation 4.1 cannot be applied directly to the data as the quantities $I_0$ and $t_0$ are unknown. It has therefore been considered acceptable by some authors \((55,56)\) to attempt to determine $n$ from equation 4.2 by plotting $\log I$ against $\log t$; the slope of this plot gives $n$ providing $I > I_0$ and $t > t_0$. The accuracy of the $n$ value thus obtained can be checked by plotting $n\log I$ against $\log t$. If a straight line with a slope of 1 is obtained then the $n$ value can be considered correct. Because this procedure is based on equation 4.2 it is applicable only to data where $I > I_0$ and $t > t_0$. In cases where $I_0$ and $t_0$ are not negligible, this method cannot be applied as was the case with the present work; the plot of $\log I$ against $\log t$ usually resulted in a curve rather than a straight line. In such cases the high $(I,t)$ values in the data set fulfil the condition $I > I_0$ and $t > t_0$ and thus these points approximate to a straight line on the $\log I$ against $\log t$ plot. Normally, however, there were too few such points to permit an accurate determination of $n$. 
in any case, it is clearly more desirable to determine x using the entire data set if possible rather than just part of it. What is required therefore for the solution of this problem is a method of compensating the data to correct for the effect of the unknown $I_0$ and $t_0$. The method that has been used for that purpose in the present work is the following: log I is plotted against log ($t + x$). As shown in figure 5, there is one value of x for which a straight line results. It is clear that the constant x has progressively less effect as I and t values increase and thus the adjusted line effectively coincides with the original at high I and t values.

![Graph showing log I vs log(t + x) with different values of x.](image)

Figure 5: There exists only one value of x which gives a straight line in a plot of log I against log(t + x).
This method is based on an assumption that equation 4.3 below is equivalent to equation 4.1

\[ I^n = k(t + x) \]  

i.e. that

\[ n = \frac{\log(k(t - t_0) + I^n)}{\log I} = \frac{\log(k(t + x))}{\log I} \]  

from which it follows that \( x = \left(\frac{I^n}{k} - t_0\right) \); the units of \( x \) are time.

Thus, providing \( x = \frac{I^n}{k} - t_0 \), a plot of \( \log I \) vs. \( \log(t + x) \) gives a straight line with a slope of \( 1/n \). Because of the large amount of calculation involved in finding the value of \( x \) which gives the best straight line, an iterative least squares computer program (appendix 3) was used to select the value of \( x \) which had the minimum residual sum of squares value. The computer result was printed out in the form

\[ \log I = a + b \log(t + x) \]  

where \( b = 1/n \), and \( a = \log k/n \).

This device of adding a factor \( x \) to the recorded time values enables the best fitting line, equation 4.5, to be drawn through the adjusted data plot; now, by reversing the procedure i.e. by removing \( x \), it is possible to use the constants \( a \) and \( b \) of equation 4.5 to generate a set of \((I, t)\) values which define the best fitting curve for the original, as recorded, data set - equation 4.6.

\[ a + b \log t = \log I' \]  

If the data is to be analysed in terms of equation 4.1,
the problem now remains of assigning values to $I_o$ and $t_o$. In so far as values of $n$ and $k$ are concerned, it is not necessary to know $I_o$ and $t_o$ since, from equation 4.4, a plot of $\log^n v \log(t+x)$ is equivalent to a plot of $\log(I^n - I_o^n)$ against $\log(t - t_o)$. It might, however, be thought desirable to determine $I_o$ and $t_o$ because they have a particular physical significance in that they describe the starting point of the grain growth process. Accepting for a moment this view, it seems reasonable to assume that the point $(I_o, t_o)$ should correspond to the instant that grain growth starts i.e. when the interfering process of sintering ceases. There are, however, two reasons why $(I_o, t_o)$ cannot be used when defined in this way. First, there is the practical difficulty in that sintering bodies approach their maximum density in an asymptotic manner so that it is impossible in practice to determine accurately the time at which sintering ceases. Second, there is the theoretical point that grain growth does not begin at the instant sintering ceases, in fact, it occurs continuously during sintering and is a necessary consequence of the densification process.

Despite these objections which imply that it may not be possible to relate the point $(I_o, t_o)$ to an event of physical significance, i.e. the end of sintering, it is clear from the form of equation 4.1 that some value of $I$ and $t$ must be assigned to $(I_o, t_o)$. It is also clear from the previous analysis that the zero point must lie on the curve defined by equation 4.6. Since it proved impossible to determine the point $(I_o, t_o)$ by direct observation, by analysis or by extrapolation of the data, it became necessary to consider
the consequences of using some fairly arbitrary zero point 
\((I_1, t_1)\) which nevertheless satisfies equation 4.6 i.e. it is 
proposed to analyse the data in terms of equation 4.7

\[ I^n - I^n_1 = k(t - t_1) \quad (4.7) \]

The effects of choosing a zero point in the above way were investigated on a set of data using a set of zero points below the smallest recorded point. This substitution was without serious consequence. In fact, the only effect of changing the chosen zero point in this way on a plot of \(\log(I^n - I^n_1)\) against \(\log(t - t_1)\) was to shift the data points along the line. The size of the shift became smaller as the distance between the data point and the zero became larger. The position and the orientation of the line on the graph with respect to the axes did not change but the line was lengthened or shortened somewhat according to the chosen value of \((I_1, t_1)\). The importance of the fact that \(I_1\) and \(t_1\) must be interdependent through equation 4.6 should be emphasised; by carefully manipulating \(I_1\) independently of \(t_1\) it is possible to make almost any set of data appear as a straight line with a slope of 1 in a plot of \(\log(I^n - I^n_1)\) against \(\log(t - t_1)\).

In view of these findings, the method was considered acceptable and all results were analysed using equation 4.7 and a chosen \((I_1, t_1)\) point. This point was chosen so that \(I_1\) was several microns smaller than the smallest observed grain size in that particular experiment; \(I_1\) was always larger than 1 micron and smaller than 11 microns, usually it was in the range 1.5 - 6 microns. This was the method used to
analyse the data in terms of kinetic exponential and preexponential factors. However, for the graphical presentation of the data, it was decided to follow the customary practice of plotting \( \log(I_3^3 - I_1^3) \) against \( \log(t - t_1) \) regardless of the value of \( n \) found in practice (it is often a non-integer). The reason for choosing \( n = 3 \) is that such a plot has an immediate physical significance: it is a function of the increase in grain volume with time. Equally well a value of \( n = 2 \) could be used which would show the rate of increase of grain cross-sectional area with time. The comparison of results would be much more difficult if every grain growth curve was plotted according to equation 4.7 using its own non-integer exponent.

So that the effect of this method of presentation can be seen clearly, simple plots of the raw data on logarithmic scales have also been included in section 4.3 for comparison.
4.3 GRAPHICAL PRESENTATION OF RESULTS

Each set of data is presented twice:

- First, as a plot of $\log I$ against $\log t$. This is the raw data.

- Second, as $\log(I_3^2 - I_1^2)$ against $\log(t - t_1)$ where $I_1$, $t_1$, and $n$ were derived from an analysis of the data as explained in the previous section. The $n$ values for each set of data are also given in tabular form.
Figure 6: Grain growth in undoped uranium dioxide
Figure 7: Grain growth in molybdenum doped uranium dioxide (higher dopant concentration)
Figure 8: Grain growth in molybdenum doped uranium dioxide (lower dopant concentration)
Figure 9: Grain growth in chromium doped uranium dioxide
Figure 10: Grain growth in nickel doped uranium dioxide
Figure 11: Grain growth in lanthanum doped uranium dioxide
Figure 12: Grain growth in aluminium doped uranium dioxide
It was stated in section 4.2 that if the kinetic exponent, \( n \), did not equal 3 then the lines resulting from a plot of \( \log(I^3 - I_0^3) \) against \( \log(t - t_0) \) would not have a slope of 1; they would also tend to be curved. The first of these effects is readily apparent from the graphs in section 4.3: curvature of the lines was negligible in most cases but is visible in the lines for nickel doped uranium dioxide at 1600°C and in three of the molybdenum doped experiments. In all these cases, however, the curvature is so slight that the curve could be replaced by a straight line without visibly worsening the fit of the line to the data.

The most striking thing about the results in general is the wide variation in the value of the kinetic exponent; the two most extreme values were 1.038 and 5.88. Not only does this variation occur between specimens containing different dopants but also within groups of specimens containing the same dopant but treated at different temperatures. Even though the variations of the exponent with temperature are large they do not appear to follow any pattern. A sudden change in kinetics even occurs part way through the experiment in the case of undoped uranium dioxide at 1600°C. In view of the range of kinetic exponents covered, it was not possible to ascribe much significance to the rate constants, \( k \), except in the case of La-doped specimens.

In fact, some results of the experiments on undoped uranium dioxide have a less regular appearance on the graph than any of the experiments with doped material. This is unfor-
tunate because it was intended that the behaviour of the undoped material should be the reference standard by which the effects of the various dopants would be judged. This intention is difficult to accomplish because of the above-mentioned irregularity. The scatter of the initial data about the line in the undoped material at temperatures of 1700°C and 1800°C is more than can be explained by the experimental errors - the inaccuracy of grain size measurement and the uncertainties, due to poorly known heating rates, in measuring time spent at the heat treatment temperature. The experiment at 1700°C was repeated later with another batch of UO₂ to provide more data. The scatter was less on this second run and the kinetic exponent was very similar to that of the 1800°C experiment. The 1700°C (2nd) and 1800°C exponents are the most typical of what would be expected from pure uranium dioxide on theoretical grounds. The behaviour in the other experiments cannot, however, be ignored.

The results suggest rather that grain growth was controlled by the residual impurities which were mainly iron and silicon. The idea that the residual impurities in the uranium dioxide used in this work could have controlled grain growth behaviour is consistent with the findings of Kasen(23) where 0.5 ppm of impurity was found to be sufficient to control grain boundary movement, even allowing for the fact that he used aluminium rather than a ceramic. That grain growth was impurity controlled appears to be the only conclusion that can be drawn, particularly in view of the change of rate from n = 5.87 to n = 1.038 in the 1600°C experiment after 10⁴ minutes, which indicates in addition that not only
one impurity was rate controlling at all times.

If this explanation is correct then it is clear from the fact that a sharp transition occurs only in the case of the 1600°C experiment that the combined effect of the impurities on grain growth is temperature dependent. The occurrence of the rate transition at only one temperature is also a reason for believing that there was some interaction between the impurities, perhaps the formation of a compound with limited stability, rather than that the transition was due to a simple change from high to low boundary conditions according to the theories of Lücke and Detert(12) and Cahn(13) although the effects of impurity segregation as a function of boundary velocity probably do play a rôle.

The value of the kinetic exponent, 1.038, after the transition is believed to be significant - it is very close to 1 which implies that boundary velocity had ceased to be a function of grain diameter. Such a condition is not covered by any of the theories since they all contain grain diameter as a function upon which boundary velocity is dependent. The only conditions under which boundary velocity can be expected to remain constant are those of a system with a liquid phase in the grain boundaries. In such a system, transport of material across the boundary is dependent only on the relative free energy of the two surfaces forming the boundary and hence the rate is independent of grain size. In instances where this phenomenon is known i.e. liquid phase sintering, the microstructure typically contains large numbers of straight sided grains. However, no such features were observed in this work even though sufficient growth occurred in the
region with linear kinetics to allow such a feature to develop: the appearance of the microstructure was no different in the \( n = 1 \) region than in the \( n = 5.87 \) region.

The fact that the expected change in microstructure did not occur may be because the quantity of liquid phase was much smaller than is usually present in liquid phase sintering where there is so much material dissolved in the liquid phase that the grain growth can almost be regarded as growth of crystals from solution compared with the situation that probably occurred in the uranium dioxide where the liquid phase would be a very thin film, just enough to permit material to be transported straight across the boundary and not enough to permit much transport along the boundary. Thus a narrow liquid film might prevent the formation of straight sided grains normally associated with the presence of liquid phases in grain boundaries and so the liquid phase hypothesis remains a feasible explanation of the linear kinetics.

The transition in kinetics after a certain time is not difficult to explain. Initially boundary migration will have been controlled by one impurity, probably the most abundant. However, if that impurity species does not have a higher energy of interaction than all other impurities it will be progressively displaced as grain growth occurs by minor impurities with higher energies of interaction until the latter become sufficiently concentrated to control the grain growth rate. In the case of the undoped uranium dioxide at \( 1600^\circ C \) it may be imagined that this happened and that the minor impurity either largely replaced the original impurity or reacted with it to form a phase which was molten at \( 1600^\circ C \).
If the mechanism responsible for the rate transition was a simple replacement of a major impurity by a minor one then the same phenomenon would also be expected to be seen at 1700°C, although perhaps not at the same position since the interaction of impurities with boundaries depends on the velocity of the boundary\(^{12,13}\) which was higher at 1700°C than at 1600°C for equivalent grain sizes or anneal times. No transition occurred at 1700°C, therefore the above replacement mechanism is inadequate. If it is admitted that a liquid was responsible for the transition at 1600°C then it must also be accepted that no liquid was present at higher temperatures. Postulating a suitable explanation for the loss of liquid is difficult, and at best, speculative.

The behaviour of the undoped material in the first stage, prior to the rate transition, where \(n = 5.87\) can best be interpreted by comparing it with that of the molybdenum doped material. In all cases except one, which will be discussed later, the value of the kinetic exponent was larger than those produced by any other dopant and, in the case of the experiment at 1645°C where \(n = 5.88\), was practically identical with that of the undoped material. This suggests that the rate controlling mechanisms may have been the same in both cases.

The solubility of molybdenum in uranium dioxide is practically zero so that the molybdenum forms small insoluble particles whose drag on the migrating boundaries is the rate controlling factor for grain growth. It would appear therefore that grain growth in undoped uranium dioxide at 1600°C was initially also controlled by an impurity
in the form of insoluble particles.

At 1700°C and 1800°C in undoped uranium dioxide none of the features discussed above for the 1600°C experiment seem to apply. In the results for the higher temperature scatter of the data is much greater than at 1600°C which indicates that the overall effect of the residual impurities became more irregular, probably due to more complex mutual interactions at the higher temperatures and boundary velocities.

Returning to the molybdenum doped material, the results are generally consistent with the expected behaviour of drag on boundaries exerted by second phase particles. The kinetic exponents are high and in three cases the lines are slightly curved in the sense normally associated with a limiting grain size effect. The only exception is the experiment at 1700°C in which the average grain diameter exceeded 63 microns without any signs of a limiting grain size effect. The kinetic exponent was also much lower than in all other molybdenum doped experiments which suggests that the grain boundary driving force in this case may have been sufficient to enable the boundary to breakaway from the particles. This explanation is indirectly supported by the fact that the material used in the 1700°C experiment was from the batch with the lower of the two molybdenum concentrations used.

By comparing the experiments performed at 1500°C with two different molybdenum concentrations, the higher concentration can be seen to have retarded grain growth the most. The 1645°C experiment at the high dopant level produced
results that seem contradictory; the exponent is very high at 5.88 indicating a very slow growth rate, yet the line lies between the 1600°C and 1700°C lines for the lower dopant level experiments which seems to indicate quite a high growth rate. This conflict can be resolved if it is assumed that the boundary driving force in the 1645°C experiment was initially high enough to cause boundary breakaway as in the 1700°C experiment but that later as the driving force decreased the boundary began to collect retarding particles. The increase in the number of particles with time would account qualitatively for the very high kinetic exponent. It can be argued that the 1600°C experiment exhibits the same effect but to a lesser extent. From the following table it can be seen that the exponent increases with temperature except at 1700°C; this is consistent with the hypothesis that boundary breakaway occurred to an increasing extent at higher temperatures, (being total at 1700°C) and that later as the boundaries slow down they begin to sweep up the particles which they had earlier left behind.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Kinetic Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500°C</td>
<td>4.32, 4.22</td>
</tr>
<tr>
<td>1600°C</td>
<td>4.92</td>
</tr>
<tr>
<td>1645°C</td>
<td>5.88</td>
</tr>
<tr>
<td>1700°C</td>
<td>3.21</td>
</tr>
</tbody>
</table>

Since at higher temperatures more particles were initially left behind, the deceleration of the boundary will be greater for the higher temperatures since there are more particles to be swept up, thus resulting in a higher kine-
tic exponent. At 1700°C the boundary velocity was still too high at the end of the experiment for the boundary to have started to sweep up the second phase particles.

The results of the experiments on molybdenum doped material will now be compared with those of the nickel and chromium doped materials. These three materials formed group 1 in section 3.3.2 which it was hoped would investigate the effect, if any, of the melting point of the impurity species on grain growth.

The nickel doped material showed two types of kinetic behaviour, one occurring at 1500°C and 1700°C was characterized by an exponent of about 3.45 and the other occurring at 1600°C and 1800°C was characterized by an exponent of between 2.17 - 2.2. Normally it would be expected that such similarities in the kinetics implied that the same rate controlling mechanism operated. However it is difficult to see why the mechanism should alternate in the way implied by the graph.

The results for the chromium doped material are rather more regular than those for nickel with one exception - the 1500°C experiment. A decrease in the kinetic exponent apparently exists although the variation is within the scatter limits.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400°C</td>
<td>2.78</td>
</tr>
<tr>
<td>1700°C</td>
<td>2.64</td>
</tr>
<tr>
<td>1755°C</td>
<td>2.42</td>
</tr>
</tbody>
</table>

Comparison of the positions of the lines on the graph indicate that the chromium doped material had a greater retarding effect on grain growth than the nickel doped specimens. Whether this is because chromium is intrinsically more effective at restricting grain growth than nickel is
difficult to say since the chromium doped specimens had a higher total impurity content which may have affected the results.

Exaggerated grain growth was encountered in the 1755°C experiment. It began after only 420 minutes and at first affected just one grain near the specimen edge. Later on other grains became affected in other places but always near the specimen edge. This suggests that the surface of the specimen may have been accidentally contaminated. A similar effect was noticed in the lanthanum doped material at 1700°C and so the phenomenon is discussed in more detail later on.

Comparison of results for both the nickel and chromium doped material with the molybdenum doped experiments shows that molybdenum was less effective initially than either chromium or nickel, due to the suspected boundary breakaway mentioned earlier. Later, however, the retardation of the molybdenum became the most effective break to grain growth except at 1700°C where the boundary velocity remained too high for the second phase particles to keep pace. If the concentrations of molybdenum had been higher the boundary breakaway effect would probably have been unable to occur and the molybdenum would have been more effective than chromium or nickel at all stages during grain growth.

The next results to be considered will be those of aluminium doped uranium dioxide. The amount of aluminium in the specimens was quite low as already mentioned in chapter 4.1; the major impurity was nickel. Therefore, to see the effects of aluminium on grain growth the results must be
compared directly with those of nickel doped material. The results at 1500°C in the two experiments are very similar, both as regards kinetic exponent and the position of the lines on the graph. However, at 1600°C and 1700°C progressively more grain growth occurred in the aluminium doped material than in the nickel doped material. Thus, compared with nickel as a dopant, aluminium is equally effective at 1500°C at restricting grain growth but progressively aids grain growth at higher temperatures.

Although the range of kinetic exponent values was approximately the same for both nickel and aluminium doped material, the value at each temperature was usually quite different. This is further evidence that a relatively small quantity of aluminium was able to override the effect of a larger amount of nickel.

The amount of lanthanum present in the lanthanum doped material was large compared with the amounts of dopants used in the other experiments. This probably accounts for the close similarity between the kinetic exponents obtained at different temperatures in the experiments with the lanthanum doped material. The rate constants, \( k \), increased with increasing temperature as would be expected. As a result of this regular behaviour it was possible to calculate an energy of activation for grain growth; a value of 40 k.cal/mole was obtained. Values given for "pure" material average 70 - 80 k.cal/mole.

The kinetic exponents lay within the range 2.61 - 2.86 and so they cannot be accounted for by the simple theories
of grain growth which predict integer exponents. The theory most appropriate for these results is one such as that of Grey and Higgins\(^{(12)}\) or Cahn\(^{(13)}\) which contains both velocity dependent and velocity independent coefficients. According to these equations the deviation from squared kinetics is due to a velocity dependent interaction between the impurity and the boundary.

An important feature of the lanthanum experiments was that exaggerated grain growth began in the 1700\(^\circ\)C experiment after 2000 minutes. Only localized areas near the edge of the specimens were affected but by the end of the experiment the largest grain had attained a diameter of 0.5mm. The rest of the specimen seemed to be completely unaffected by this local exaggerated grain growth and the grain size measurements in the later stages of the experiment were confined to the unaffected regions. The rate of growth of the grains affected by the exaggerated growth was such that the smaller grains frequently became completely surrounded by the large grains and were isolated inside them until they were consumed.

There is only one theory which accounts for abnormal grain growth and that is the Hillert defect model (section 2.2.4.3). However, this model predicts that exaggerated growth will occur, probably by coalescence of second phase particles, after a limiting grain size has been reached. No limiting grain size effect was found in the lanthanum doped material and so this theory cannot provide an explication. However, according to Hillert’s theory of grain growth in pure materials (section 2.2.1.2) it is stated that for normal grain growth to occur the grain size distribution must fall
between certain limits, if it does not then abnormal growth will occur until a normal size distribution is obtained.

A disturbance of the normal grain size distribution could therefore have been the cause of the observed abnormal grain growth behaviour. Such a disturbance could have been the result of an external event, for example, a foreign particle may have stuck to the specimen surface and diffused into it and subsequently modified the local growth rate thus changing the grain size distribution.

An explanation of this type would seem the most probable in view of the localized nature of the phenomenon. It may be of significance that in the two cases where abnormal grain growth occurred - chromium doped material at 1755°C and lanthanum doped material at 1700°C - the temperature was relatively high and so a high boundary driving force may be a contributory factor.

Comparing the lanthanum, aluminium and molybdenum doped materials (group 2 of section 3.3.2) it can be seen that the aluminium and lanthanum doped materials were comparable with much greater amounts of grain growth than in the molybdenum doped uranium dioxide. In view of the low concentration of aluminium in the aluminium doped specimens which will have reduced the effectiveness of this dopant compared with the lanthanum doped material, it can be concluded that the mobility of the controlling impurity species is a rate controlling factor.
CHAPTER 5 SUMMARY AND CONCLUSIONS
High purity uranium dioxide has been prepared from $\text{UO}_2\text{F}_2$ by reaction with ammonia followed by reduction in hydrogen to form a fine powder with a specific surface area, as determined by B.E.T. gas adsorption, of 18 - 20 $\text{m}^2/\text{g}$.

The doping technique used to introduce impurities into the $\text{UO}_2$ was only partially successful because the dopant compounds used volatilized to an undesirable extent before decomposing. This resulted in lower dopant levels than anticipated and also to contamination of the uranium dioxide with previously used dopants. As a result less information could be obtained from the experiments than would otherwise have been possible.

Cold pressed uranium dioxide pellets have been sintered to 100% density at 1400°C in a wet hydrogen atmosphere. This treatment was successful for all doped and undoped materials which had been compacted at a pressure of 150 MPa.

The grain growth behaviour of the undoped material was not typical of pure materials. It was concluded that the observed behaviour was determined by the residual impurities and that very low levels of impurity can radically affect the intrinsic grain growth behaviour.

The behaviour of the undoped material at 1600°C indicated that two rate controlling mechanisms operated sequentially. In the early stages the behaviour strongly resembled that of molybdenum doped uranium dioxide. This suggested that the grain growth in the undoped material had initially been controlled by drag from second phase particles. A change
in kinetic exponent from 5.88 to 1.038 after $10^4$ minutes indicated that the grain boundary velocity had ceased to be dependent on grain size. A liquid phase in the grain boundaries was believed to be responsible for this behaviour.

The undoped material treated at 1800°C and one of the experiments at 1700°C showed large amounts of scatter in the data which are believed to be the result of a more complex interaction of the impurities with the grain boundaries than occurred at 1600°C.

The experiments on molybdenum doped material produced very high kinetic exponents except at the highest temperature 1700°C. This behaviour is interpreted in terms of drag by second phase particles after initial breakaway of the boundary from these particles. A dependence of growth rate on dopant concentration was found and it was clear that a concentration as low as 50 ppm of molybdenum was sufficient to enable it to be the rate controlling species.

Experimental results for nickel doped uranium dioxide gave kinetic exponents that varied considerably with temperature. At 1500°C and 1700°C it was about 3.45 in both cases but at 1600°C and 1800°C it was about 2.19. This is believed to be due to some complex interaction of the main dopant with other impurities.

The chromium doped material showed a trend for the kinetic exponent to decrease with increasing temperature. The results with this dopant showed that slightly more grain growth had occurred in the nickel doped material.
The effect of aluminium as a dopant compared with nickel was to increase the rate of grain growth above 1500°C. It was shown that a small amount of aluminium was capable of replacing a larger amount of nickel as the rate controlling species.

Lanthanum as a dopant permitted the largest rates of grain growth. The kinetic exponent changed very little with temperature and an energy of activation for grain growth of 40 kcal/mole was calculated. This is to be compared with an average of 70 - 80 kcal/mole previously found for "pure" uranium dioxide. The fact that the kinetic exponents were not integers is best explained in terms of a solute drag theory with both velocity dependent and velocity independent coefficients.

In conclusion the following statements can be made about the effects of impurities on grain growth:

1. It is probably impossible at present to measure the intrinsic grain growth characteristics of pure materials. The residual impurities in "pure" materials always determine the grain growth behaviour.

2. The combined effects of concentration and energy of interaction are important. Thus a solute with a low energy of interaction and present in a relatively high concentration will be progressively displaced during grain growth by those with higher energies of interaction even if the latter are present in lower concentrations. In the case of second phase particles, even if they have a high energy of interaction, they will not prevent the
boundary from breaking away from them if their concentration is too low.

3. In addition to concentration and interaction energy, the mobility of the impurity in the grain boundary is very important. Species whose diffusion coefficient is lower than that of the unimpeded boundary will tend to slow it down by a degree depending of the difference in mobilities, energy of interaction and concentration. Species whose mobility is at least as great as that of the boundary will exert no drag whatever the energy of interaction or concentration of the impurity. In cases where the mobility of the impurity is greater than that of the boundary and, in addition, the atoms of the base material diffuse faster through the impurity species than across the "clean" grain boundary, then the rate of growth may be accelerated.

The interaction between the boundary and the impurity is dependent on the velocity of the boundary.

4. Factors such as melting point and atomic diameter of the impurity species are important only to the extent to which they affect the mobility of the species as described above.
In this appendix the experimentally recorded time and average intercept values are listed under the headings TIME and INTERCEPT. Time values are in minutes and intercept values are in microns. Beneath these lists the results of the computer analysis are given. These are:

a. The equation of the best fitting straight line for the processed data expressed in the form:

\[ \log I = a + b \log(t+x) \]

b. The time correction factor, \( x \), that was applied in the above equation.

c. The standard deviation for the best straight line.

d. The constant, \( k \), from the equation \( \log k = a/b \).

e. The grain growth exponent, \( n \), from \( n = b^{-1} \).

The data for the experiment on \( \text{UO}_2 \) at 1600\(^\circ\)C was split up before analysis so that more than one set of processed results was obtained. The experiment on \( \text{UO}_2 \) at 1700\(^\circ\)C was repeated so that two sets of data were recorded; these were analysed separately.
**UNDOPED \( \text{UO}_2 \) AT 1600°C**

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
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<td>25</td>
<td>3.03</td>
<td>9700</td>
<td>8.43</td>
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<tr>
<td>75</td>
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<td>195</td>
<td>4.62</td>
<td>19900</td>
<td>18.12</td>
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<td>25500</td>
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</tr>
<tr>
<td>5425</td>
<td>7.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. The first 6 points.
   a. \( \log I = 0.23456 + 0.17036 \log(t+x) \)
   b. \( x = +1 \)
   c. S.D. = 0.028978
   d. \( k = 23.81491 \)
   e. \( n = 5.87 \)

2. The last 5 points.
   a. \( \log I = -1.78457 + 0.72291 \log(t+x) \)
   b. \( x = -3977 \)
   c. S.D. = 0.007081
   d. \( k = 0.00340 \)
   e. \( n = 1.038 \)

**UNDOPED \( \text{UO}_2 \) AT 1700°C (first run).**

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
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<td>2.98</td>
<td>400</td>
<td>11.30</td>
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<td>30</td>
<td>4.99</td>
<td>1400</td>
<td>18.04</td>
</tr>
<tr>
<td>110</td>
<td>9.87</td>
<td>7000</td>
<td>59.20</td>
</tr>
</tbody>
</table>

a. \( \log I = 0.01081 + 0.43291 \log(t+x) \)

b. \( x = +3 \)

c. S.D. = 0.100757

d. \( k = 1.05918 \)

e. \( n = 2.31 \)
**UNDOPED UO₂ AT 1700°C (second run).**

<table>
<thead>
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<th>INTERCEPT</th>
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<th>INTERCEPT</th>
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</thead>
<tbody>
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<td>840</td>
<td>16.99</td>
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<td>120</td>
<td>9.13</td>
<td>3780</td>
<td>28.55</td>
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<tr>
<td>240</td>
<td>10.19</td>
<td>7680</td>
<td>35.03</td>
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<tr>
<td>480</td>
<td>15.13</td>
<td>16200</td>
<td>45.10</td>
</tr>
</tbody>
</table>

a. \( \log I = 0.3666 + 0.3031 \log(t+x) \)
b. \( x = -24 \)
c. S.D. = 0.078500
d. \( k = 16.19951 \)
e. \( n = 3.299 \)

**UNDOPED UO₂ AT 1800°C.**

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7.20</td>
<td>300</td>
<td>27.60</td>
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<tr>
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<td>11.15</td>
<td>435</td>
<td>30.67</td>
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<td>85</td>
<td>14.20</td>
<td>1350</td>
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<td>105</td>
<td>14.56</td>
<td>1600</td>
<td>45.00</td>
</tr>
<tr>
<td>145</td>
<td>22.40</td>
<td>4485</td>
<td>50.33</td>
</tr>
<tr>
<td>235</td>
<td>29.50</td>
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</tr>
</tbody>
</table>

a. \( \log I = 0.63852 + 0.30683 \log(t+x) \)
b. \( x = -5 \)
c. S.D. = 0.064417
d. \( k = 120.50972 \)
e. \( n = 3.26 \)
### Chromium Doped UO₂ at 1400°C

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>6.15</td>
<td>2600</td>
<td>6.27</td>
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<td>5.11</td>
<td>4000</td>
<td>6.72</td>
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<td>244</td>
<td>6.44</td>
<td>8000</td>
<td>7.85</td>
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<td>344</td>
<td>5.30</td>
<td>9500</td>
<td>10.24</td>
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<tr>
<td>1200</td>
<td>6.15</td>
<td>11000</td>
<td>8.93</td>
</tr>
<tr>
<td>1300</td>
<td>7.09</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- \( \log I = -0.5435 + 0.35988 \log (t + x) \)
- \( x = +3914 \)
- \( S.D. = 0.048141 \)
- \( k = 0.0308 \)
- \( n = 2.78 \)

### Chromium Doped UO₂ at 1500°C

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>5.96</td>
<td>7200</td>
<td>15.78</td>
</tr>
<tr>
<td>100</td>
<td>7.29</td>
<td>10000</td>
<td>15.50</td>
</tr>
<tr>
<td>300</td>
<td>8.05</td>
<td>17200</td>
<td>24.92</td>
</tr>
<tr>
<td>600</td>
<td>7.67</td>
<td>22800</td>
<td>26.33</td>
</tr>
<tr>
<td>1600</td>
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</tr>
<tr>
<td>3000</td>
<td>8.65</td>
<td>35000</td>
<td>28.75</td>
</tr>
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</table>

- \( \log I = -1.06894 + 0.55767 \log (t + x) \)
- \( x = +2500 \)
- \( S.D. = 0.049475 \)
- \( k = 0.01223 \)
- \( n = 1.79 \)
### CHROMIUM DOPED UO₂ AT 1700°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>6.80</td>
<td>2700</td>
<td>18.82</td>
</tr>
<tr>
<td>100</td>
<td>9.28</td>
<td>4000</td>
<td>21.40</td>
</tr>
<tr>
<td>330</td>
<td>10.96</td>
<td>8000</td>
<td>29.45</td>
</tr>
<tr>
<td>1300</td>
<td>14.30</td>
<td>11000</td>
<td>33.86</td>
</tr>
</tbody>
</table>

a. \( \log I = -0.02072 + 0.37824 \log(t+x) \)
b. \( x = +206 \)
c. S.D. = 0.033608
d. \( k = 0.88255 \)
e. \( n = 2.64 \)

### CHROMIUM DOPED UO₂ AT 1755°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>6.30</td>
<td>420</td>
<td>14.28</td>
</tr>
<tr>
<td>34</td>
<td>7.65</td>
<td>1366</td>
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</tr>
<tr>
<td>65</td>
<td>8.78</td>
<td>2800</td>
<td>33.56</td>
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<tr>
<td>120</td>
<td>10.78</td>
<td>4227</td>
<td>39.58</td>
</tr>
<tr>
<td>300</td>
<td>13.52</td>
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<td></td>
</tr>
</tbody>
</table>

a. \( \log I = 0.06835 + 0.41367 \log(t+x) \)
b. \( x = +54 \)
c. S.D. = 0.039146
d. \( k = 1.4638 \)
e. \( n = 2.42 \)
### Nickel Doped UO₂ at 1500°C

<table>
<thead>
<tr>
<th>Time</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.82</td>
</tr>
<tr>
<td>100</td>
<td>5.14</td>
</tr>
<tr>
<td>1400</td>
<td>9.56</td>
</tr>
</tbody>
</table>

\[ \log I = 0.05968 + 0.2995 \log(t+x) \]
\[ x = +29 \]
\[ \text{S.D.} = 0.019826 \]
\[ k = 1.5827 \]
\[ n = 3.34 \]

### Nickel Doped UO₂ at 1600°C

<table>
<thead>
<tr>
<th>Time</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>8.94</td>
</tr>
<tr>
<td>100</td>
<td>9.92</td>
</tr>
<tr>
<td>300</td>
<td>11.07</td>
</tr>
<tr>
<td>1250</td>
<td>14.73</td>
</tr>
</tbody>
</table>

\[ \log I = -0.36533 + 0.46032 \log(t+x) \]
\[ x = +769 \]
\[ \text{S.D.} = 0.034261 \]
\[ k = 0.16122 \]
\[ n = 2.17 \]
NICKEL DOPED UO$_2$ AT 1700$^\circ$C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.90</td>
<td>615</td>
<td>13.67</td>
</tr>
<tr>
<td>30</td>
<td>6.92</td>
<td>1575</td>
<td>17.13</td>
</tr>
<tr>
<td>100</td>
<td>8.60</td>
<td>3250</td>
<td>25.36</td>
</tr>
<tr>
<td>320</td>
<td>11.38</td>
<td>7500</td>
<td>27.95</td>
</tr>
</tbody>
</table>

a. log$I$ = 0.36742 + 0.28056 log(t+x)
b. $x = 6$
c. S.D. = 0.030778
d. $k = 20.342$
e. $n = 3.56$

---

NICKEL DOPED UO$_2$ AT 1800$^\circ$C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>8.09</td>
<td>300</td>
<td>42.49</td>
</tr>
<tr>
<td>35</td>
<td>19.02</td>
<td>1296</td>
<td>79.33</td>
</tr>
<tr>
<td>100</td>
<td>17.92</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. log$I$ = 0.47314 + 0.45418 log(t+x)
b. $x = 0$
c. S.D. = 0.098058
d. $k = 10.966$
e. $n = 2.20$
MOLYBDENUM(I) DOPED UO₂ AT 1645°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>.40</td>
<td>7.79</td>
<td>2500</td>
<td>18.10</td>
</tr>
<tr>
<td>100</td>
<td>9.78</td>
<td>7000</td>
<td>19.54</td>
</tr>
<tr>
<td>1100</td>
<td>13.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. \( \log I = 0.64224 + 0.17 \log(t+x) \)

b. \( x = -9 \)

c. S.D. = 0.034781

d. \( k = 5988.5 \)

e. \( n = 5.88 \)

MOLYBDENUM(I) DOPED UO₂ AT 1500°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
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<td>30</td>
<td>2.00</td>
<td>8500</td>
<td>8.54</td>
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<tr>
<td>100</td>
<td>2.69</td>
<td>16800</td>
<td>8.68</td>
</tr>
<tr>
<td>1100</td>
<td>5.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. \( \log I = -0.00882 + 0.23163 \log(t+x) \)

b. \( x = -9 \)

c. S.D. = 0.027689

d. \( k = 0.91772 \)

e. \( n = 4.32 \)
MOLYBDENUM(II) DOPED UO₂ AT 1500°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>3.29</td>
<td>4225</td>
<td>10.11</td>
</tr>
<tr>
<td>55</td>
<td>4.46</td>
<td>9862</td>
<td>13.34</td>
</tr>
<tr>
<td>155</td>
<td>5.07</td>
<td>15470</td>
<td>14.94</td>
</tr>
<tr>
<td>365</td>
<td>6.90</td>
<td>22575</td>
<td>16.39</td>
</tr>
<tr>
<td>735</td>
<td>8.11</td>
<td>31155</td>
<td>20.90</td>
</tr>
<tr>
<td>1705</td>
<td>9.35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. \( \log I = 0.20789 + 0.23674 \log (t+x) \)

b. \( x = -2 \)

c. S.D. = 0.036022

d. \( k = 7.545 \)

e. \( n = 4.22 \)

MOLYBDENUM(II) DOPED UO₂ AT 1600°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
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<td>175</td>
<td>6.97</td>
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<td>317</td>
<td>8.31</td>
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<td>17.89</td>
</tr>
<tr>
<td>632</td>
<td>9.19</td>
<td>30521</td>
<td>19.93</td>
</tr>
<tr>
<td>1618</td>
<td>10.95</td>
<td>48901</td>
<td>22.83</td>
</tr>
</tbody>
</table>

a. \( \log I = 0.37677 + 0.20315 \log (t+x) \)

b. \( x = 6 \)

c. S.D. = 0.026872

d. \( k = 71.488 \)

e. \( n = 4.92 \)
MOLYBDENUM(II) DOPED $\text{UO}_2$ AT 1700°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>4.57</td>
<td>2667</td>
<td>30.02</td>
</tr>
<tr>
<td>35</td>
<td>6.88</td>
<td>6561</td>
<td>38.22</td>
</tr>
<tr>
<td>152</td>
<td>11.24</td>
<td>10745</td>
<td>44.68</td>
</tr>
<tr>
<td>281</td>
<td>14.06</td>
<td>16400</td>
<td>48.29</td>
</tr>
<tr>
<td>473</td>
<td>17.08</td>
<td>22285</td>
<td>55.23</td>
</tr>
<tr>
<td>1423</td>
<td>24.10</td>
<td>31900</td>
<td>63.63</td>
</tr>
</tbody>
</table>

a. $\log I = 0.39417 + 0.31113 \log(t+x)$
b. $x = -8$
c. S.D. = 0.0113
d. $k = 18.432$
e. $n = 3.21$

LANTHANUM DOPED $\text{UO}_2$ AT 1500°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>2.40</td>
<td>5930</td>
<td>13.37</td>
</tr>
<tr>
<td>90</td>
<td>3.08</td>
<td>9830</td>
<td>23.15</td>
</tr>
<tr>
<td>295</td>
<td>6.10</td>
<td>17063</td>
<td>23.50</td>
</tr>
<tr>
<td>730</td>
<td>8.24</td>
<td>25280</td>
<td>24.21</td>
</tr>
<tr>
<td>1626</td>
<td>9.94</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. $\log I = -0.1245 + 0.35152 \log(t+x)$
b. $x = -5$
c. S.D. = 0.056437
d. $k = 0.44279$
e. $n = 2.845$
### Lanthanum Doped UO₂ at 1600°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4.68</td>
<td>5611</td>
<td>23.59</td>
</tr>
<tr>
<td>92</td>
<td>5.70</td>
<td>6640</td>
<td>24.23</td>
</tr>
<tr>
<td>300</td>
<td>7.58</td>
<td>15340</td>
<td>29.68</td>
</tr>
<tr>
<td>1291</td>
<td>12.27</td>
<td>25010</td>
<td>32.43</td>
</tr>
</tbody>
</table>

a. \( \log I = 0.01429 + 0.34956 \log(t+x) \)
b. \( x = +42 \)
c. S.D. = 0.031
d. \( k = 1.0986 \)
e. \( n = 2.86 \)

### Lanthanum Doped UO₂ at 1700°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>11.30</td>
<td>1502</td>
<td>36.80</td>
</tr>
<tr>
<td>38</td>
<td>13.00</td>
<td>2800</td>
<td>45.50</td>
</tr>
<tr>
<td>99</td>
<td>15.65</td>
<td>4080</td>
<td>50.10</td>
</tr>
<tr>
<td>211</td>
<td>19.35</td>
<td>8117</td>
<td>75.97</td>
</tr>
<tr>
<td>402</td>
<td>23.27</td>
<td>18227</td>
<td>95.50</td>
</tr>
</tbody>
</table>

a. \( \log I = 0.3448 + 0.3836 \log(t+x) \)
b. \( x = +58 \)
c. S.D. = 0.018827
d. \( k = 7.984 \)
e. \( n = 2.61 \)
### ALUMINIUM DOPED UO$_2$ AT 1500°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>5.94</td>
<td>10530</td>
<td>17.80</td>
</tr>
<tr>
<td>1080</td>
<td>8.50</td>
<td>16205</td>
<td>23.54</td>
</tr>
<tr>
<td>2400</td>
<td>12.25</td>
<td>23095</td>
<td>23.62</td>
</tr>
<tr>
<td>5127</td>
<td>15.23</td>
<td>30090</td>
<td>25.25</td>
</tr>
</tbody>
</table>

\[ \text{a. } \log I = -0.0745 + 0.33378 \log(t+x) \]

\[ \text{b. } x = 188 \]

\[ \text{c. } \text{S.D.} = 0.046246 \]

\[ \text{d. } k = 0.5212 \]

\[ \text{e. } n = 3.00 \]

---

### ALUMINIUM DOPED UO$_2$ AT 1600°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>547</td>
<td>11.02</td>
<td>6043</td>
<td>25.49</td>
</tr>
<tr>
<td>587</td>
<td>12.73</td>
<td>11483</td>
<td>32.15</td>
</tr>
<tr>
<td>667</td>
<td>14.26</td>
<td>15563</td>
<td>36.11</td>
</tr>
<tr>
<td>858</td>
<td>14.14</td>
<td>25213</td>
<td>37.80</td>
</tr>
<tr>
<td>1808</td>
<td>16.50</td>
<td>36304</td>
<td>44.91</td>
</tr>
<tr>
<td>3258</td>
<td>21.28</td>
<td>41429</td>
<td>44.19</td>
</tr>
</tbody>
</table>

\[ \text{a. } \log I = 0.28408 + 0.29802 \log(t+x) \]

\[ \text{b. } x = -71 \]

\[ \text{c. } \text{S.D.} = 0.024644 \]

\[ \text{d. } k = 8.9552 \]

\[ \text{e. } n = 3.35 \]
ALUMINIUM DOPED UO$_2$ AT 1700°C.

<table>
<thead>
<tr>
<th>TIME</th>
<th>INTERCEPT</th>
<th>TIME</th>
<th>INTERCEPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>13.88</td>
<td>4580</td>
<td>56.49</td>
</tr>
<tr>
<td>190</td>
<td>15.39</td>
<td>7100</td>
<td>61.44</td>
</tr>
<tr>
<td>440</td>
<td>16.97</td>
<td>12165</td>
<td>70.65</td>
</tr>
<tr>
<td>1430</td>
<td>30.09</td>
<td>23163</td>
<td>90.49</td>
</tr>
</tbody>
</table>

a. $\log I = 0.04904 + 0.44426 \log(t+x)$
b. $x = +178$
c. S.D. = 0.039307
d. $k = 1.2896$
e. $n = 2.25$
Assumption - Boundaries migrate in response to the pressure difference existing across them.

Hence \[ V \propto \Delta P = M \cdot \Delta P \]  \hspace{1cm} A1

For a spherical body \( \Delta P = 2\gamma / r_c \). That is, the internal pressure is proportional to the ratio of boundary area to the volume of material enclosed by the boundary. Hence it is maintained that \( R = r_c \) for spheres & \( R = k r_c \) for non spheres, where \( k > 1 \).

\[ V = M \cdot \gamma \cdot \frac{2}{R} \]  \hspace{1cm} A2

Consider two isolated spherical grains of radius \( R_1 \) & \( R_2 \) respectively where \( R_1 > R_2 \). The pressure differences across their boundaries are thus \[ \Delta P_1 = \gamma \cdot \frac{2}{R_1} \] \hspace{1cm} & \hspace{1cm} \[ \Delta P_2 = \gamma \cdot \frac{2}{R_2} \]  \hspace{1cm} A3

These two grains are brought into contact. A boundary forms between them with \( r_c = r_{c3} \). The pressure drop across this boundary, \( \Delta P_3 \), is given by \[ \Delta P_3 = \Delta P_1 - \Delta P_2 = 2\gamma \left( \frac{1}{R_1} - \frac{1}{R_2} \right) \]

\[ r_{c3} = \frac{2\gamma}{\Delta P_3} = \frac{R_2 \cdot R_1}{R_2 - R_1} \]  \hspace{1cm} A4

Generalizing this equation for a given grain, \( l \), in relation to the surrounding grains, \( S \), gives \[ \frac{r_{c1}}{\text{average}} = \frac{R_S \cdot R_l}{R_S - R_l} \]  \hspace{1cm} A5

Taking the average situation a grain \( \bar{R} \) surrounded by other grains, \( \bar{R} \) will not grow in relation to other grains, \( \bar{R} \), but what is required is the absolute growth rate of \( \bar{R} \), or, its growth rate with respect to grains that do not grow i.e., those of \( D = D_{\text{crit}} \). Therefore \[ r_{c\bar{R}} = \frac{R_{\text{crit}} \cdot \bar{R}}{R_{\text{crit}} - \bar{R}} \]  \hspace{1cm} A6
the equations:

\[ \Sigma y = b \Sigma x + n.a \]
\[ \Sigma xy = b \Sigma x^2 + a\Sigma x \]

where \( n \) is the number of data points. The formula of the line to which
the data is fitted is

\[ y = a + b.x \]

The program first reduced each of the set of time values for an experimental
run by the largest possible amount without creating any negative values.
The least squares data fitting calculation was then performed and the
resulting values stored. Each of the set of time values was now increased
by 1 and the process repeated. This occurred 1000 times. The 1000 values
of the residual sum of squares values were then compared and the smallest
selected. The time values corresponding to this value were then printed
out together with the formula of the straight line and the residual sum
of squares value and the standard deviation.
C DATA ENHANCEMENT PROGRAM
0001 DIMENSION TIME(17), CEPT(17), X(1000,17), Y(1000,17), S(1000)
0002 DIMENSION B(1000), A(1000), T(1000), L(1000), R(17), U(17)
0003 DIMENSION TIM1(17)
0004 DO 71 I=1,30
0005 READ(5,30) TIME
0006 READ(5,30) CEPT
0007 30 FORMAT(9F8.2)
0008 IF(TIME(I).EQ.0.0) GOTO 72
C REDUCE ALL TIME VALUES WITHOUT CREATING NEGATIVE VALUES.
0009 N=0.0
0010 DO 40 K=1,17
0011 IF(CEPT(K).LT.0.10) GOTO 44
0012 N=1+N
0013 40 TIM1(K)=TIME(K)-TIME(1)+1
C ADD 1 TO TIME VALUES AND DO LEAST SQUARES FIT, REPEAT 1000 TIMES
0014 44 CONTINUE
0015 DO 41 J=1,1000
0016 SUMX=0.0
0017 SUMY=0.0
0018 SUMXY=0.0
0019 SUMSQX=0.0
0020 SUMSQY=0.0
C SET ALL VARIABLES AT ZERO
0021 DO 42 K=1,N
0022 TIM1(K)=TIM1(K)+1
0023 X(J,K)=ALOG10(TIM1(K))
0024 SUMX=SUMX+X(J,K)
0025 Y(J,K)=ALOG10(CEPT(K))
0026 SUMY=SUMY+Y(J,K)
0027 SUMXY=SUMXY+X(J,K)*Y(J,K)
0028 SUMSQX=SUMSQX+X(J,K)**2
0029 SUMSQY=SUMSQY+Y(J,K)**2
0030 42 CONTINUE
0031 E=(SUMSQ-(SUMX**2)/N)
0032 D=(SUMXY-(SUMX*SUMY)/N)
0033 B=SLOPE A=CONSTANT S=RESIDUAL SUM OF SQUARES T=STANDARD DEVIATION
0034 C  B(J)=D/E
0035 A(J)=(SUMY-B(J)*SUMX)/N
0036 S(J)=SUMSQY-((SUMY**2)/N)-B(J)*(SUMXY-(SUMX*SUMY/N))
0037 T(J)=SQRT(S(J)/(N-2))
0038 41 CONTINUE
0039 42 CONTINUE
0040 43 CONTINUE
0041 CONTINUE
0042 CONTINUE
0043 CONTINUE
0044 CONTINUE
0045 CONTINUE
0046 CONTINUE
0047 CONTINUE
0048 CONTINUE
0049 CONTINUE
0050 CONTINUE
0051 CONTINUE
0052 CONTINUE
0053 CONTINUE
0054 CONTINUE
0055 CONTINUE
0056 CONTINUE
0057 CONTINUE
0058 CONTINUE
0059 CONTINUE
0060 CONTINUE
0061 CONTINUE
0062 CONTINUE
0063 CONTINUE
DO 51 K=1,N
U(K)=EXP(2.303*X(1,K))
R(K)=EXP(2.303*Y(1,K))
51 CONTINUE
WRITE(6,33)
33 FORMAT(6X,'DOPED',2X,'U02',2X,'AT',7X,'DEGREES',2X,'C',3X,'PROCESS
CED',2X,'DATA')
WRITE(6,19)
19 FORMAT(6X,'DATETIME',2X,'DATACEPT',6X,'TIM1',4X,'LOGT',4X,'LOGI',2
CX,'NEWCEPT',3X,'NEWTIME')
DO 20 K=1,N
20 WRITE(6,21) TIME(K), CEPT(K), TIM1(K), X(1,K), Y(1,K), R(K), U(K)
WRITE(6,45) S(1)
45 FORMAT(6X,'RESIDUAL',2X,'SUM',2X,'OF',2X,'SQUARES',2X,'=',',F10.6)
WRITE(6,48) T(1)
48 FORMAT(6X,'STANDARD',2X,'DEV',2X,'=',',F10.6)
WRITE(6,46) A(1), B(1)
46 FORMAT(6X,'LOGINTERCEPT',2X,'=',',F10.5,2X,'+',',F10.5,'LOGTIME///)
71 CONTINUE
72 STOP
END
55. N. Murty, Phil. Mag., 20, 855, 1969.