FACTORS DETERMINING THE UNIDIRECTIONAL SOLIDIFICATION BEHAVIOR OF THE SYSTEM UO₂-W

A THESIS

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The Faculty of the Graduate Division
by
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In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Ceramic Engineering

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SUMMARY

Unidirectional solidification of oxide-metal composite mixtures produced structures consisting of metallic fibers uniformly embedded in the oxide matrix. In particular, the system UO$_2$-Tungsten was investigated and was found to give tungsten fiber densities between 15 and $42 \times 10^6$ fibers per cm$^2$ by varying the growth rate from 1.9 to 9.0 cm/hr. Much higher growth rates produced problems with oxide stoichiometry. Preliminary investigation into the effects of impurity additions were studied also to determine their effects on the solidification behavior of the system UO$_2$-tungsten. Finally, studies into the solubility of tungsten in molten UO$_{2+x}$ lead to the conclusion that an O/U ratio of approximately 2.10 was necessary to allow enough tungsten to go into solution and result in good fiber growth.
CHAPTER I

INTRODUCTION

Since the discovery of rod-type growth in oxide metal composites, much interest has been expressed insofar as electrical applications of these composites are concerned. This interest is based on the fact that there are millions of highly conducting rods in a square centimeter of an insulating matrix, which is an essentially ideal situation for use in microcircuits and electron emission.

To be of use in these functions, however, more information must be known about this area of eutectic fiber growth in an oxide-metal system. Since work is very limited in this area, basic questions, such as the effect of growth rate on fiber densities, the correct composition of raw materials and the effect of impurities on the system, need to be answered.

Because there was limited knowledge in the UO$_2$-W composite area, this was the system chosen for further investigation. It was known that during unidirectional solidification certain composites of UO$_2$-W will form a eutectic matrix. With this as a starting point, the behavior of this composite were explored to determine if it would be suitable for the above applications, and to serve as a guidepost for the investigation of other oxide-metal systems.
CHAPTER II

SURVEY OF THE LITERATURE

In the field of eutectic alloy solidification, a technique\textsuperscript{1-6,14} has recently been discovered by which the microstructure of a given system can be controlled by the direction and rate of heat removal. Generally, this technique is employed by obtaining a molten pool of a mixture of two metals and removing heat from a single direction so as to pass a solidification front through the molten material. The method is commonly referred to as unidirectional solidification and leads generally to structures with lamellae or rod type growth of one metal in another metal matrix.

Considerable theory\textsuperscript{1-7,10} is available on the metal-metal systems; however, work in the oxide-metal systems, i.e. where an oxide serves as the matrix and the metal solidifies as fibers or lamellae, is very limited at present. Recently it has been shown that unidirectional eutectic growth is possible in certain of these systems, and there is considerable effort in the oxide-metal system at this time.

Due to the paucity of information in oxide-metal systems this survey will primarily deal with the metal-metal system, and should be understood that the information presented may or may not hold true for the oxide-metal system. Due, however, to the similarity of the growth mechanism, it is as at least a starting point for further investigation.

Chadwick\textsuperscript{1}, in his article on eutectic alloy solidification, discusses the growth of lamellar eutectic alloys and states that the
average composition of the solid is exactly the same as the composition of the liquid from which it freezes, even though the component phases of alpha and beta in the solid can be of widely different compositions. During the solidification the $\alpha$ phase rejects the atoms of B, and the $\beta$ phase rejects the atoms of A. However, under steady state growth conditions, the rate of rejection of B atoms by the $\alpha$ phase is equal to the rate of rejection of A atoms by the $\beta$ phase (see Figure 1).

A mathematical solution is difficult, and has never been evaluated quantitatively. Solidification in eutectic systems is controlled by the extraction of heat from the system. If the rate of the extraction of heat is controlled externally the rate of growth of the solid is fixed and the inter-lamellar spacing of the alloy is constant. The solid-liquid interface must be undercooled below the equilibrium eutectic temperature to drive the solidification process along at a specified growth rate. Since the temperature of the interface cannot be controlled by external devices but is fixed by the system itself, the only thing that can be controlled is the amount of undercooling present in the system. In the analysis of a eutectic growth system, it must be understood that there are three general types of undercooling:

$\Delta T_c$, which is the constitutional undercooling due to the enrichment of the liquid by the solute; $\Delta T_r$, which is the undercooling due to the curvature of the solid surface in contact with the liquid; and $\Delta T_k$, the undercooling required by the kinetic process of solidification.

The value of $\Delta T_k$ can be assumed to be negligible when compared with the other two terms. The equation can then be written for total undercooling that:
Figure 1. Concentration Distribution Ahead of Eutectic Interface (a), and Shape of Eutectic Interface, (b).

- $C^L_\alpha$ = concentration in the liq ahead of $\alpha$ phase
- $C^L_\beta$ = $\beta$ concentration in the liq ahead of $\beta$ phase
- $C_E$ = Eutectic concentration
- $\sigma$ = inter-surface energy
\[ \Delta T = \Delta T_c + \Delta T_r \]

which in turn equals

\[ \frac{n_i \Delta C_i + \sigma_i T_E}{L_i \rho_i r_i} \]

in which:

i designates either \( \alpha \) or \( \beta \),

\( n \) = slope of the liquidus lines at the eutectic composition,

\( \Delta C \) = the difference between the eutectic composition and the composition of the liquid at any position across the interface,

\( \sigma \) = solid-liquid inter-surface energy,

\( T_E \) = equilibrium eutectic temperature,

\( L \) = latent heat of solidification per unit mass of liquid,

\( \rho \) = density, and

\( r \) = radius of curvature at any point on the interface.

**Influence of Impurities**

Chadwick also investigated the effect of impurities or additives on a metal-metal system with relation to lamellae structure. He found that the addition of impurities leads to the formation of a colony structure, which is the result of the fact that the growth rate of the individual lamellae at the cellular interfaces is not constant across the interface but in fact decreased as a function of the distance from the center of a colony or cell. The curvature of the solid-liquid interface at the cell top increased toward the cell wall; and,
since the lamellae were seen to grow normal to the solid-liquid interface, the lamellae curved as they got closer and closer to the wall of each cell and at the cell wall were actually almost perpendicular to the direction of growth. He concluded from further investigation that the colony structure within the grain of the eutectic alloys was due to the formation of a zone of constitutionally supercooled liquid ahead of the interface which was due to the rejection of the impurities in the growing solid. When the eutectic phases were found to have different partition coefficients with the same impurity element, the lamellar structure may become unstable, and if so may be replaced by a rod-type structure. The solute will build up ahead of the alpha and beta lamellae and will attain different steady state values ahead of each phase according to the formulas:

\[
C^\alpha_x = \frac{C_0 + C_{x\alpha} (1-k^\alpha_x)}{(k^\alpha_x)} \exp \left[ \frac{-Rx}{D} \right] \tag{2(a)}
\]

\[
C^\beta_x = \frac{C_0 + C_{x\beta} (1-k^\beta_x)}{(k^\beta_x)} \exp \left[ \frac{-Rx}{D} \right] \tag{2(b)}
\]

in which

\[D = \text{liquid diffusion coefficient}\]

\[R = \text{Growth Rate}\]

\[k^\alpha_x \text{ and } k^\beta_x = \text{the two partition coefficients in the } \alpha \text{ and } \beta \]
phases.
Where $k^\beta_x$ is less than $k^\alpha_x$, the amount of solute at the $B$ lamellae interface is greater than that at the $\alpha$ lamellae interface; therefore, the equilibrium freezing point of the liquid in contact with the $\beta$ lamellae is lower than that of the liquid in contact with the $\alpha$ lamellae interface. This means the eutectic interface is no longer isothermal, and the $\beta$ phase will grow at a finite distance behind the $\alpha$ phase (see Figure 2). Some distance ahead of the interface, of course, it is to be expected that the solute will be evenly distributed across the interface. Hence the effective value of the partition coefficient of the interface as a whole is not the algebraic mean of the individual partition coefficients $k^\alpha_x$ and $k^\beta_x$ due to the entrapment of some of the solute and pockets of high solute concentration in regions ahead of the $\beta$ lamellae and between the $\alpha$ lamellae. Since the $\alpha$ lamellae are ahead of the $\beta$ lamellae, it is obvious that the $\alpha$ lamellae are supercooled with respect to the $\beta$ solid solution. This means that if in some way a protrusion on the $\beta$ lamellae is formed, rejection of $A$ atoms from it now will be radial and, therefore, form a bridge over the $\beta$ lamellae by the $\alpha$ lamellae on either side of it. Then, what we have is the projection of the $\beta$ lamellae surrounded by the $\alpha$ phase, which is in effect now a rod. This could happen many times along the length of a $\beta$ lamellae. Lamellae type growth has transitioned into rod-type growth as shown in Figures 3 and 4. These rods of the $\beta$ phase are of course growing in the direction of the solidification front. Chadwick postulates that the addition of impurities is responsible for two growth effects within a eutectic alloy system. First, such additions breaks the system down into a colony type structure, and instead of one single
Figure 2. Profile of a Lamellar Eutectic Interface in the Presence of an Impurity Element Where $k^\alpha_x > k^\beta_x$.

Figure 2a. Composition of the Liquid Ahead of the Interface of Figure 2.

Figure 2b. Equilibrium Freezing Temperatures of the Liquid Ahead of the Interface.
Figure 3. Schematic Drawings Illustrating the Development of a Rod-type Structure from a Lamellar Structure.
Figure 4: Schematic Drawings Showing the Development of a Cellular Structure from a Planar Interface, and the Increase in the Proportion of the Rod-type Structure with Increasing Amounts of Impurity Element.
grain or crystal it becomes many smaller grains or colonies. Secondly, this breaks down the lamellae type structure into a rod-like structure; and this addition of impurities, in fact, is the only thing that will break the lamellae type structure into the rod like structure.

A Mathematical Approach to the Influence of Growth Rate

In attempting to explain mathematically the effect of variance of growth rate on the systems during eutectic or off-eutectic solidification, most work was done around an equation that was first derived by Tiller\(^2\) in 1958. He showed generally that as growth rate increased, interlamellae or interrod spacing decreased. Tiller used the ideal case and solved a simple diffusion equation by dimensional and phenomenological arguments. First, considering interface cooling, since undercooling is the controlling factor in eutectic solidification rate, the interface undercooling was given a value consisting of \(\Delta T_c\) (undercooling due to solute build-up ahead of lamella) and \(\Delta T_B\) (the undercooling required to form phase boundaries). Tiller then went on to develop equations for solute rejection at a particular growth rate \(R\), and a diffusion equation for flux between adjacent lamellae (see Figure 5). This lead to an equation for solute build-up ahead of the interface such that:

\[
\Delta C = \frac{R(1 - k\alpha) C_E \lambda\alpha}{4D}
\]

in which:

\[\begin{align*}
R &= \text{Growth Rate} \\
\lambda\alpha &= \text{width of a lamella}
\end{align*}\]
Figure 5. Idealized Diagram of Solid-Liquid Interface for Tiller’s Analysis.
\( k_\alpha \) = the partition coefficient of B in \( \alpha \).

Undercooling at the interface in the planar case was then:

\[
\Delta T_c = -m_\alpha \left( \frac{C^L_\alpha}{\alpha} - C_E \right) = m_B \left( C_E - \frac{C^L_B}{\beta} \right) \tag{4}
\]

in which: \( \frac{C^L_\alpha}{\alpha} \) and \( \frac{C^L_B}{\beta} \) = average composition of liquid in contact with the solid phases

\( C_E \) = the eutectic composition

\( m \) = liquid line slope.

If (4) is solved for \( C_E \) and substituted in (3), the undercooling is then given as

\[
\Delta T_c = \frac{R(1-k_\alpha) C_E}{\lambda_\alpha} \frac{1}{4D \left( \frac{1}{m_\beta} - \frac{1}{m_\alpha} \right)} \tag{5}
\]

Now, if \( \Delta T_B \) is formulated in terms of liquid latent heat of fusion \( L \), eutectic temperature \( T_E \), and interphase boundary energy, the result is

\[
\Delta T_B = \frac{2\sigma_{\alpha\beta}}{L\rho} \frac{T_E}{\lambda} \tag{6}
\]

If \( \Delta T_c \) and \( \Delta T_B \) are summed, and the extremum condition of minimum entropy of \( \frac{d\Delta T}{d\lambda} = 0 \) is applied, the result is:

\[
\lambda^2 R = \frac{8\sigma_{\alpha\beta} T_E D \left( \frac{1}{m_\beta} - \frac{1}{m_\alpha} \right)}{\sigma L (1-k_\alpha) C_E} \tag{7}
\]

which is seen to be equivalent to

\[
\lambda^2 R = \text{constant}.
\]
Now, although Tiller's derivation gives a correct relationship between $\lambda$ and $R$, as seen experimentally, the condition that $\frac{dT}{d\lambda} = 0$ is considered to be invalid.¹

Other investigators such as Li and Weart ³ used correct extremum conditions but came up with incorrect results. In an analysis given in Chadwick's paper by Jackson and Chalmers, and not published elsewhere, the use of entropy considerations was eliminated. As a base for their calculations, Jackson and Chalmers used actual lamellar terminations as a stability condition (see Figure 6). Assumptions taken here are that solid-liquid interface exists and that total interface undercooling is a combination of two causes, lamellae curvature effects and solute enrichment of the liquid. They analyzed the undercooling at two points on the lamellae and, for equilibrium conditions, said that undercooling must be equal in the ideal case where phase lamellae widths were equal to symmetrical interface boundaries.

The geometrical considerations of surface energies at lamellae tips were expressed as

$$\frac{\sigma_{\alpha L}}{r} = \frac{2\sigma_{\alpha \beta}}{\lambda} \quad (8)$$

in which: $\sigma_{\alpha L}$ and $\sigma_{\alpha \beta}$ = surface energies between the $\alpha$ phase and the liquid phase, and the $\alpha$ phase and $\beta$ phase respectively,

$r$ = radius of curvature of lamellae, assumed equal for $\alpha$ and $\beta$ phases.

This relationship Equation (8) applied to the Gibbs-Thomson formula
Figure 6. Section through Solid-Liquid Interface According to Jackson and Chalmer's Analysis.
gives an equation for undercooling due to the radial nature of lamellae tips, or

$$\Delta T_r = \frac{2\sigma T_E \beta}{\lambda L}$$  \hspace{1cm} (9)

Tiller's equation for $\Delta T_c$ was substituted in the equation 1(a)

$$\Delta T = \Delta T_r + \Delta T_c$$

to give an expression for total undercooling of

$$\Delta T = \frac{2\sigma T_E \beta}{\lambda L} + \frac{(1-k)C_E R_{\lambda m}}{8 D}$$  \hspace{1cm} (10)

An expression for $\Delta T$ was also developed using the second condition, that of lamellae termination, where

$$\Delta T = \frac{4\sigma T_E \beta}{\lambda L} + \frac{(1-k)C_E R_{\lambda m}}{16 D}$$  \hspace{1cm} (11)

Since (10) and (11) are both equal to $\Delta T$, setting them equal to each other gives

$$\lambda^2 R = \frac{32\sigma T_E \beta D}{m (1-k) C_E L}$$  \hspace{1cm} (12)

or again,

$$\lambda^2 R = \text{constant.}$$

Both derivations above assume lamellar structure and eutectic composition for the system at the time of growth. Jackson and Hunt\(^4\), in 1966, derived a steady state solution for the diffusion equation for
a lamellar eutectic growing with a plane surface for the general case.

There were no restrictions on the relative volumes of the two phases, and the melt could be on or off the eutectic. This was taken further to the case of a rod-like eutectic structure, and expressions were obtained for average composition at the interface and average curvature at the interface.

To do this Jackson and Hunt considered a plane interface in which $S_\alpha$ and $S_\beta$ represented the half widths of the $\alpha$ and $\beta$ phases, and originated the coordinate system at the center of the $\alpha$ phase interface, with the $X$ axis parallel to the eutectic interface and the $Z$ axis perpendicular to it (see Figure 7). The $Y$ axis is parallel to the lamellae in the interface. For steady state growth with velocity $V$, in the $Z$ direction, the diffusion equation is

$$v^2_c + \frac{V}{D} \frac{\partial C}{\partial Z} = 0 \quad (13)$$

with boundary conditions

$$C = c_E + c_\infty \text{ at } Z = \infty$$

$$\left. \frac{\partial C}{\partial X} \right|_{Z=0} = 0 \text{ at } X = 0 \text{ and } X = S_\alpha + S_\beta$$

Using a conservation of energy argument, the following requirements must be met:

$$\left( \frac{\partial C}{\partial Z} \right) Z = 0 = \frac{-VC_\alpha}{D} \quad 0 \leq X < S_\alpha \quad 14(a)$$

$$\left( \frac{\partial C}{\partial Z} \right) Z = 0 = \frac{VC_\beta}{D} \quad S_\alpha < X \leq S_\alpha + S_\beta \quad 14(b)$$
Figure 7. Planar Lamellar Eutectic Interface Showing Definition of $S_\alpha$ and $S_\beta$ and the Coordinate System.
in which:

\[ D = \text{diffusion coefficient}, \]
\[ C_E = \text{eutectic composition}, \]
\[ C_\infty = \text{the difference between eutectic composition and actual composition far from the interface.} \]
\[ C_0^\alpha \text{ and } C_0^\beta = \text{amounts of B and A rejected when unit volume of } \alpha \text{ and } \beta \text{ freeze (see Figure 8).} \]

Equation (13) is solved and reduced to give

\[ C = C_E + C_\infty + B_o e^{-\left(\frac{V}{D}Z\right)} + \sum_{n=1}^{\infty} B_n \cos \left(\frac{\pi n x}{S_\alpha + S_\beta}\right) e^{-\left(\frac{\pi n Z}{S_\alpha + S_\beta}\right)} \]  

Then using Equations 14(a) and (b) to evaluate the Fourier coefficients in Equation (15) gives:

\[ B_o = \frac{C_0^\alpha S_\alpha - C_0^\beta S_\beta}{S_\alpha + S_\beta} \]  

16(a)

And

\[ B_n = \frac{2}{(n \pi)^2} \left(\frac{S_\alpha + S_\beta}{S_\alpha + S_\beta}\right) \frac{V}{D} C_0 \sin \left(\frac{n \pi S_\alpha}{S_\alpha + S_\beta}\right) \]  

16(b)

in which

\[ C_0 = C_0^\alpha + C_0^\beta \]

The average composition in the liquid at \( Z = 0 \) at the \( \alpha \) phase interface is then given as:
Figure 8. Phase Diagram Showing Definition of $C_0$, $C_0^\alpha$, and $C_0^\beta$. 
\[ \overline{C}_\alpha = C_E + C_\infty + B_0 + \frac{1}{S} \int \sum_{n=1}^{\infty} B_n \cos \left( \frac{n \pi x}{S_\alpha + S_\beta} \right) \, dx \]

\[ = C_E + C_\infty + B_0 + \frac{2(S_\alpha + S_\beta)^2}{S} \frac{D}{v} C_0 P \]  \hspace{1cm} 17(a)

and similarly at the \( \beta \) phase interface

\[ \overline{C}_\beta = C_E + C_\infty + B_0 - \frac{2(S_\alpha + S_\beta)^2}{S} \frac{D}{v} C_0 P \]  \hspace{1cm} 17(b)

where

\[ P = \sum_{n=1}^{\infty} \left( \frac{1}{n \pi} \right)^3 \sin^2 \left( \frac{n \pi S_\alpha}{S_\alpha + S_\beta} \right) \]

Much the same was done for rod-like growth with the exception that the cosine series is replaced with a Bessel function series.

Again,

\[ \nabla^2 C + \frac{v}{D} \frac{\partial C}{\partial Z} = 0 \]  \hspace{1cm} 18(a)

and

\[ C = C_E + C_\infty \text{ at } Z = \infty \]  \hspace{1cm} 18(b)

\[ \frac{\partial C}{\partial r} = 0 \text{ at } r = 0 \text{ and } r = r_\alpha + r_\beta \]  \hspace{1cm} 18(c)

\[ \left( \frac{\partial C}{\partial Z} \right)_Z = 0 = -\frac{v}{D} C_0^\alpha \quad 0 \leq r < r_\alpha \]  \hspace{1cm} 18(d)

\[ \left( \frac{\partial C}{\partial Z} \right)_Z = \frac{v C_0^\beta}{D} \quad r < r \leq r_\alpha + r_\beta \]  \hspace{1cm} 18(e)

where \( r \) is defined as the radius of a circle equivalent in area to a
polygonal boundary at \( r = r_\alpha + r_\beta \). Solving the equations (18) gives:

\[
C = C_E + C_\infty + A_o e^{-\frac{v_2}{D}} + \sum_{n=1}^{\infty} A_n J_0 (\frac{\gamma_n r}{r_\alpha + r_\beta}) e^{-\frac{(\lambda_n)^2}{r_\alpha + r_\beta}}
\]

(19)

in which:

\( \lambda_n \) = a root of \( J_1 (x) = 0 \), i.e. approximately \( n\pi \).

and,

\[
A_o = \frac{r_\alpha}{r_\alpha + r_\beta}^2 (C_o - C_\beta)
\]

\[
A_n = \frac{2vr_\alpha}{D} C_o J_1 \left( \frac{\lambda_n r_\alpha}{r_\alpha + r_\beta} \right) \frac{J_1 (\frac{\gamma_n r}{r_\alpha + r_\beta})}{\lambda_n J_0 (\lambda_n)^2}
\]

(20)

The average composition in front of the \( \alpha \) and \( \beta \) phases is given by:

\[
\overline{C_\alpha} = \frac{4v}{D} \frac{(r_\alpha + r_\beta)^2}{C_o} M + C_E + C_\infty + A_o
\]

(21a)

and,

\[
\overline{C_\beta} = -\frac{4r_\alpha^2 (r_\alpha + r_\beta)^2}{(r_\alpha + r_\beta)^2 - r_\alpha^2} \frac{v}{D} C_o M + C_E + C_\infty + A_o
\]

(21b)

in which

\[
M = \sum_{n=1}^{\infty} \frac{1}{\lambda_n^3} \frac{J_1^2 (\frac{\gamma_n}{r_\alpha + r_\beta})}{J_0 (\lambda_n)^2}
\]

Jackson and Hunt went into the derivation of an expression for average curvature of a lamellar or rod type interface which is dependent upon the angles at the phase boundaries and upon the lamellar or rod
type interface, which is dependent upon the angles at the phase boundaries and upon the lamellar or rod spacing. These equations can be combined with (17) or (21) to give total average interface undercooling.

By taking the origin at the center of a lamellae (see Figure 9), the slope will be zero at \( x = 0 \), and the average curvature can be given by:

\[
\left( \frac{1}{r(x)} \right) = \frac{1}{S} \sin \theta
\]  

(22)

in which

\[ S = \frac{1}{2} \text{ width of lamellae} \]

\[ \theta = \text{angle of interface at lamellae edge}. \]

For a rod-type surface the derivation becomes more complex, and two expressions are needed. One, \( \frac{1}{\rho_1} \), is the radius of curvature in the plane of the paper and equals

\[
\frac{1}{\rho_1} = - \frac{d^2 z}{d r^2} \left[ 1 + \left( \frac{dz}{dr} \right)^2 \right]^{-3/2}
\]

in which: \( z(r) = \) equation of the surface in the plane of the paper.

The other, \( \frac{1}{\rho_2} \), is in the plane normal to the paper and equals

\[
\frac{1}{\rho_2} = \frac{-\sin \theta}{r}
\]

in which

\[ \tan \theta = \frac{dz}{dr} \]
Figure 9. Schematic Drawing of Lamellar Interface Showing Definition of \( S \) and \( \theta \).
Now, \( \frac{1}{\rho} = \frac{1}{\rho_1} + \frac{1}{\rho_2} \), and the average curvature between \( r_1 \) and \( r_2 \) is, after simplification,

\[
\left\langle \frac{1}{\rho} \right\rangle = \frac{-2}{r_2^2 - r_1^2} \left( r_2 \sin \theta_2 - r_1 \sin \theta_1 \right)
\]  

(23)

For \( \alpha \) rods in a \( \beta \) matrix,

\[
r_2 = r_\alpha', \quad r_1 = 0, \quad \theta_2 = \tan^{-1} \left( \frac{dy}{dx} \right)_2 = -\theta_\alpha, \quad \theta_1 = 0
\]

and then,

\[
\left\langle \frac{1}{\rho_\alpha} \right\rangle = \frac{2}{r_\alpha} \sin \theta_\alpha
\]  

24(a)

And for the \( \beta \) phase,

\[
r_2 = r_\alpha + r_\beta', \quad r_1 = r_2, \quad \theta_1 = \theta_\beta, \quad \theta_2 = 0
\]

and

\[
\left\langle \frac{1}{\rho_\beta} \right\rangle = \frac{2 r_\alpha}{(r_\alpha + r_\beta)^2 - r_\alpha^2} \sin \theta_\beta
\]  

24(b)

In 1967 Mollard and Flemings expanded on the work of Jackson and Hunt to include the factors affecting solute redistribution along the growth direction.

Starting with equation (13)

\[
\nabla^2 C + \frac{R}{D} \frac{\partial C}{\partial x'} = 0
\]

and assuming that the interface is a flat plane (see Figure 10), the special case where
Figure 10. Interface Morphology for a Two-phase Alloy Growing Unidirectionally with Plane Fronts (a) Actual Interface; (b) Assumed Interface for Analysis.
\[ (S^*_\alpha + S^*_\beta) \ll 2 \pi \left( \frac{D}{R} \right) \]

and,

\[ C \approx C^*_E \text{ at } x' = 0, \]

the solution to (13) becomes

\[
\frac{C - C_o}{C^*_E - C_o} = e^{-\frac{R}{D} x'} + \frac{1}{C^*_E - C_o} \sum_{n=1}^{\infty} B_n \cos \left( \frac{n \pi x'}{S^*_\alpha + S^*_\beta} \right) e^{-\frac{R}{D} x'} \]

which is seen to be the same as Equation (15). Now, unless \( C^*_E \) is almost equal to \( C_o \), the second expression in this equation is small when compared with the first, so that the equation becomes

\[
\frac{C - C_o}{C^*_E - C_o} = e^{-\frac{R}{D} x'} \]

(25)

if the solid is assumed to be completely homogeneous. It must be remembered that Equation (25) can be used only to describe liquid composition ahead of a growing plane front, two phase interface, when the growth is at a steady state and no convection is present. The effects of changes in growth velocity on solute redistribution were studied, again assuming a two-phase system with plane front growth, and again using the assumptions \( C = C^*_E \) at \( x' = 0 \), etc., used above.

Under these assumptions, if an alloy of composition \( C_o \) is solidifying along a plane front, the solid forming \( \bar{C}_S \) must be average
composition of $C_0$, and the solute concentration along the $x'$ direction must be approximately given by equation (25). An increase in the growth rate must decrease the thickness of the boundary layer, and conservation of solute then requires that the solid forming $C_s$ must increase to a $\beta$ content greater than $C_0$. The reverse also holds true as a decrease in growth rate must result in $C_s$ below $C_0$. The diffusion equation for the non-steady state must then be

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x'^2} + R \frac{\partial C}{\partial x'}$$  

in which

- $t = \text{time}$
- $C = C_E$ at $x' = 0$  \hspace{1cm} 26(a)
- $C = C_0$ at $x' = \infty$  \hspace{1cm} 26(b)

Then, conservation of matter at the interface gives

$$\left(\frac{\partial C}{\partial x'}\right)_{x'} = 0 = -\frac{R}{D} (C_E - C_s)$$  \hspace{1cm} 26(c)

Now, considering $R = R_1$ at $t = 0$

$$\frac{C - C_0}{C_E - C_0} = e^{-\frac{R_1}{D} x}$$  \hspace{1cm} 26(d)

which gives the initial condition.

If, then, there is an infinitely fast acceleration from $R_1$ to $R_2$, conservation of matter before the velocity change requires that

$$(C_E - C_0) R_1 = -D \left(\frac{dc}{dx'}\right)$$  \hspace{1cm} (27)
and just after the velocity change,

\[(C_E - \overline{C_s}^*) R_2 = -D \left( \frac{dc}{dx'} \right) \tag{28} \]

in which \( \overline{C_s}^* \) = solid composition forming just after velocity change.

Dividing (27) and (28), and rearranging,

\[\frac{\overline{C_s}^* - C_o}{C_E - C_o} = 1 - \frac{R_1}{R_2} \tag{29} \]

It is simplest to assume that equation (25) holds up to the interface. The interface can then be expected to be stable when the gradient of constitutional supercooling at the interface in the \( x' \) direction is equal to or less than zero,

\[\frac{dS}{dx'} \leq 0 \tag{30} \]

in which \( S = \) constitutional undercooling (°C).

The liquidus temperature \( T_L \) can then be related to liquid composition at \( x' \) by the slope of the liquidus line, \( m \),

\[\frac{dT_L}{dx'} \bigg|_{x'=0} = m \left( \frac{dc}{dx'} \right) \bigg|_{x'=0} \tag{31} \]

in which \( m < 0 \) for simple eutectic systems.

Conservation of matter at the interface, assuming steady state conditions, can be re-written as

\[\left( \frac{dc}{dx'} \right)_{x'=0} = \frac{R}{D} (C_E - C_o) \tag{32} \]
and by combining (31) and (32)

\[
\frac{dT}{dx'} x'=0 = -\frac{m R (C_E - C_o)}{D}
\]

The gradient of constitutional undercooling is defined as

\[
\left( \frac{dS}{dx'} \right) x'=0 = \left( \frac{dT}{dx'} \right) x'=0 - G
\]

in which \( G \) = imposed temperature gradient in the liquid, \( \left( \frac{dT}{dx'} \right) x'=0 \) for

\[
\left( \frac{dS}{dx'} \right) x'=0 \leq 0,
\]

\[
\frac{G}{R} \geq -\frac{m (C_E - C_o)}{D}
\]

Mollard and Flemings proved their calculations experimentally in the lead-tin alloy system. They found that the conditions which could cause a breakdown of the interface to the cellular dendritic type structure were generally as predicted by their constitutional supercooling criterion. The structures of alloys of near eutectic composition that solidified with a plane front exhibited a lamellar structure and the interlamellar spacing decreased as predicted (see Figure 11), while the alloys furthest from the eutectic exhibited a rod-like structure. A binary lead-tin system of compositions ranging from 12 to 26 atomic % lead was unidirectionally solidified in a convection free system. They also showed that the assumptions used in previous calculations for solute redistribution along a two-phase system were reasonable for the lead-tin alloys.
Figure 11. Lamellar Spacing as a Function of Growth Rate for Pb-Sn Alloy Composites of Compositions from 12.6 Atomic Percent Pb to Eutectic Composition. Data of Chadwick and Davies are for Eutectic Composition.
Other investigators such as Hunt and Chilton have somewhat confirmed these results by indicating that the growth rate is not the determining factor in the break-up of a structure from the lamellae to the rod-like structure in metal-metal systems. Since they used the same composition in all their investigations, the work by Hunt and Chilton would tend to indicate that there has to be a change in the ratios of the two components used before the break-up to the rod-like structure will take place.

Eutectic Growth in Oxide-Metal Systems

All of the work surveyed above was for metal-metal systems. None of the investigators looked into the oxide-metal type system or gave it any consideration in their theoretical or mathematical analyses. Chapman et al.\(^7\) showed that in fact using a modified internal centrifugal zone growth technique, they could produce metal fibers in an oxide substrate. Powders in the required weight percentage ratios were pressed to form a cylinder and then sintered inside a molybdenum tube in an inert atmosphere to densify and preheat the material. Preheating is necessary with oxides because the oxide must be raised above a certain temperature to increase its electrical conductivity to a point at which it will couple to an rf induction heating field. After this preheating and sintering the molybdenum heater was lowered, and the sample was exposed to an rf field of 3 to 33 MHz depending on the material to be melted. The temperature was then raised until the surface temperature of the pellet was about 2000\(^\circ\)C, which gave an interior temperature in the neighborhood of 3000\(^\circ\)C. Considering the high rate
of heat loss and the inherent low thermal conductivity of the oxides, the skin temperature of the rod was maintained below the eutectic temperature, thereby allowing the rod to be its own crucible and avoiding the problem of contaminants. The fiber growth was then obtained by moving the solidification front up through the rod by lowering the rod down into the molybdenum preheater, which effectively controlled the amount of undercooling in the rod. A cavity was then formed in the rod just above the molten zone; and, as the rod was lowered further into the rf field, the material above the cavity would melt, maintaining the molten pool large enough to sustain growth. During growth of pure oxides it was advantageous to rotate the rod at speeds above 300 rpm. This rotation casts the molten material against the sides of the rod, thereby flattening out the liquid interface, allowing the crystallization to begin from the center of the rod and promoting more uniform growth of one crystallographic orientation across the entire solidified zone. Good oxide-metal structures were found in UO$_2$-W, stabilized ZrO$_2$-W, and a combination U-Th-O$_2$W. The unidirectional solidification technique gave fiber concentrations in the millions of less than 1 micron in diameter tungsten fibers per square centimeter. These were seen to be uniformly distributed in the refractory oxide matrix. Although the best results so far were obtained with the materials given above, several other oxides are being entered as candidates for use in this field. These oxide-metal type composites have some very interesting electrical as well as thermal and mechanical characteristics.
CHAPTER III

EXPERIMENTAL EQUIPMENT AND TECHNIQUES

A. Sample Preparation

Sample preparation started with 325 mesh UO₂ powder purchased from Nuclear Metals and Equipment Corporation, and 325 mesh tungsten powder from the Fairmount Chemical Company, Inc., by mixing the required weight percentage ratios in a mortar and pestle. A typical chemical and/or spectrographic analysis of the UO₂ and tungsten powders is presented in Appendix I. As later investigation was to show, the UO₂ powder was actually UO₂.14, and when a requirement existed for a lower O/U ratio, this powder was reduced by firing to 650°C and maintaining this temperature for 12 to 20 hours in a continuous flow of hydrogen, then slow cooling the powder to room temperature and allowing controlled oxidation to take place so that the resultant O/U ratio was 2.03. The powder was then stored at 0 to -10°F to maintain this O/U ratio.

If impurities were to be added to the sample, the mixing technique was essentially the same except that, due to the small amount of impurity present, the samples were tumbled for periods ranging from 15 to 30 minutes. The only impurities investigated were Al₂O₃ and Fe₂O₃, both being obtained from the Fisher Chemical Company.

The pellet was formed by pouring the powder mixture into a 1.9 cm x 10 cm die that had been lubricated with a saturated solution of stearic acid in acetone, and the die then tapped to settle the powder. Additional powder was then added to top off the die, and this was pressed
to 4000 psi. The pressure was released, raised to 4000 psi again, and finally released. The sample was removed from the die and was then ready for firing.

B. Growth Facility

The green sample was then placed in the apparatus shown in Figure 12, which was designed to permit the necessary freedom in vertical translation of the sample, variable positioning of the molybdenum preheaters, and control of the firing atmosphere.

The sample was placed on an $\text{Al}_2\text{O}_3$ spacer which was fitted over a steel rod that ran through the table to the hydraulic cylinder used to lower the sample. The use of a hydraulic cylinder rather than a mechanical system allowed smooth lowering, minimizing growth fluctuations caused by any jerking in the lowering rate by providing a more stable liquid-solid solidification front. A ceramic spacer was used to hold the lower molybdenum shield in position around the pellet. An upper molybdenum tube also was used in later experiments to control the shape of the rf field and thereby limit the size of the growth zone in the pellet, and prevent the top of the pellet from bulging during lowering. All of these components were enclosed inside a 25mm ID vycor tube which enables evacuation of the system and the use of controlled atmospheres, usually nitrogen or nitrogen-hydrogen mixtures.

Finally, a $6 \frac{1}{2}$ turn flat tube copper coil from a Lepel Model $\#T-10-3-DF1-E-HW$ rf generator, set up to run at 4 MHz, was placed outside the vycor tube at the level of the sample. Placement of the coil outside the vycor tube eliminated problems associated with obtaining a satisfactory high frequency rf lead into a closed system, and reduced
Figure 12. Schematic Diagram of the Facility for the Growth of Oxide-Metal Composites.
the tendency to arc from the coil to the sample at high power settings. One anticipated problem with placement of the work coil external to the system was the inability to obtain a close sample-coil spacing to improve coupling efficiency, but this was not found to be a hindrance with $\text{UO}_2\cdot\text{W}$. After sufficient preheating, the 4MHz rf field coupled easily to the sample, although the runs with an O/U ratio of 2.03 required a higher preheat temperature.

C. Composite Growth Procedure

Prior to heating, the system was evacuated to less than 200 $\mu\text{Hg}$ of mercury and nitrogen pumped in until the pressure stabilized at 1.5 psi above atmospheric. As soon as the flow of nitrogen into the system dropped to zero, indicating no leaks in the apparatus, the exhaust valve was opened and the nitrogen flow set at 500 cc/min. The flow was allowed to continue for approximately 10 minutes to purge the system of any remaining oxygen and the rf then turned on, with the nitrogen flow held constant at 500 cc/min.

The power was slowly raised by a temperature controlling device until it reached 1300-1400°C, which required about 2 hours. This gave a fairly steady temperature rise, and sample cracking was avoided. At about 1100°C, the sample would begin sintering, which was completed by about 1300°C. At this time the molybdenum preheaters were separated to expose 35 mm of the sample to the rf field, which allowed direct coupling to the field and melting of the interior of the pellet. The internal melting technique is more thoroughly described in the Survey of Literature starting on page 31. As soon as coupling was evident, hydrogen was turned on at 60 cc/min to react with any oxygen present and reduce the
oxide stoichiometry toward UO$_{2.00}$, and also to protect the tungsten from oxidation. Since the small volume of the apparatus enabled rapid changes in atmosphere for stoichiometry control, this procedure appears to have successfully attained both these objectives. These, then, are the standard growth conditions; and, unless stated otherwise, they are the conditions under which the samples in the Discussion of Results section were grown.

The temperature of the pellet was then raised to a skin temperature of about 2000°C and allowed to stabilize to assure a fairly homogeneous molten zone, whereupon the solidification front was moved by lowering the pellet into the Mo preheater at the rate desired. When the sample had been almost completely lowered into the molybdenum preheater, the preheater would be raised back up into the coil, the hydrogen flow stopped, and the sample cooled at about the same rate it was heated, or from approximately 1300°C to room temperature in about 2 hours. The cooling rate of the sample proved to be very critical to the success of the run in that, if cooled too fast, the sample would develop numerous cracks in the growth area which were avoided by careful control of the cooling rate.

**D. Analysis of the Sample**

The sample was sliced with a diamond wheel, mounted, polished using various grits of SiC from 180 to 320, final polishing was accomplished with 1 µ diamond paste on a nylon cloth covered wheel. Samples were viewed in a light microscope, and in a scanning electron microscope (SEM). Samples prepared for SEM viewing by etching in a solution of
20 ml saturated chromic acid  
10 ml glacial acetic acid  
7 ml concentrated nitric acid  
5 ml 48% hydrofluoric acid

by clipping the polished wafer to a shaft rotating at 20-30 rpm and immersing in the solution for 10 minutes. After etching, the samples were rotated in water for 10 minutes and then cleaned in a bath of acetone in an ultrasonic cleaner. The samples were mounted on an SEM pin using silver paste for attachment.

SEM examinations were made in the emissive mode, at magnifications between 25 and 10,000X. The pictures were used to determine fiber cross sections, fiber geometries in the oxide matrix, and fiber diameter and density. The determination of fiber diameter was made by simply measuring the diameter of fibers on an SEM photograph of known magnification, and then by dividing by the magnification to give actual fiber diameter. In order to determine fiber density, an SEM photo of known magnification was used. The number of fibers inside a 16 cm² area was counted and this number was multiplied by the reciprocal of the area and the square of the magnification, or

$$\text{fiber density} = \left( \frac{\text{fibers}}{16 \text{ cm}^2} \right) (\text{magnification})^2$$ (36)

The effect of growth rate and impurity content on grain size was investigated and a method was developed to determine a usable grain size value. One difficulty that immediately arose was the fact that all standard grain size determination procedures assume spherical geometry, or at best, irregular shapes with the x, y, and z dimensions being
approximately the same. Since the very nature of unidirectional solidification produces grains (cells) with highly preferred orientations, none of these methods was deemed appropriate for use, and another method was needed.

The simplest approach for finding a useful average grain size number was first to etch a transverse section of the sample to make the grains stand out, then to photomicrograph the etched surface at 50X. The grains were then counted along several parallel lines of known lengths, and these numbers averaged to give the average number of grains crossed per mm of length. This number was then squared to give the average number of grains per square millimeter, on the assumption that there was no preferred orientation in the plane of the cross section analyzed. The reciprocal of this number then gives the average area of each grain in millimeters squared.
CHAPTER IV

RESULTS AND DISCUSSION

The results of this work fall broadly into five areas, each of which is dependent on the others yet distinct enough to be discussed separately. First, the effect of varying the tungsten concentration and UO$_2$/W ratio was determined. Secondly, the optimum UO$_2$/W ratio found was used in studies to determine the effect of various growth rates on fiber size and density. Thirdly, some preliminary work showed the effect of certain impurity additions on the system and how these effect growth in the optimum system. Fourthly, the upper limit of growth rate was investigated, and some problems associated with this are discussed. And lastly, as a consequence of the fast growth rate studies, the problems of tungsten solubility in UO$_{2+x}$ were looked into more thoroughly.

A. Determination of the Optimum Oxide/Metal Ratio and the Effects of Varying the Oxide/Metal

The first area of investigation concentrated on determination of the effects of varying tungsten concentrations on the type of eutectic structure that resulted. Tungsten concentration was varied from 2 to 20 weight %, and the result of each experiment analyzed for the presence of fibers and continuity of any fibers present. All the experiments in this phase were made with UO$_{2,14}$ powder, and Table 1 shows the raw data from these runs. Figure 13 is a photomicrograph of a typical UO$_2$-10% tungsten longitudinal section showing good continuous fiber growth,
Table 1. Effects of Varying Oxide-Metal Ratio On Unidirectionally Solidified UO$_2$-W Composites

<table>
<thead>
<tr>
<th>Starting Composition</th>
<th>Type Growth</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_{2.14}$ • 2% tungsten</td>
<td>Pothole</td>
<td>Large Areas of Excess Primary Phase</td>
</tr>
<tr>
<td>UO$_{2.14}$ • 5% tungsten</td>
<td>Banded</td>
<td>See Discussion</td>
</tr>
<tr>
<td>UO$_{2.14}$ • 7% tungsten</td>
<td>Pothole</td>
<td></td>
</tr>
<tr>
<td>UO$_{2.14}$ • 8% tungsten</td>
<td>Good in Lower Half, Pothole in Upper Half</td>
<td></td>
</tr>
<tr>
<td>UO$_{2.14}$ • 10% tungsten</td>
<td>Good</td>
<td>Very Good Fibers</td>
</tr>
<tr>
<td>UO$_{2.14}$ • 11% tungsten</td>
<td>Pothole at Bottom, Good at Top</td>
<td></td>
</tr>
<tr>
<td>UO$_{2.14}$ • 12.5% tungsten</td>
<td>Fair</td>
<td>Some Good Growth But Large Areas of Excess Tungsten</td>
</tr>
<tr>
<td>UO$_{2.14}$ • 20% tungsten</td>
<td>None</td>
<td>Large Areas of Excess Tungsten</td>
</tr>
</tbody>
</table>

A Growth Atmosphere of 500 cc/min nitrogen flow and 60 cc/min hydrogen flow was used for these and all subsequent runs unless otherwise noted.
Figure 13. Longitudinal Section of a Typical UO$_2$ - 10\%W Sample Displaying "Good" Fiber Growth. 600X
while Figure 14 is an SEM photograph of the same sample showing a transverse section of the fibers after chemical etching was employed to expose the fibers. These photos show the uniformity of the microstructure that is called "good fiber growth" in Table 1 and in subsequent descriptions of composite growth. Figures 15 and 16 show a transverse and longitudinal section, respectively, under dark field at approximately 600X, of compositions with less than 8% tungsten concentration. It will be noted in the side view that there are fibers that have grown in some areas while in between these there are areas of pure primary phase oxide. The top view shows the primary phase areas to be somewhat circular, with areas of typical eutectic growth surrounding each. Due to the appearance of the samples, this type structure came to be called "pothole" growth. Samples below 8% tungsten generally showed either this or a horizontal banded type structure shown in Figure 17. The growth direction was from the bottom to the top, and the fibers can be seen nucleating from a few points and fanning out. Once the fibers stop, the area between them is again primary phase UO$_2$.

The best explanation for the formation of pothole type structure is one given by Chapman, et al.,$^{18}$ in which they state that as cooling of the oxide-rich melt proceeds, the primary phase oxide will solidify at a higher temperature than the eutectic temperature; therefore, the composition of remaining liquid will move down the liquidus line toward the eutectic composition. Since there will be, at some later time, sufficient undercooling to initiate nucleation of the remaining melt, the result will be areas of primary phase UO$_2$ surrounded by areas of typical tungsten fiber growth, as in Figures 15 and 16. A more thorough
Figure 14. Scanning Electron Micrograph of a Typical UO₂-10%W Sample Showing "Good" Fiber Growth. (Transverse Section) 630X

Figure 15. Scanning Electron Micrograph of a Typical UO₂ 5%W Sample Showing "Pothole" Growth (Transverse Section) 1280X
Figure 16. Scanning Electron Micrograph of a Typical UO₂ - 5% Tungsten Sample Showing "Pothole" Growth (Longitudinal Section) 600X

Figure 17. Photomicrograph of a Typical UO₂-5%W Sample Showing Horizontal Banding (Transverse Section) 600X
discussion as well as a phase diagram of the UO$_2$-W system is presented by Chapman.

The type banding shown in Figure 17 is apparently an expression of the same problem, namely an oxide-rich system. The explanation of this phenomena is that as the zone is moved through the molten zone, the area just in front of the zone is critical to the type structure obtained. If, for example, initially there is enough tungsten in solution just ahead of the solidification front, normal growth of fibers will take place. Then, since this area naturally becomes depleted of tungsten, growth suddenly will stop, an area or band of pure UO$_2$ will precipitate until, as the front moves along, the tungsten concentration ahead of it builds up high enough to again, nucleate fibers. The process then repeats itself as shown in Figure 17. As stated earlier, this is a typical growth pattern of samples containing less than 8% tungsten.

In samples with 11% tungsten or greater, the melt was apparently too far on the tungsten-rich side of the eutectic to allow good fiber growth, and the result is shown in Figure 18. This is a picture of a UO$_2$ - 20% tungsten sample, and results remained much the same until the tungsten concentration was reduced below 11%, as the melt is still metal-rich until under that composition. At 11% tungsten it will be noted that the growth became good in the upper half of the solidified zone but was still poor in the lower half. The reason it was potholed in the lower half is possibly due to the fact that there were large areas of tungsten in "globs" around this part of the zone, which produced a tungsten poor melt in this area.

Compositions around 90 wt% UO$_2$ plus 10 wt% tungsten was found
Figure 18. Photomicrograph of a Typical UO$_2$-20%W Sample Showing Large "Globs" of Excess W. 600X
to give consistently good growth over a wide range of conditions. At 10% tungsten there was enough metal in the melt to maintain a eutectic tungsten concentration of about 4% W as found by Chapman. This did not allow the area ahead of the solidification front to become depleted of tungsten and yet did not contain so much tungsten that it would begin to precipitate out in globs. This ratio was used to explore the effect of growth velocity on the composite structure.

B. The Effect of Growth Rate on the System UO$_2$ - 10% W

Once an oxide-metal ratio of 90% UO$_2$ + 10% W was decided upon, the effect of growth rate on fiber size, fiber density and cell size was investigated. Initially growth rates between 1.5 and 9.0 cm/hr were studied. The results for the fiber size and density are listed in Table 2 and Figure 19 shows the results of the cell size determinations. Much higher growth rates were also explored, but the discussion of these will be in a later sub-section. The relationship between growth rate and fiber density is graphically displayed in Figures 20 and 21. As expected, an increase in the growth rate increased the fiber density and decreased the fiber diameter. Figures 22 and 23 show two SEM photos under similar magnifications to indicate the relative difference in fiber density caused by an increase in the growth rate from 1.6 cm/hr to 9.0 cm/hr.

The growth rate versus interfiber spacing data obtained from the UO$_2$ + 10% W system does not appear to follow the relationship developed in the Survey of Literature of $\lambda R = \text{constant}$. Interfiber spacing data is presented in Table 2, and plotted versus growth rate in Figure 24. By using a least squares to fit to the logarithms of the growth rate
Table 2. Influence of Growth Rate on Tungsten Fiber Density and Diameter During the Unidirectional Solidification (Without Rotation) of UO$_{2.14}$ Plus 10 Weight Percent Tungsten Mixtures

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Growth Rate cm/hr</th>
<th>Fiber Density Per cm$^2 \times 10^{-6}$</th>
<th>Fiber Diameter Microns</th>
<th>Interfiber Spacing, $\lambda$ (microns)</th>
<th>Cell Size mm$^2 \times 10^2$</th>
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<tr>
<td>3-14</td>
<td>1.6</td>
<td>14.8</td>
<td>0.49</td>
<td>2.80</td>
<td>2.6</td>
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<tr>
<td>3-11a</td>
<td>1.9</td>
<td>19.5</td>
<td>0.45</td>
<td>2.44</td>
<td>2.4</td>
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<tr>
<td>3-11</td>
<td>3.0</td>
<td>17.3</td>
<td>0.45</td>
<td>2.59</td>
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<tr>
<td>3-13a</td>
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<td>-</td>
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<tr>
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<td>5.0</td>
<td>25.0</td>
<td>0.33</td>
<td>2.15</td>
<td>-</td>
</tr>
<tr>
<td>3-9a</td>
<td>9.0</td>
<td>42.0</td>
<td>0.28</td>
<td>1.66</td>
<td>1.45</td>
</tr>
<tr>
<td>3-10a</td>
<td>0.0</td>
<td>No Fibers</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.80</td>
</tr>
<tr>
<td>3-18a</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.50</td>
</tr>
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</table>
Figure 19. Effect of Growth Rate and Doping on Grain (Cell) Size of UO₂ Composites.
Figure 20. Effect of Growth Rate on Tungsten Fiber Density for UO$_2$-W Composites.

Figure 21. Effect of Growth Rate on Tungsten Fiber Diameter for UO$_2$-W Composites.
Figure 22. Scanning Electron Micrograph of UO$_2$ - Tungsten Composite Containing Approximately 14.8 Million 0.49 Micron Diameter Tungsten Fibers per cm$^2$/570X.

Figure 23. Scanning Electron Micrograph of UO$_2$ - Tungsten Composite Containing Approximately 42 Million 0.28 Micron Diameter Tungsten Fibers per cm$^2$/540X.
Figure 24. Graph Showing the Effect of Growth Rate on Interfiber Spacing for UO$_{2.14}$ + 10% Tungsten Samples.
versus interfiber spacing as plotted in Figure 24, it appears that a relationship of
\[ 4X K = \text{constant} \] (37)
may hold true for the UO₂ + 10% tungsten composite. The values for interfiber spacing were obtained from the fiber density values, assuming a hexagonal array of fibers.

Figure 19 is a graphical display of the effect that growth rate has on cell size. It can be noted from the curve on the right that as growth rate increase, cell size decreased. Since grain size, theoretically, should approach infinity at some infinitely slow growth rate, the curve probably tails off as indicated.

C. The Effect of Fe₂O₃ and Al₂O₃ Additions

Some preliminary work was next done in the area of doping samples with 1% additions of Fe₂O₃ and Al₂O₃ to determine the effects of these additions on composite structure and grain size. In the case investigated, 1% Fe₂O₃, the grain size was reduced when compared to an undoped sample grown under the same conditions. Micrographs of samples lightly etched in a solution of

\[ 70 \text{ ml } H_2O \]
\[ 10 \text{ ml } H_2SO_4 \text{ (concentrated)} \]
\[ 30 \text{ ml } 30\% H_2O_2 \]

to expose the grain boundaries are seen in Figures 25 and 26, which are two samples of the same growth rate, one doped and one undoped. The effect of Al₂O₃ additions on cell size was unclear due to reasons that will be explained below.
Figure 25. Photomicrograph of a Typical UO$_2$-10\%W Sample Lightly Etched to Expose the Grain Boundaries. (Transverse Section) 50X

Figure 26. Photomicrograph of a UO$_2$+10\%W+1\%Fe$_2$O$_3$ Sample Lightly Etched to Expose the Grain Boundaries (Transverse Section) 50X
A decrease in cell size was not the only effect of impurity additions, as Figures 27 through 31 illustrate. The Fe$_2$O$_3$ doped samples, Figures 27 and 28, etched to a much rougher surface than undoped UO$_2$-W samples. The reason for this is unknown.

The Al$_2$O$_3$ doped sample, on the other hand, was changed drastically. Figures 29 through 31 show that the Al$_2$O$_3$ doped sample had a ring of very dense fiber growth around the outside of the solidified zone (Figure 29), then suddenly changed to an area in the center of pothole type growth. The SEM photograph in Figure 31 shows a view of the overall melt zone, which shows clearly the demarcation between these two growth areas. It should also be noted that the sample is cracked very badly, which is typical of Al$_2$O$_3$ doped samples and effectively precluded drawing any conclusions about the cell size.

Occasionally a plate of tungsten was noted in a grain boundary as seen in Figure 30. This type growth is not necessarily caused by Al$_2$O$_3$ additions, and the best explanation is that as the solidification front passes through the sample, a certain amount of undercooling occurs which normally produces fiber growth. When this undercooling becomes so great that the composition becomes effectively tungsten rich, the tungsten nucleates and begins to come out of solution as shown in Figure 30.

D. Solidification Behavior of UO$_2$-W Samples at Growth Rates Above 10 cm/hr

Since the curve shown in Figure 22 indicated that the higher the lowering rate used the finer the fibers would be, attempts were made
Figure 27. Scanning Electron Micrograph of a UO$_2$+10\%W+1\%Fe$_2$O$_3$ Sample Showing the Rough Oxide Matrix After Etching (Transverse Section) -6100X

Figure 28. Scanning Electron Micrograph of a UO$_2$+10\%W+1\%Fe$_2$O$_3$ Sample Showing the Rough Oxide Matrix After Etching (Transverse Section) -1225X
Figure 29. Scanning Electron Micrograph of a UO$_2$+10\%$W+1\%$Al$_2$O$_3$ Sample Showing Dense Fiber Growth in Outer Ring (Transverse Section) 220X

Figure 30. Scanning Electron Micrograph of a UO$_2$+10\%$W+1\%$Al$_2$O$_3$ Sample Showing "Pothole" Fiber Growth in Central Area (Transverse Section) 650X
Figure 31. Scanning Electron Micrograph of a UO$_2$ + 10% W + 1% Al$_2$O$_3$ Sample Showing the Demarcation Between the Good Growth Area Around the Outside and the "Pothole" Growth Area in the Center (Transverse Section) 26X.
to find the maximum growth rate conducive to good fiber growth, and therefore the finest fibers and the greatest fiber density. These results are shown in Table 3.

When fast growth rates were investigated, a problem immediately arose of large voids forming in the molten zone, interrupting growth and now allowing continuous fibers to be formed, as is shown in Figure 32. At first this was thought to be caused by oxygen being released by the UO₂ during melting, as a determination of the oxygen to uranium ratio in the UO₂ powder showed it to be UO₂.14 before firing. After the melting and growth process, the O/U ratio was reduced to UO₂.00. To alleviate this problem, the O/U ratio of a batch of UO₂.14 powder was reduced as described in the Experimental Equipment and Techniques Section. This powder was then used to rerun some of the fast growth rate tests. The results in Table 3 show, however, that this met with little success; most of the problems still existed, with the additional observation that large areas of undissolved tungsten existed in the melt. This led to the solubility studies described in the next sub-section.

E. Tungsten Solubility in Molten UO₂²⁺ₓ

Since no growth was evident in samples run at high growth rates with low O/U ratio powder, attempts were made to return to normal growth rates with low O/U powder to try to pin down the cause of the failures. Table 4 shows that no growth was obtained from these samples, even though tungsten concentration was varied somewhat to alleviate the excess tungsten problem. Although there was ample tungsten present in the system, the resulting growth was typical of tungsten poor samples such as the
Table 3. Effect of Very Fast Growth Rate Studies
On Unidirectionally Solidified $\text{UO}_2\cdot\text{10\% tungsten}$ Composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth Rate</th>
<th>Composition</th>
<th>Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-19a</td>
<td>255 cm/hr</td>
<td>$\text{UO}_2\cdot\text{10% tungsten}$</td>
<td>None</td>
</tr>
<tr>
<td>3-20a</td>
<td>77 cm/hr</td>
<td>$\text{UO}_2\cdot\text{10% tungsten}$</td>
<td>Poor</td>
</tr>
<tr>
<td>3-21a</td>
<td>40 cm/hr</td>
<td>$\text{UO}_2\cdot\text{10% tungsten}$</td>
<td>Poor</td>
</tr>
<tr>
<td>3-24</td>
<td>38 cm/hr</td>
<td>$\text{UO}_2\cdot\text{10% tungsten}$</td>
<td>Very Poor</td>
</tr>
<tr>
<td>3-25a</td>
<td>35 cm/hr</td>
<td>$\text{UO}_2\cdot\text{10% tungsten}$</td>
<td>Fair</td>
</tr>
<tr>
<td>3-26</td>
<td>16 cm/hr</td>
<td>$\text{UO}_2\cdot\text{10% tungsten}$</td>
<td>Very Poor</td>
</tr>
<tr>
<td>3-26a</td>
<td>6,5 cm/hr</td>
<td>$\text{UO}_2\cdot\text{10% tungsten}$</td>
<td>Banded</td>
</tr>
<tr>
<td>3-27a</td>
<td>39 cm/hr</td>
<td>$\text{UO}_2\cdot\text{10% tungsten}$</td>
<td>None</td>
</tr>
<tr>
<td>3-28</td>
<td>29 cm/hr</td>
<td>$\text{UO}_2\cdot\text{10% tungsten}$</td>
<td>None</td>
</tr>
</tbody>
</table>
Figure 32. Photograph of a Typical $\text{UO}_{2.14} + 10\% \text{ W}$ Sample Showing the Large Voids Forming in the Molten Zone at Fast Growth Rates (Longitudinal Section) 3X.
Table 4. Effects of Stoichiometry Changes on Fiber Growth in Unidirectionally Solidified UO$_2$-Tungsten Composites

<table>
<thead>
<tr>
<th>Composition</th>
<th>Type Growth</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_{2.03}$+10% W</td>
<td>Banded</td>
<td>Large Amounts of Excess W</td>
</tr>
<tr>
<td>UO$_{2.03}$+7.7% W</td>
<td>Banded</td>
<td>Large Amounts of Excess W</td>
</tr>
<tr>
<td>45% UO$<em>{2.14}$+45% UO$</em>{2.04}$+10% W</td>
<td>Very Good</td>
<td></td>
</tr>
<tr>
<td>20% UO$<em>{2.14}$+70% UO$</em>{2.04}$+10% W</td>
<td>Fair</td>
<td>Large Area of Excess W in Center of Growth Area</td>
</tr>
<tr>
<td>UO$_{2.03}$+10% W+0.3% WO$_3$</td>
<td>Fair</td>
<td>Same</td>
</tr>
<tr>
<td>UO$_{2.03}$+8.8% W+1.2% WO$_3$</td>
<td>Good</td>
<td></td>
</tr>
<tr>
<td>UO$_{2.03}$+7.2% W+2.7% WO$_3$</td>
<td>Very Good</td>
<td>Some Areas of U WO$_3$ at Top of Melt Zone</td>
</tr>
<tr>
<td>UO$_{2.03}$+8.23% W+1.77% WO$_3$</td>
<td>Very Good</td>
<td>Gives Final O/U Ratio of 2.10</td>
</tr>
<tr>
<td>UO$_{2.03}$+7.35% W+2.65% WO$_3$</td>
<td>Very Good</td>
<td>Excess W Evident at Bottom and Sides of Melt Zone</td>
</tr>
<tr>
<td>UO$_{2.03}$+5% W+5% WO$_2$</td>
<td>Good in Upper Half</td>
<td>Pothole in Bottom Half</td>
</tr>
</tbody>
</table>
5% tungsten samples discussed earlier. This could only mean that the tungsten was not going into solution in the melt when low O/U ratio powder was used.

Once it was realized that a solubility problem existed in the low O/U ratio powder, work was directed toward finding the proper O/U ratio powder that would allow enough tungsten solubility so that fiber growth was possible. Table 4 shows the data obtained from some of these runs, and Figure 33 shows the large amount of excess tungsten left in the solidified zone after cooling. Urania powders with an O/U ratio of 2.14 and 2.03 were mixed to give a final ratio of approximately 2.09, which produced growth that was as good as any previously seen. The Table also shows that attempts to use a lower proportion of UO$_2$ did not give good results. Attention was directed toward the addition of various amounts of WO$_3$ and WO$_2$, hoping that these compounds would break down at temperature, giving tungsten and releasing the oxygen to raise the O/U ratio. Figures 34 and 35 show some of the more successful attempts at melting UO$_2$ + tungsten with WO$_2$ and WO$_3$ additives.

An article by Latta and Fryxell showed that the solubility of tungsten in molten UO$_2$ was related to the stoichiometry of the UO$_2$, and that the solubility increased by a factor of 10 as the O/U ratio increased from 2.03 to 2.10, Figure 36. From this graph and the optimum O/U ratio determined above, it can be seen that the solubility of the tungsten must be high enough to allow on the order of 4 weight % tungsten to go into solution before well ordered eutectic growth may be expected. To obtain this range of solubility, the O/U ratio must be on the
Figure 33. Photomicrograph of UO$_2$, $0_3 + 10\%$ W Sample Showing Large Globs of Excess W Remaining in the Molten Zone (Transverse Section) 200X.
Figure 34. Photomicrograph of a Typical UO$_2$ + 5\% W + 5\% WO$_2$ Sample Showing "Good" Fiber Growth (Transverse Section) 600X.

Figure 35. Photomicrograph of a Typical UO$_2$ + 5\% W + 5\% WO$_2$ Sample Showing "Good" Fiber Growth (Longitudinal Section) 600X.
Figure 36. Graph of Tungsten Solubility in Molten UO₂\(^{2+}\) (after Latta and Fryxell).
order of 2.10, but a number of methods may be used to introduce the necessary oxygen to raise the O/U ratio of the starting powder as described.

It should be noted that the formation of $U_xWO_3$ as described in Latta and Fryxell's article was seen in some of the samples. This was a fairly common occurrence, particularly in samples displaying less than ideal growth. Figures 37 and 38 show typical examples of this compound. Within the $U_xWO_3$ grains there appears to be platelets of tungsten. This phenomena is unexplained.
Figure 37. Photomicrograph of a UO$_2$ + 8.8% W Sample Showing an Area of U$_x$WO$_3$, 1000X.

Figure 38. Photomicrograph of a UO$_2$ + 10% W Sample Showing the Formation of U$_x$WO$_3$ in the Grain Boundaries, 1000X.
CHAPTER V

CONCLUSIONS

1. A composition of $^{\text{UO}_2}_{1.14} + 10\%$ tungsten melted in an atmosphere of 7 parts nitrogen to 1 part hydrogen gives the most consistent oxide-metal microstructures using the unidirectional solidification technique insofar as fiber geometry and continuity of fibers is concerned, although tungsten concentration may be as much as 11\% or as low as 8\%.

2. $^{\text{UO}_2}_{1.14} +$ tungsten mixtures containing less than 8\% tungsten resulted in "pothole" or banded type growth with large areas of primary $\text{UO}_2$ and discontinuous fibers, probably because the solidification took place on the tungsten poor side of the eutectic.

3. $^{\text{UO}_2}_{1.14} +$ tungsten samples with over 11\% tungsten were tungsten rich, and the excess metal precipitated out in globs throughout the solidified zone, precluding good growth and leaving large areas of primary phase $\text{UO}_2$.

4. The growth rate and the fiber density are directly related in that the faster the growth rate used, the higher the fiber density, and therefore the lower the interfiber spacing; i.e. a growth rate of 1.9 cm/hr gives fiber densities of $15 \times 10^6$ fibers/cm$^2$ while a growth rate of 9.0 cm/hr gives a fiber density of $42 \times 10^6$ fibers/cm$^2$.

5. The growth rate is inversely proportional to the fiber diameter.
6. Growth rate and cell size are related inversely.

7. Tungsten solubility is an extremely important variable that must be controlled in the UO$_2$-W system if fiber growth is to be accomplished.

8. An O/U ratio of 2.10 in the molten uranium dioxide is optimum for good fiber growth, and gives a tungsten solubility on the order of 4 weight % tungsten, which is close to the eutectic composition.

9. The oxygen needed to raise the O/U ratio to 2.10 may be included by a variety of methods such as replacement of a portion of the tungsten with WO$_2$ or WO$_3$, while maintaining the total tungsten content at 10 weight percent.

10. The upper limit of growth rate is somewhere in the area of 35 cm/hr due to problems with bubbles of gas forming in the melt.

11. An addition of 1% Fe$_2$O$_3$ to UO$_2$-W mixtures reduces the grain size of a sample, if all other variables are held constant.

12. The addition of 1% Al$_2$O$_3$ causes considerable cracking in the solidified zone.

13. An addition of 1% Al$_2$O$_3$ also causes unusual growth geometries, such as a band of good growth around the outer ring of the melt zone, and pothole growth in the center.
APPENDIX I

MANUFACTURER'S ANALYSIS OF AS RECEIVED
TUNGSTEN METAL POWDER, 99.95%

SPECTROGRAPHIC ANALYSIS

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<thead>
<tr>
<th>Element</th>
<th>PPM</th>
<th>Element</th>
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<td>Mn</td>
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<td>Mg</td>
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PARTICLE SIZE DISTRIBUTION
BY PHOTOMETER
(ASTM B430 - 65 T)

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APPENDIX I (cont'd.)

MANUFACTURER'S ANALYSIS OF AS RECEIVED UO$_2$ POWDER

CHEMICAL ANALYSIS

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</tr>
<tr>
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<tr>
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<tr>
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<tr>
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<tr>
<td>Pb</td>
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<tr>
<td>Si</td>
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<td>Ti</td>
<td>10</td>
</tr>
<tr>
<td>V</td>
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W   50

Dy  .02
Eu  .01
Gd  .02
Sm  .02

O/U (dry)  2.055

(Results in Parts Per Million)

SIEVE ANALYSIS

<table>
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<tr>
<th>Result</th>
<th>Test</th>
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<tr>
<td>+ 100</td>
<td>28.12%</td>
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<tr>
<td>- 100 + 170</td>
<td>29.14</td>
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<tr>
<td>- 170 + 200</td>
<td>18.08</td>
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<tr>
<td>- 200 + 230</td>
<td>8.36</td>
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<tr>
<td>- 230 + 270</td>
<td>6.62</td>
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<td>- 270 + 325</td>
<td>3.90</td>
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BIBLIOGRAPHY


