# UNIDIRECTIONAL SOLIDIFICATION OF $Y_2O_3(CeO_2)$ -Mo AND $Y_2O_3(CeO_2)$ -W COMPOSITES

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UNIDIRECTIONAL SOLIDIFICATION OF Y<sub>2</sub>O<sub>3</sub>(CeO<sub>2</sub>)-Mo AND Y<sub>2</sub>O<sub>3</sub>(CeO<sub>2</sub>)-W COMPOSITES

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#### CHAPTER I

#### INTRODUCTION

The floating zone method of growing oriented fibers of a conducting metal in a semiconducting or insulating matrix has been utilized to produce UO<sub>2</sub>-W composites suitable for high field electron emission devices. Due to the anisotropic shapes and properties of melt-grown oxide-metal composites, other composite systems under investigation are attributed potential as high strength, high temperature components in mechanical and structural systems. Further magnetic and electronic applications of oxide-metal components are envisioned.

The  $Y_2O_3$  -  $CeO_2$  - Mo system was thought to be a prospective composite growth system for several reasons:

1. These refractory materials possess the necessary stability at high temperatures.

2. The results of previous oxide-metal composite growth investigations indicated that mixtures of  $Y_2O_3$  - CeO<sub>2</sub> - Mo might be susceptible to direct rf eddy current heating.

3. A  $Y_2^0_3$  - CeO<sub>2</sub> solid solution range was known to exist.

In the present unidirectional solidification

investigation, the objective was to produce uniformly ordered oxide-metal composites after characterizing any existing  $Y_2O_3(CeO_2)$  - Mo eutectic. It was also necessary to determine the effects of compositional variables as several composite growth morphologies were observed. Other parameters of importance were growth atmospheres and growth rates.

Several conditions controlling successful composite growth were examined:

 The formation of a dynamic liquid structure necessary for compatibility of the oxide and metal in the liquid state.

2. The relationship between entropy of fusion of the components and composite growth.

3. The importance of the presence of "excess" oxygen in the melt on metal solubility.

 Origins of composite cracking and metal fiber discontinuities.

#### CHAPTER II

#### SURVEY OF LITERATURE

During the last decade, increased interest has been shown in the growth of oriented composite materials. The field has become extensive and a number of review papers have appeared: Tiller, 1958<sup>1</sup>; Winegard, 1961<sup>2</sup>; Chadwick, 1973<sup>3</sup> and 1963<sup>4</sup>; Kerr and Winegard, 1966<sup>5</sup>; Kraft, 1966<sup>6</sup>; Hunt, 1968<sup>7</sup>; Durand, 1968<sup>8</sup>; and Hogan et al., 1970<sup>9</sup>.

### Classification of Binary Eutectics

Scheil<sup>10</sup> classified eutectics based on their mode of solidification rather than on their morphology. Division is made into three classes:

- (a) normal
- (b) anomalous
- (c) degenerate

These classes are illustrated in Figures 1, 2 and 3, respectively. Figure 1 illustrates the highly organized nature of the normal eutectic structure. Lamellar and rodlike structures are typical.

Figure 2 shows an anomalous eutectic in which the two phases are still closely intermingled, but there is much less regularity. The white-etching antimony occurred



Figure 1. Normal Eutectic Structure in Cadmium-Zinc Alloy. (a) Lamellar (X250), (b) Rod-like (X150) - after Scheil



Figure 2. Anomalous Eutectic Structure in a Lead-Antimony Alloy. (X150) - after Scheil<sup>10</sup>

in a semi-dendritic form which suggests it may have grown first from the melt, the lead following behind and filling in the spaces. The growth of the two phases is clearly much less closely coupled than in the normal eutectic structures.

Figure 3 shows a degenerate eutectic in which the association of the two phases has been reduced to a minimum.

#### Solidification of Binary Eutectics

Numerous attempts have been made to speculate on the mechanism of the formation of eutectics. The views of Hogan<sup>11</sup> and Tiller<sup>1</sup> are discussed below.

#### (a) Normal Eutectic Structures

(1) The "pure" eutectic structure, containing no primary crystals, does not necessarily occur at the eutectic point as given by the phase diagram. Under suitable conditions of freezing it may be found at compositions deviating substantailly from the equilibrium eutectic composition.

(2) The two phases of a normal eutectic grow simultaneously in a close physical association, so that their growth can be said to be closely "coupled." The two solid phases grow into the liquid by movement of a uniform front which may be almost planar. The lamellae or rods lie parallel to the growth direction and normal to the crystallization front. This uniform crystallization front is one of the major characteristics of a normal eutectic.

(3) These crystallization fronts, growing from



Figure 3. Degenerate Eutectic Structure in Aluminum-Tin Alloy. (X200) - after Scheil<sup>10</sup>

different centers, meet to form "grains," analogous to the grains of a single-phase alloy, in which each phase has a uniform orientation, so that a eutectic grain consists effectively of two inter-penetrating single crystals.

(4) Normal eutectics tend to occur when the liquiduslines are roughly symmetrical about the eutectic point.(b) Characteristics of Anomalous Eutectic Structures

(1) The composition of the "pure" eutectic structure is inclined to vary even more strongly from the equilibrium eutectic point than in the case of normal eutectics, or it may be difficult to obtain a pure eutectic structure at all.

(2) Coupled growth is present but with much less regularity in the mutual arrangement of the two phases. It is difficult or impossible to observe a uniform crystallization front normal to the growth direction.

(3) Boundaries between eutectic grains are very seldom present and the absence of grain boundaries may be regarded as positive evidence of anomalous crystallization.

The Coupled Zone Concept of Eutectic Solidification

The theory<sup>1,10,11</sup> of eutectic solidification is based on the assumption that the rate of growth of a given solid phase from the melt is proportional to the degree of supersaturation of the melt with respect to that phase. Some

slight degree of supersaturation, produced by supercooling, is necessary for growth to occur, and the rate of growth will increase with increasing supersaturation.

Slightly below the eutectic temperature the growth rate of the two phases will be equal, and they can grow with a common crystallization front to form a "pure" eutectic microstructure. With increasing supercooling the growth rates should increase, but processes occur which produce a difference in the rate for both phases.

Figure 4a represents a binary phase diagram for mutually insoluble metals A and B. The liquidus lines have been extended below the eutectic point. These are saturation curves passing through  $C_{ma}$  and  $C_{mb}$  representing the compositions and temperatures at which the liquid is just saturated with respect to metals A and B, respectively.

The degree of supersaturation of the melt will increase at different rates for a given melt composition unless the saturation curves are symmetrical. For example, if a melt of composition  $C_e$  is supercooled to  $T_o$ , it will be supersaturated with respect to A in proportion to the distance  $C_{ma}-C_e$ , and with respect to B in proportion to the smaller distance  $C_e-C_{mb}$ .

Hence the solid phase A should grow much more rapidly than B at  $T_0$ . The melt composition would have to shift to the intermediate value  $C_0$  to produce equal supersaturation and therefore equal growth rates.



Figure 4. Concentration Distribution at the Crystallization Front in Ideal Eutectic Crystallization - after Hogan<sup>11</sup>

However, there are many systems in which a eutectic alloy, of composition  $C_e$ , does give a normal eutectic at rapid rates of cooling, with no primary crystals present. Further analysis is necessary.

As crystals of A grow, atoms B are rejected into the melt, so that ahead of the lamellae of A the melt composition moves along the  $T_o$  isotherm towards  $C_{ma}$ , similarly, atoms of A are rejected from the lamellae of B and the melt composition here moves toward  $C_{mb}$ .

Let the growth velocity of A equal  $V_a$  and of B equal  $V_b$ . These velocities will depend on the degree of supersaturation of the melt in contact with each phase. If the melt ahead of A actually reaches  $C_{ma}$  then it will be exactly saturated with respect of A, so that the growth of this phase will stop, i.e.  $V_a = 0$ . Hence the melt enrichment at this point is shown as  $C_a$  (Figure 4b), slightly less than  $C_{ma}$ . Similarly the local limit of concentration of B to maintain growth is  $C_b$ .

The compositions  $C_a$  and  $C_b$  will be reached only in the melt in contact with the center of each lamella. The composition must change progressively across the interface, as shown, so that where the two lamellae join the melt will have the intermediate composition  $C_o$ . Tiller<sup>1</sup> represented the distribution of the  $\beta$  constituent as a build up of the  $\beta$ constituent ahead of the  $\alpha$  phase, and a deficiency ahead of the  $\beta$  phase (Figure 5). It should be noted that Hogan<sup>11</sup>



Figure 5. Schematic Representation of Solute Profiles for the & Constituent in the Liquid Ahead of the & and Phases - after Tiller.<sup>1</sup>



Figure 6. Probable Form of Crystallization Front in Lamellar Eutectic Crystallization - after Hogan.ll The transfer of the Rejected Material Across the Interface due to the Lateral Concentration Gradient is Represented in the Figure by the Diffusion Distances da and db. called the crystallized phases A and B, while Tiller defined them in terms of  $\alpha$  and  $\beta$ .

Consider the situation when  $V_a > V_b$  so that the A lamellae tend to grow out in advance of the B lamellae. It has been proposed by Tiller<sup>1</sup> that the interface will be of the form shown in Figure 6. In order to have a steady-state  $\beta$  distribution in the liquid the concentration profiles for the  $\beta$  constituent ahead of the  $\alpha$  and  $\beta$  phases must be as shown in Figure 5.

The interface can show several possible morphologies (Figure 7). The concentration in the liquid at the point of junction of the  $\alpha$  and  $\beta$  phases will be that concentration at which the liquidus lines cross, i.e.,  $C_e$  if the curvature of the surfaces are zero at this point. The equilibrium temperature at this point will be  $T_e$  if the curvature of the interface is zero as shown in Figure 7b and below T<sub>e</sub> if the curvature is positive as in Figure 7a. In order to have a steady state solute distribution in the liquid the concentration profiles for the  $\beta$  constituent ahead of the  $\alpha$  and  $\beta$ phases must be as shown in Figure 5. This requires that the interface temperature be below the eutectic temperature. The interface shape shown in Figure 7a satisfies this condition. Mechanical equilibrium will occur at the liquid- $\alpha$ ,  $\beta$  junction to balance the solid-liquid interfacial tensions and the  $\alpha$ ,  $\beta$  phase boundary tension, and Tiller proposes the formation of a deep groove at this junction caused by the



Figure 7. Two Possible Interface Shapes for the Lamellae on a Microscopic Scale - after Tiller<sup>1</sup>

greater magnitude of the  $\alpha$ ,  $\beta$  phase boundary energy compared to the solid-liquid interfacial energy.

In order to maintain a steady state concentration distribution in the liquid, there must be a continuous redistribution of the atoms rejected from the respective advancing solid lamellae. The flux of  $\beta$  rejected from the  $\alpha$  interface per unit time must diffuse to the  $\beta$  interface in unit time (Figure 6, d<sub>a</sub> and d<sub>b</sub>). The liquid composition at the base of the groove has a constant value, C<sub>o</sub>. If the diffusion distances concerned are d<sub>a</sub> and d<sub>b</sub>, the average concentration gradients over the two distances must be equal, and so,

$$\frac{(C_{a}-C_{o})}{d_{a}} = \frac{(C_{o}-C_{b})}{d_{b}}$$
(1)

Now, any change in the lead distance, S, changes the ratio  $d_a/d_b$ . If S increases, then  $d_a$  will increase without significant change in  $d_b$ , and either  $C_a$  or  $C_b$  or both must increase to maintain the equality. Figure 4a shows that such a shift of concentration to the right will decrease the supersaturation of the liquid with respect to A, increase it with respect to B, and thus cause an increase in the growth velocity of B with respect to A. Thus if A has, initially, the faster growth rate, the A lamellae will advance ahead of B until a critical lead distance, S, is

reached at which the growth rates are equal. For any growth rate, lateral concentration gradients are set up ahead of the interface to give the required amount of diffusion of atoms of two species to stabilize the steady state interlamellar spacing.

It can be seen that the line through  $C_0$  in Figure 4a represents the compositions at which a lamellar eutectic can form with a completely planar interface, at various degrees of supercooling. If, however, the composition varies from  $C_0$ , a normal lamellar eutectic may still be formed if one phase grows a little in advance of the other. Therefore a region is defined around the line through  $C_0$  in which closely coupled eutectic growth is possible. Possible coupled eutectic growth regions, derived from experimental work, are shaded in Figure 8.

In type (a) the coupled region is almost symmetrical, so that it would be difficult to produce anything but a normal eutectic structure. Alloys immediately on either side of the composition  $C_e$  would always solidify as pure eutectic at sufficiently high cooling rates, such that the eutectic solidification occurs within the coupled region. Hence the eutectic point would appear to vary with conditions of freezing.

Type (b) represents a quite different situation which appears to be typical of anomalous eutectic structures. If a melt of eutectic composition supercools before nucleation



Possible Limits of the Coupled Region - after Hogan.11 Figure 8.

occurs then crystallization takes place in a region where coupled growth to form a normal eutectic structure is not possible. The structure must depend on the relative ease with which either phase can form nuclei.

## Relation Between Entropies of Fusion of Components and Structure of Binary Eutectics

Many attempts have been made to connect the different tendencies of substances to be supercooled and to form oriented microstructures with parameters such as: the heat of fusion, the shape of the liquidus curves within binary and ternary systems, and the bond energies and other thermodynamic properties. The experimental methods and theoretical developments of Jackson<sup>12,13,14</sup> and Filonenko<sup>15,16</sup> have shown that eutectic morphology is directly related to the entropy of melting.

Jackson's classification of the morphology of crystal growth was based on the surface roughness of the crystalliquid interface as predicted by the entropy of fusion (melting). If the two solidifying phases have low entropies of fusion, the eutectic should be lamellar or rod-like and if one or both phases have a high entropy of fusion, the eutectic should be unordered. This classification follows from Jackson's prediction that phases with high entropies of fusion would grow with a faceted interface, while those with low entropies of fusion would grow with an atomically

rough interface. High entropy elements have a "smooth" interface, so crystals grow by a mechanism requiring greater supercooling than in the case of a "ragged" solidliquid boundary. Where there is considerable supercooling before the moving front, it is quite possible for crystallization centers of any orientation to be nucleated in the volume of the liquid, and this results in the formation of misoriented, irregular structures. High entropy eutectics cannot therefore be crystallized in the form of ordered eutectic structures.

However, Filonenko regards this conclusion as erroneous, because the theory of Jackson does not account for the structure of the melt and the possibility of its affecting the growth mechanism of crystals. Experimental verification of Jackson's theory has usually been carried out in organic systems. As compared with these "flawless" organic liquids of high entropy, which form irregular eutectics, crystallization of ordered structures is possible in high entropy liquids of the "fissured" type-liquids which are permeated by a large number of surfaces of rupture at any given instant. A fissured liquid has a high entropy because of the higher mobility and greater disorder of its particles. Over a short range the structure of liquid microportions of this type of binary eutectic has a close resemblance to the structure of a solid. In comparison, the anions in a flawless, isovalent liquid are mobile within

the anionic part and the cations within the cationic part of the structure and easy supercooling is possible. Just before nucleation occurs, the supercooling of the low viscosity, fissured binary melt is much less than the supercooling of the high viscosity, flawless liquid and thus the oriented crystallization of high entropy phases can occur.

Filonenko's<sup>15,16</sup> results showed that the presence of a quasieutectic structure (Tiller's<sup>1</sup> partitioning diffusion) in the melt is still not sufficient for formation of an ordered structure. In his investigation of eutectic mixtures of semiconductors, Filonenko found that for stable formation of a regular composition in the process of directional crystallization the interface of each phase would have to be identical. This condition can be satisfied if there is an equality, or only a slight difference, in the entropies of melting of the solid phases. On the basis of his results, binary eutectic systems should be classified according to the entropy ratio of the phases. If  $S_{\alpha}/S_{\beta}$  = 1.0 to 1.5, then there is a possibility of getting regular structures in the process of directional crystallization (whatever the value of  $S_{melt}$ ); if  $S_{\alpha}/S_{\beta} >> 1.5$ , then the structures have phases with random orientation.

Morphological Features of Binary Eutectics

Tiller<sup>1</sup> developed a concept of how ordered eutectics

nucleate and an explanation of the transition from rod or lamellar morphology to globular morphology. Hopkins and Kraft<sup>17</sup> demonstrated the necessity of a certain growth direction and orientation relationship (preferred habit planes) between the phases of a binary eutectic to obtain a lamellar, rather than an irregular structure.

It is also well known<sup>18</sup> that addition of small amounts of a third component to a lamellar binary eutectic produces a cellular structure. The third component results in curvature of the solid-liquid interface and since the lamellae tend to grow normal to this interface, they may curve away from the macroscopic growth direction. The size of the eutectic cells, and hence the radius of curvature, has been found related to both the growth rate and the solute content<sup>19</sup>. It has been demonstrated experimentally by Weart and Mack<sup>18</sup> that the colony structure of lamellar eutectics is associated with the presence of a cellular structure superimposed on the lamellar eutectic structure.

## Melting of Oxides by Direct High Frequency Induction

Crystalline samples of refractory metal oxides (MgO,  $Al_2O_3$ ,  $SiO_2$ , CaO,  $Y_2O_3$ ,  $ZrO_2$ , etc.)<sup>20,21,22,23,24</sup> carbides and borides<sup>25,26,27</sup> have been prepared by various modifications of the radio frequency induction melting technique. In the case of relatively low conductivity oxides, the

primary advantage of high frequency melting is the possibility of solidifying the substances in oxidizing or neutral conditions without contamination of the material during fusion. Other features include:

(1) Precise heating and cooling rate control

(2) Mixing of the melt is obtained by convection currents due to radial and vertical temperature gradients.

(3) Sufficient power can be concentrated in a restricted volume to form a stable and reproducible molten zone.

Heating is accomplished  $^{28,29}$  by subjecting the samples to an alternating magnetic field, produced by energizing a coil with an alternating current. Consequently eddy currents are produced in the sample by the induced electromotive force and  $I^2R$  heating of the sample results.

The distribution of current induced in a conductor by a harmonically changing magnetic field  $^{28}$  is given by

$$\nabla^2 J = j 8 \pi^2 \mu f \sigma X 10^{-3} \overline{J}$$
 (2)

where  $\overline{J}$  is the vector current density (amps/cm<sup>2</sup>),  $\mu$  is the permeability of the material,  $\sigma$  is the conductivity of the material ( $\mu$ mho/cm), f is the frequency and j =  $\sqrt{-1}$ . Equation 2 shows that the current density decreases exponentially from the surface to the interior of a conductor carrying alternating current. Thus the cylinder to be heated

contains an inner cylindrical region of low current density, surrounded by a region of comparatively high current density. This "skin effect" is shown in Figure 9.

The skin depth  $\delta$ , defined as the depth below the surface of the conductor where the current density has been reduced to  $1/\varepsilon$  (approximately 37% of the surface density, is the depth at which the total current can flow uniformly and produce the same heating effect as the current expressed by Equation 2. The ratio of specimen radius to skin depth  $(r/\delta)$  has been related<sup>30</sup> to the power absorbed by a solid cylindrical specimen from an oscillating magnetic field in the manner shown in Figure 10 (A\* =  $r/\delta$ ). Thus  $r/\delta$  is a measure of the heating efficiency of the induction coil and is directly related to the ability to establish eddy-current heating in a material. From Figure 10, it is clear that a value of  $r/\delta$  greater than four or five is required for efficient operation. With sufficient power available, however, values of  $r/\delta$  as low as 0.1 may be acceptable.

The skin depth  $\delta$  (cm) is dependent on the frequency (hertz) and the electrical conductivity  $\sigma$  (ohm cm)<sup>-1</sup> by the equation

$$\delta = (\pi \mu f \sigma)^{-1/2}$$
(3)

Unfortunately, the operating frequency of commercial rf generators (3-5 megahertz) is not large enough for an







Figure 10. Power Absorbed From an Oscillating Magnetic Field as a Function of A\*, the Radius-to-Skin Depth Ratio - after Hill.29

adequate skin effect in insulating (low  $\sigma$ ) oxide materials. Also the frequency is limited by other considerations. Above a frequency of 30 MHz, the current is very difficult to contain on the surface of copper tubing. In addition, the high voltage which builds up across the coil at such frequencies causes turn-to-turn arcing within the coil, as well as to the specimen. Atmospheric gasses ionize easily at this frequency. Therefore it is necessary to preheat oxide materials before attempting to couple directly to them with the induction coil in order to increase their extremely low electrical conductivity, allowing an acceptable yield at practical frequencies.

The magnitude of the thermal conductivity also plays an important role in the induction melting of oxides. Because of the inherent low value of the thermal conductivity<sup>31</sup> and the extensive cooling by surface radiation (heat fluxes varying between 12 and 100 W/cm<sup>2</sup> are radiated from UO<sub>2</sub> in the range 1400-2300°C), the outer part of the material may be kept solid, the center being melted. So oxides act as their own crucible and contamination can be avoided.

A number of refractory metal oxides have been melted using induction heating devices. Hill<sup>29</sup> has successfully initiated internal molten zones in pellets of  $CeO_2$ ,  $TiO_2$ ,  $Ca_{.1}^{Zr}.9^{O}_{1.9}$ ,  $Cr_2^{O}_3$ , and  $BaTiO_3$  using fields of 6 to 30 MHz. In their investigation of melt-grown oxide-metal composites,

Chapman, et al.<sup>36</sup> melted a number of refractory oxide compounds including: NiO·TiO<sub>2</sub>, TiO<sub>2-x</sub>,  $Cr_2O_3 + 40$  weight %  $2rO_2$ , and 2nO + 20 weight %  $Nb_2O_5$ . Chapman and  $Clark^{32}$ succeeded in growing single crystals of  $UO_2$  up to two inches long and up to 3/8 inch in diameter. The crystals were grown from polycrystalline  $UO_2$  rods by initiating a molten zone in the center of each rod and moving the zone up the rod. The power source for the induced eddy current heating was a 3 to 10 MHz rf generator. A molybdenum susceptor was used to preheat the samples to 1500°C prior to direct coupling to the sample. In addition the molybdenum was used to heat the areas above and below the molten zone to reduce thermal gradients.

#### Unidirectional Eutectic Solidification

#### of Oxide-Metal Composites

Aligned eutectic structures, consisting of single crystal rods of metal embedded in a continuous oxide matrix, have been observed in the following oxide-metal systems:  $UO_2-W^{33}$ ,  $ZrO_2-W^{34}$ ,  $HfO_2-W^{35}$ , and rare earth oxide-metal<sup>36</sup>. Other oxide-metal binary eutectics include<sup>37</sup>: MgO-W,  $Cr_2O_3$ -Re,  $Cr_2O_3$ -Mo,  $Cr_2O_3$ -W, (A1,Cr)\_2O\_3-Mo, and (A1,Cr)\_2O\_3-W systems.

Chapman, et al.<sup>33</sup> melted pressed UO<sub>2</sub>-5 to 15 weight % W rods, then used a modified floating zone process to produce well ordered UO<sub>2</sub>-W structures. Both metallic lamellar and

fiber arrays were observed in the solidified composites.

Watson et al.<sup>34</sup> was successful in employing a similar rf melting and solidification technique to grow crystals of zirconia containing areas of well ordered, parallel tungsten fibers in the system  $\text{ZrO}_2(\text{GaO stabilized})$ -5 to 20 weight % W. Johnson et al.<sup>35</sup> determined the fiber density to be as high as 7.2 X  $10^7/\text{cm}^2$  and the fiber diameter to be 0.15 µm for their HfO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub> stabilized)-W composites.

Another advantage of the floating zone method of unidirectional eutectic solidification is the possibility of obtaining with relatively simple apparatus crystals having shape and dimensions suitable for further analysis. In their review of zone melting, Vigodorovich et al.<sup>38</sup> state:

> Zone melting with a temperature gradient is characterized by the spontaneous movement of the liquid zone in a crystal in the stationary field of a temperature gradient. Movement of the zone is caused by the process of dissolving and crystallization at its boundaries and diffusion transfer of the substances being dissolved to the crystallization front in the melt. In addition, the processes of evaporation of the components of the zone and convective agitation in the melt have an influence on the rate of movement on the zone.

Kopetskii and Marchenko<sup>39</sup> determined that the shape of the crystallization front of vanadium samples (1 cm in diameter) during growth was a function of the thermal conditions: A concave front occurred when heat removal from the lateral surface predominated over axial removal.

The furnace and growth facility used by Chapman and

co-workers<sup>36</sup> to grow oxide-metal composites is shown in Figures 11 and 12. In this technique uniaxially or isostatically pressed rods of the oxide-metal mixture are sintered inside rf heated molybdenum tubes in the desired atmosphere ( $N_2$ ,  $H_2/N_2$ ,  $H_2/H_20$ ,  $CO/CO_2$ ) to densify and preheat the material. When the temperature has increased sufficiently to allow direct rf coupling to the oxides the molybdenum tube heaters are separated to expose the rod to an rf field of 3 to 30 MHz, depending on the material to be melted. If the resulting increase in temperature, electrical conductivity, and resistance heating is effective, the interior of the rod (at temperatures up to 3000°C) melts. Unidirectional solidification is achieved by moving the molten zone upward by slowly lowering the rod through the rf field.

Melt-grown oxide-metal composite structures were developed and produced by Chapman and co-workers<sup>36</sup> for high field electron emission testing. The induction melting and unidirectional solidification technique was used to form aligned metallic fibers in the oxide matrix for a number of refractory oxide-metal mixtures:  $UO_2$ -W,  $ZrO_2(Y_2O_3)$ -W,  $HfO_2(Y_2O_3)$ -W,  $UO_2$ -Ta,  $Gd_2O_3(CeO_2)$ -Mo or W,  $Nd_2O_3(CeO_2)$ -Mo or W,  $La_2O_3(CeO_2)$ -Mo or W, and  $CeO_2$ -Mo. In this investigation, the parameters influencing composite growth (Table 1) are presented and characterized. Regarding the above oxide-metal systems, Hart<sup>41</sup> observed:


Figure 11. RF Generator and Composite Growth Assembly



Figure 12. Schematic Diagram of the Facility for the Growth of Oxide-Metal Composites.

Table 1. Parameters Influencing Composite Growth in Refractory Oxide-Metal Systems after Chapman et al.<sup>36</sup>

- 1. Oxide-metal ratio
- 2. Growth rate
- 3. Metal powder characteristics
- 4. High-temperature electrical conductivity
- 5. Rf frequency
- 6. Mixing of the liquid (sample rotation)
- 7. Melting (eutectic) temperature
- 8. Preheat temperature
- 9. Sample density
- 10. Sample-rf coil geometry
- 11. Quantity of liquid and void size
- 12. Oxygen partial pressure
- 13. Pre- and post-heater separation
- 14. Vapor pressure
- 15. Variable oxide stoichiometry

"Phase diagrams for these systems have not been rigorously established. Criteria necessary for establishing eutectic structures in oxide-metal systems are presently not understood. High purity alumina does not exhibit eutectic behavior when combined with refractory metals; however, doping the system with Cr<sub>2</sub>O<sub>3</sub> does yield eutectic structures in the Al<sub>2</sub>O<sub>3</sub>-W and Al<sub>2</sub>O<sub>3</sub>-Mo systems. What role the dopant plays is not understood."

# Nonstoichiometry and Electrical Conductivity

 $\frac{\text{of } Y_2 \underline{O}_3 - \text{CeO}_2 \text{ Solid Solutions}}{\text{Anderson and Wuensch}^{42} \text{ reported that McCullough and}}$ Britton<sup>43</sup> and Brauer and Gradinger<sup>44</sup> had found complete solid solubility between  $CeO_2$  and  $Y_2O_3$  at 1100 to 1400°C, but Bevan et al. 46 found miscibility gaps from 42 to 62 mole % YO<sub>1.5</sub> at 1700°C. At percentages of YO<sub>1.5</sub> greater than approximately 15 mole %, the C-type solid solution is formed, consisting of a defect fluorite structure with anions missing at the ends of the body diagonal. In the C-phase region, the  $Ce^{4+}$  and  $Y^{3+}$  ions are randomly distributed and anions are present as an interstitial structure.

In general, pure  $Y_2^{0_3}$  is an electrical conductor  $^{47}$ whose level of conductivity is dependent upon temperature and oxygen partial pressure. Changes in either parameter cause small deviations in stoichiometry which in turn establish a concentration of electronic charge carriers. The equilibrium charge carrier density is the principal determinant of conductivity level as the mobility of these carriers is thought to be only slightly affected by changes in temperature and  $p_{0_2}$ . Since a dependence upon  $p_{0_2}$  exists, slight deviations in stoichiometry depend upon ionic charge transfer, which for  $Y_2^{0_3}$  is thought to take place by oxygen ion diffusion. In fact  $Y_2^{0_3}$  loses some oxygen without undergoing a structural change at high temperatures in low oxygen environments: The free energy change associated with the reaction

$$YO_{1.5}(s) = YO_{1.491}(s) + 0.009\frac{1}{2}O_2$$
 (4)

will be less than that associated with the decomposition reaction

$$Y_2 O_3(s) = 2YO(g) + 0$$
 (5)

Ceria is essentially a pure electronic semiconductor<sup>46</sup>. A distinguishing feature of the cerium ion<sup>47</sup> is the nature of its transition from the tetra- to tri- valent state. Dissociation of  $CeO_2$  to  $CeO_{1.99}$  begins at 800°C under an oxygen pressure of  $10^{-18}$  atm, and reaches the final limit  $(CeO_{1.5})$  at  $10^{-27}$  atm. This corresponds to a change in thermodynamic potential of about 30 kcal/mole  $CeO_2$ . Such a property of cerium oxide facilitates defect formation in the anionic sublattice and increases the ease of solid solution formation.

Two methods exist for increasing the  $Y_2^{0}$  electrical

conductivity: by forming a substoichiometric composition or by adding a controlled amount of a doping agent such as  $CeO_2$ . In both cases a defect solid solution forms with anion vacancies. It has been determined<sup>47</sup> that the presence of oxygen interstitials introduced a significant ionic contribution which is responsible for the magnitude of electrical conductivity in solid solutions being much higher<sup>46</sup> than either of the parent oxides (Table 2).

Table 2. Electrical Conductivity of Y	203-CeO2 System <sup>40</sup>
---------------------------------------	-------------------------------

Tempera	ature = 701°C	$p_{0_2} = 10^{-3}$ atm	
Comp	position	x 10 <sup>6</sup> 11	
(* LeO <sub>2</sub>	<sup>1n</sup> <sup>2</sup> <sup>2</sup> <sup>3</sup> <sup>-</sup> <sup>2</sup> <sup>2</sup>	dc x 10 8hm cm	
	0	0.1	
2	20	4.5	
2	25	0.04	
4	2.9	87.0	
7	0	135.0	
8	37.5	97.9	
10	0	32.0	

34

### CHAPTER III

# DISCUSSION OF UNIDIRECTIONAL SOLIDIFICATION EXPERIMENTS AND EQUIPMENT

# 1. Sample Preparation

The  $Y_2O_3 - CeO_2$  - Mo mixtures were prepared by mixing the required weight percentage ratios of -325 mesh  $Y_2O_3$ powder (Kerr-McGee Chemical Corp., 99.98% purity), CeO<sub>2</sub> powder (Fisher Chemical Co., 99.6% purity), and molybdenum powder (Teledyne Wah Chang, 99.9% purity) in a mortar. Two methods were used to fabricate feed rods. Pellets were formed by pouring the powder mixture into a 1.9 cm X 10 cm steel die (after lubricating the die walls and punches with a saturated stearic acid-acetone solution), and pressing the mixture to 8,000 psi. Longer rods were pressed by packing the mix into a 8-1/2" X 1-1/4" (3/8" wall thickness) rubber mold (Trexler Rubber Co.) and isostatically compressing to 30,000 psi.

## 2. Growth Assembly

The green sample was placed in the assembly shown in Figure 12, which permits vertical translation of the sample rod, vertical adjustment of the molybdenum pre- and post-heat tubes (one inch o.d., 1 mm. wall thickness), and selection and control of sintering and growth atmosphere. The sample rod rested on an insulating  $Al_2O_3$  pedestal which was fitted over a hardened steel rod extending through the table to a hydraulic cylinder. A porous  $Al_2O_3$  spacer fixed the lower Mo preheater in position around the pellet and supported the 25 mm. i.d. Vycor tube. After evacuating the Vycor tube to 500 millitorr with a mechanical pump, controlled ratios of  $N_2:H_2$  were passed through the system (entering at the bottom and exiting at the top) at rates between 400 and 500 cc/min.

A Lepel dual frequency rf generator (model T-10-3-MC-HW), operating at 3.7 MHz was used in all experiments. Temperatures were optically measured with no correction for radiation losses due to the vitreous silica tube or to vapor deposits.

During preheat, the power was automatically controlled and increased from room temperature to approximately 1750°C, which required fifty minutes. Sintering occurred during this period.

# 3. Formation of a Stable Zone

Forming and maintaining a stable molten zone in polycrystalline rods requires that sufficient power is introduced into a limited volume to balance heat losses when the volume is at a temperature exceeding the melting point. The distribution of heat generated in the rod by induced currents depends on the coil configuration, the resistivity of the

material and rf frequency. The mechanism and the rate at which heat is lost depends on material properties: melting point, thermal conductivity and emissivity. Also the continuous gas flow through the growth system causes a heat loss, which is a function of the heat capacity of the atmospheric component(s). Chapman, et al.<sup>36</sup> have undertaken an empirical approach in studying the effect of rf coil geometry on the concentration of power in the area of the zone of refractory oxide-metal mixtures. One satisfactory arrangement, also used in this investigation, consists of 7-1/2 turns of equal radius wrapped upward in a clockwise direction, with turns spaced approximately 3-4 mm. apart (Figure 13). The coils were made of rectangular copper tubing (1/8" x 1/4" O.D. x .032" wall thickness).

It is necessary that the melt volume remain unchanged if a stable molten zone is to be maintained during growth, or that the masses of material melting or freezing per unit time be the same. It should be noted that if the rod diameter is too small, it is difficult to maintain a stable molten zone at normal power levels.

Uniform rod density was obtained by two methods (Chapter III, Section 1). Uniaxially pressing the mixtures to 8,000 psi produced a 1.9 cm dia. rod that was of satisfactory density and diameter for coupling. Isostatically pressing at 30,000 psi proved more desirable; although the rods initially had the same diameter as that achieved with



Figure 13. Configuration of Work Coil Used in Composite Growth Experiments.

the uniaxial method, the higher pressed density decreased the shrinkage of the sintered rod making coupling significantly easier. Also a result of isostatic pressing was a longer rod--approximately six cm. versus a maximum uniaxial pressed length of four cm., allowing the growth of a correspondingly longer composite.

#### 4. Solidification and Composite Growth

Direct coupling to the heated rod was accomplished by decreasing the power (to avoid arcing), lowering the Mo preheater well below the coil, increasing the power and observing the effect of the increase on the temperature of the central portion of the sample rod; as the temperature increased and melting became apparent, the power was lowered to avoid melting through the solid skin from the interior. Melting was detected by an increase in the plate current and a simultaneous decrease in the plate voltage of the rf generator.

After coupling and melting were achieved and power input stabilized, the lower Mo tube was raised inside the coil (about two turns) and the upper Mo tube was pushed down inside the coil (about two turns) over the pellet, leaving a fixed separation of 35 mm centered about the solidification front (Figure 14). Optimum placement of the Mo tube shields was based on their concentrating effect on the rf field as developed by Chapman, et al.<sup>36</sup>.



Figure 14. Upper and Lower Preheat Tube Position During Composite Growth (35 mm. spacing) and Resulting Thermal Gradient.

Growth was initiated by lowering the rod at the desired rate. After a length of composite was produced, the upper Mo tube was closed down until it contacted the lower tube and cooling began at a controlled rate.

#### CHAPTER IV

#### RESULTS AND DISCUSSION

Tiller<sup>1</sup> has shown that in order to maintain a steadystate concentration distribution in the liquid, there must be a continuous redistribution of the atoms rejected from the respective advancing solid lamellae. For the necessary diffusion of the oxide and metal constituents before the solidification front to occur it is required that the system assume a dynamic structure in which the various cation species are mobile.

Also, as the reshuffling of ions takes place, the system must meet certain geometrical conditions. Weyl and Marboe<sup>50</sup> have shown that the presence of a cation of high charge density requires a more intense shielding by electrons than can be supplied by the number of electrons that neutralize the excess charge of the cation--thus for the various chemical species to remain compatible in the melt all cations must be screened to the extent that the thermal energy available is sufficient to obviate precipitation of compounds as a means of obtaining the necessary liquid stability. Screening of the cations of a eutectic liquid is compensated for by two conditions: maintaining an anion-tocation ratio large enough to provide a symmetrical environment

of  $0^{2^{-}}$  ions for each cation species and the inherent potential of the oxygen anion to be polarized.

Since compatibility is a solubility phenomenon, the solubility of the oxide-metal components depends on temperature. At some temperature greater than the eutectic temperature, enough kinetic energy is available to make both the cations of the oxide and the solute metal cations mobile and therefore the components of the oxide-metal liquid are mutually soluble. However as the entropy of the system decreases with cooling, the coordination conditions do not permit mobility and the eutectic liquid phase separates into two phases: an oxide-rich liquid consisting of a symmetrical framework of  $0^{2}$  ions in which the screened cations are mobile and a metal-rich liquid. The metal cations can only achieve screening by aggregation into a liquid lattice in which screening is accomplished by the formation of a large number of mobile electrons. Solubility of the metal is further increased in the presence of excess screening  $0^{2}$ ions- in the  $UO_2$ -W system, an increase of oxygen concentration was developed by increasing the O/Uratio of the liquid eutectic from 2.03 to 2.10, consequently raising the W solubility by an order of magnitude<sup>51</sup>. Thus, as Tiller concluded, oriented structures are characterized by a phaseseparated structure in the liquid which promotes advance of a stable interface.

In terms of the Tiller<sup>1</sup> and Filonenko<sup>15,16</sup> model of

the structure of the crystal-melt boundary, the measure of compatibility is taken to be  $S_{\alpha}/S_{\beta}$ , the ratio of the entropies of fusion of the crystallizing phases. A comparison of the values of the ratio of the entropies of melting and the growth morphology of the liquids of refractory oxidemetal mixtures is given in Table 3. Oxide-metal eutectics that crystallize into ordered structures fall into the range  $0.72 \leq S_{\alpha}/S_{\beta} \leq 3.9$ ; for  $S_{\alpha}/S_{\beta} \geq 4.3$ , the mixtures do not form ordered eutectic.

The magnitude of the  $S_{\alpha}/S_{\beta}$  values calculated for these oxide-metal mixtures are generally larger than Filonenko's ratios. This variation is expected considering that the oxide crystal lattices are much more complex than the structures of the co-precipitating metals whereas Filonenko solidified isomorphous metal and semiconducting elements (Ge, Au, Si, etc.) of similar lattice types.

In this investigation several compositions in the system  $Y_2O_3 - CeO_2$  - Mo were unidirectionally solidified in nitrogen or nitrogen-hydrogen atmospheres at growth rates varying from two to four centimeters per hour (Table 4). Experiments were directed toward developing uniform composite growth throughout the length of a rod by establishment of an optimum starting composition.

The different types of microstructures observed were a function of the oxide-metal composition:

1. Normal eutectic composite structures were produced

Eutectic (Chapter II)	S <sub>oxide</sub>	Properties <sup>52,53</sup> S <sub>metal</sub>	(kcal/deg mole) <sup>S</sup> oxide/metal
		Oriented Struc	tures
UO2-W	6.0	2.3	2.6
UO <sub>2</sub> -Ta	6.0	2.3	2.6
MgO-W	6.0	2.3	2.6
ZrO <sub>2</sub> -W	7.0	2.3	3.1
Cr <sub>2</sub> 0 <sub>3</sub> -W	1.65	2.3	0.72
Cr <sub>2</sub> 0 <sub>3</sub> -Cr	1.65	1.61	1.0
ThO2-W	9.03	2.3	3.9
		Irregular Stru	ctures
Y <sub>2</sub> 0 <sub>3</sub> -W	10.0	2.3	4.3
A1 <sub>2</sub> 0 <sub>3</sub> -W	12.2	2.3	5.3

Table	3.	Entropy of	Melting	of Phases
		and Eutect	ic Micros	structure

Table 4. Summary of  $Y_2^{0.5}(\text{CeO}_2)$ -Mo Composite Growth

Morphology	two oxide phases plus metal globs	oxide plus large metal globs	oxide plus large metal globs	oxide-rich and normal	normal and anomalous	Mo-rich and anomalous	anomalous	normal	normal
Atmosphere	$N_2:H_2 = 10:1$	$N_2:H_2 = 10:1$	$N_2:H_2 = 10:1$	$^{\rm N}_{\rm Z}$	$^{\rm N}_{\rm Z}$	N2	$^{\rm N}_{\rm Z}$	$N_2$	N2
Rate(cm/hr)	1	unconstrained	2.1	2.1	2.7	2.4	3.4	3.4	2.4
w/o Mo	15	10	10	10	20	15	15	15	15
w/o CeO <sub>2</sub>	0	20	25	25	25	35	35	50	5.0
Exp No.	06	77	78	79	83	86	91	93	94

during solidification of  $(Y_2O_3 - 50 \text{ weight } \text{CeO}_2) + 15 \text{ weight}$ % Mo (Figure 15).

2. Anomalous eutectic micromorphologies were produced from  $(Y_2O_3 - 35 \text{ weight } CeO_2) + 15 \text{ weight } Mo$  (Figures 16 and 17).

3. For oxide-rich compositions the eutectic reaction was preceded by primary phase growth (Figure 18).

4. For molybdenum-rich compositions the microstructure consisted of molybdenum dendrites in a matrix of eutectic colonies (Figure 19).

5. Very limited metal solubility was found to exist for yttrium oxide and molybdenum conbinations (Figure 20).

The addition of  $\text{GeO}_2$  to increase the electrical conductivity permitted direct rf coupling and melting of  $Y_2O_3(\text{GeO}_2)$ -Mo at 3.6 MHz. A temperature of 1840°C was found to be the maximum preheating temperature obtainable with the Lepel rf generator and associated experimental apparatus. Preheating to this temperature did not sufficiently increase the conductivity of  $Y_2O_3$ -Mo mixtures to allow coupling. Sample 90 was obtained when a small portion of a  $Y_2O_3$ -Mo rod was melted by an arc while attempting to couple to the rod following the normal procedure. Several other attempts at inductively melting undoped  $Y_2O_3$ -Mo failed. Direct coupling was accomplished with a ceria addition of 20 weight % and further additions increased the coupling efficiency proportionately (Table 5).



Figure 16. An Example of anomalous eutectic morphology Found in Samples 83, 86 and 91 (X200, Dark Field).



Figure 17. Anomalous Eutectic Morphology (X600, Dark Field). Light Area on Right Side of Photograph is a Crack.



Figure 18. Oxide-Rich Growth (X200, Dark Field).



Figure 19. Molybdenum Dendrites Surrounded by Eutectic Growth (X600, Dark Field).



Figure 20. Solidified Y<sub>2</sub><sup>O</sup><sub>3</sub> - Mo Showing Two Oxide Phases and Insoluble Molybdenum (X600, Bright Field).

Composition	Minimum Coupling Temperature (°C)
Y <sub>2</sub> 0 <sub>3</sub> + 15 w/o Mo	>1840
(Y <sub>2</sub> 0 <sub>3</sub> - 20 w/o CeO <sub>2</sub> ) + 10 w/o Mo	1800
(Y <sub>2</sub> 0 <sub>3</sub> - 25 w/o CeO <sub>2</sub> ) + 20 w/o Mo	1760
(Y <sub>2</sub> 0 <sub>3</sub> - 35 w/o CeO <sub>2</sub> ) + 15 w/o Mo	1680
(Y <sub>2</sub> 0 <sub>3</sub> - 50 w/o CeO <sub>2</sub> ) + 15 w/o Mo	1520

Tab1e	5.	Effect of Conductivity		of Y	Y203-Ce02-Mc	Mixtures
		on Minimum	Temperature	for	Successful	Coupling

When the oxide-metal mixture was not  $\text{CeO}_2$  doped, the association between the liquid yttria and molybdenum was minimized resulting in solidification of large dispersed spheres of insoluble molybdenum (Figure 20). Another oxide phase, possibly of the form  $Y_x \text{MoO}_z$ , was also precipitated from the melt. An addition of ceria greater than or equal to 20 weight % of the total oxide content and the resulting interaction of the oxide and metal components produced an eutectic melt.

Optimization of the starting composition with respect to fiber growth was closely approached using a mixture of  $(Y_2O_3 - 50 \text{ weight } CeO_2) + 15 \text{ weight } Mo$ . The oxygen potential of a 20 weight \$ ceria melt was found far too low to keep the required amount of molybdenum screened and soluble. Large globules of metal (up to 6 mm. in diameter in sample 77 and 4 mm. in diameter in sample 78) settled to the bottom of the interior liquid pool of these sample rods and froze. The solidified rod was almost entirely oxide above the metal deposit. Similarly in sample 83, doubling the molybdenum concentration over previous experiments, eutectic growth was obtained over a 4.5 cm. length but the longest Mo sphere-free zone was only 7 mm. (Figure 21--note that sample 77 contained 20 weight \$ CeO<sub>2</sub>, sample 78 contained 25 weight \$ CeO<sub>2</sub> and sample 83 contained 25 weight \$ CeO<sub>2</sub>).

One viable method of improving the metal solubility of the  $(Y_2O_3 - 25 \text{ weight } CeO_2) + 10 \text{ weight } Mo \text{ melt is to}$ 



Figure 21. Y<sub>2</sub>O<sub>3</sub> (CeO<sub>2</sub>) - Mo Composite Rod Containing Deposites of Insoluble Molybdenum.

increase the oxygen pressure of the growth atmosphere, but the increased volatility of the oxides and metal is most The procedure for controlling the stoichiometry troublesome. of composites grown from the melt is complicated because there is a tendency for the melts to change composition due to excess vaporization losses of the metal component, thus the melts and the material solidifying behind the zone tend to have a lower metal content than the feed rod. A typical example is shown in Figure 22. Ordered growth persisted for about one centimeter (thirty minutes of growth) in sample 79, but, as shown by the definitive separation of eutectic growth from oxide-rich growth, it appears that the Mo concentration in the melt was lowered below a critical level and a sharp transition of the solidifying material from eutectic to primary oxide occurred.

A more feasible alternative for maintaining liquid stability is in taking advantage of the tendency of ceria to go substoichiometric at high temperatures and low oxygen pressures<sup>\*</sup> (Chapter II, Nonstoichiometry and Electrical Conductivity of  $Y_2O_3$ -CeO<sub>2</sub> Solid Solutions). Ceria additions were increased to 35 weight % but the solidified microstructure was composed entirely of the semi-sendritic "anomalous" form

<sup>\*</sup>The initial concept of adding CeO<sub>2</sub> to sesquioxides as a mechanism of increasing the refractory metal solubility has been described for the system CeO<sub>2</sub>-doped Gd<sub>2</sub>O<sub>3</sub>-Mo<sup>36</sup> and this work was accomplished by J. W. Stendera.



Figure 22. A Typical Example of the Transition from Eutectic to Oxide-Rich Growth in  $Y_2^{O_3}$  (CeO<sub>2</sub>) - Mo (X200, Dark Field).

of growth (Figures 16 and 17). Tiller's description of this situation (Chapter II, The Coupled Zone Concept) seems applicable. The anomalous growth is poorly oriented with respect to the solidification direction. It appears as if the numerous parallel Mo fibers grew from the melt first, changed the composition within the eutectic limits, and nucleation and coupled growth of a normal structure followed. Also, no colonies were found, the absence of which Hogan<sup>11</sup> regards as positive evidence of anomalous growth.

Improved screening of the molybdenum cations, obtained by adding more oxygen to the melt (by increasing the anion-tocation ratio) in the form of 50 weight % ceria, organized the liquid-solid interface into a geometry favorable to oriented composite growth. The increase in  $\text{CeO}_2$  content provided coupled growth of the metal phase with the oxide phase even though the supersaturation of the melt with respect to the metal was unchanged. The solidified micromorphology of the 50 weight % ceria samples was free of anomalous and primary phases and contained an average of 12 x 10<sup>6</sup> fibers/cm<sup>2</sup> (Figures 23 and 24).

Cracking and banding are two types of defects that cause discontinuities in fiber growth. Two different banding modes within a single sample are common.

In one case the discontinuity appears as an oxide layer containing molybdenum spheres (Figure 25). Recent work<sup>36</sup> has identified flucuations in line voltage as the origin of



Figure 23. Ordered Eutectic Growth of  $(Y_2O_3-50 \text{ Weight} \% \text{ CeO}_2) + 15 \text{ Weight} \% \text{ Mo}$  (Longitudinal Section, X600, Dark Field).



Figure 24. Transverse Section of (Y203-50 Weight % Ce02) + 15 Weight % Mo Composite (X200 Dark Field).



Figure 25. Power Fluctuation Banding in  $Y_2O_3$  (CeO<sub>2</sub>) - Mo Sample. (X600, Bright Field).

this type banding. A temporary increase in power input slightly enlarges the size of the molten zone and remelts a layer of the deposited composite. When the power returns to the set-point the corresponding shrinkage of the zone quenches a layer of the composite without the occurrence of supercooling and nucleation necessary for fiber growth.

Banding often occurs in a rhythmic pattern (Figure 26) in which a discontinuity in fiber growth extends across the entire solidified rod. Fibers are renucleated and uniform growth is resumed (Figure 27). No mechanism for this phenomenon has been proposed, other than a sudden, simultaneous decrease or depletion of molybdenum content across the growth front.

Composite cracking has been a problem which has not been completely solved. When cooling was accomplished by turning the power off and allowing the composite to cool naturally, the solidified polycrystalline rods were severely cracked (Figure 28), presumably resulting from differential expansion between the oxide and metal phases. The differences in thermal expansion coefficients of the oxide and metal would be anticipated as a major source of internal stress. Cracking may be minimized if equilibrium cooling rates are employed. Lowering the thermal gradient in the sample rod between the melt zone in the rod and cooler solidified area below the melt zone was investigated as a means of eliminating composite cracking. Once the melt zone was initiated



Figure 26. Rhythmic Banding in  $Y_2^0_3$  (CeO<sub>2</sub>) - Mo Sample (X200, Dark Field).



Figure 27. Fan Type Banding in Y<sub>2</sub><sup>0</sup><sub>3</sub> (CeO<sub>2</sub>) - Mo Sample (X600, Dark Field).



Figure 28. Typical Microcracking in a Quenched  $Y_2^0_3$  (CeO<sub>2</sub>) - Mo Composite Rod.

in a sample rod, the Mo preheater (which had been lowered to allow direct rf heating of the rod) was raised two turns into the rf coil, and around the coupled rod to a point just below the rod's molten zone (Chapter III, Procedure). The upper end of the Mo tube was heated since it was in the rf field. As the rod was lowered, it passed into this postheater (at approximately 1100°C), and the solidified portion of the rod was maintained at a higher temperature than normal due to radiant heat losses. This procedure in effect lowers the thermal gradient between the molten and solidified zones of the rod. After solidification of the desired length of composite, the upper Mo preheating tube (Figure 12) was closed down over the top of the rod so that the entire rod was enclosed in the postheater. One crack was found in a four centimeter length of a composite cooled under these conditions at a controlled rate to approximately 300°C.

Other  $Y_2O_3(CeO_2)$ -metal mixtures were successfully melted. A  $(Y_2O_3 - 25 \text{ weight } CeO_2) + 16 \text{ weight } W \text{ rod was}$ melted and solidified at 2.2 cm/hr. The microstructure contained anomalous and platelet growth, as well as the more typical rod-like growth. Many areas of high tungsten platelet density were present (Figures 29 and 30). Presumably the uniformity of the tungsten platelet or fiber growth could be improved with further experimentation. Yttria-ceria mixtures containing titanium and zirconium were easily melted, but no stable zone could be formed at 3.6 MHz.



Figure 29. Longitudinal Section of Y203 (CeO2) - W Sample Containing W Lamellae (X600, Dark Field).



Figure 30. Skewed Section of Y<sub>2</sub>O<sub>3</sub> (CeO<sub>2</sub>) - W Sample W Lamellae (X200, Dark Field).

#### CHAPTER V

#### CONCLUSIONS AND RECOMMENDATIONS

## Conclusions

1. Near eutectic compositions of the  $Y_2O_3(CeO_2)$ -Mo system form ordered composite structures containing aligned metal fibers when unidirectionally solidified using a modified floating zone technique.

2. Composites grown from the optimum composition,  $(Y_2O_3 - 50 \text{ w/o CeO}_2) + 15 \text{ w/o Mo}$ , at a growth rate of 2.4 cm/hr in a N<sub>2</sub> atmosphere contained fiber densities of approximately 12 X  $10^6/\text{cm}^2$ .

3. The solubility of Mo in the molten  $Y_2O_3(CeO_2)$  oxide mixture increased as the CeO<sub>2</sub> content was increased to 50 w/o.

4. The addition of increasing amounts of  $CeO_2$  reduced the preheat temperature required for coupling to the feed rod from >1840°C for  $Y_2O_3$  - 15 w/o Mo to 1520°C for  $(Y_2O_3 - 50 \text{ w/o} \text{ CeO}_2)$  + 15 w/o Mo.

5. Severe cracking of  $Y_2O_3(CeO_2)$ -Mo composites can be greatly reduced by controlled cooling.

6. Composites consisting of well-oriented tungsten platelet structures can be produced by unidirectionally solidifying the mixture  $(Y_2O_3 - 35 \text{ w/o CeO}_2) + 16 \text{ w/o W at}$
2.2 cm/hr in a  $N_2:H_2 = 10:1$  growth atmosphere.

7. Two types of oxide banding can occur in  $Y_2O_3(CeO_2)$ -Mo composites.

## Recommendations

Complete characterization of the  $Y_2O_3$ -CeO<sub>2</sub> - metal composite growth system requires further investigation as outlined below:

1. Various rf frequencies should be employed to determine if  $CeO_2$ -doped  $Y_2O_3$  mixtures containing metals such as Ti, Ta and Zr form eutectics.

2. Growth atmospheres of  $N_2:H_2/H_2O$  and  $CO/CO_2$  may have significant effects on metal solubility and composite growth and should, therefore, be studied.

3. The relationship between growth rate and fiber density and diameter, well documented for other oxide-metal composite systems, should be determined.

4. Chemical etching of both oxide matrix and metal fibers should be studied as a means of exploiting the properties of the unidirectionally solidified composites. The objective of composite etching studies are threefold:
(a) formation of electron field emission arrays<sup>36</sup> by etching away an oxide layer to expose the metal pins; (b) removing the metal pins completely to produce an oxide wafer containing an array of micrometer sized holes; and (c) removing the oxide matrix completely leaving the metal fibers to be gathered.

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The need for investigation of other chemical, electrical and mechanical properties may arise as other applications of oxide-metal composites are envisioned.

## BIBLIOGRAPHY

- W. A. Tiller, "Polyphase Solidification," Am. Soc. Mets. Symp. Liquid Metals and Solidification, A.S.M., Cleveland, Ohio, 1958, 276-318.
- W. C. Winegard, "Fundamentals of the Solidification of Metals," Metallurgical Reviews, 6(21) 57-99 (1961).
- G. A. Chadwick, "The Growth of Eutectic and Eutectoid Composites," Proc. Conf. In Situ Composites, National Academy of Sciences--National Academy of Engineering, Pub. NMAB-308-I, Washington, D. C., 1973, 25-50.
- 4. G. A. Chadwick, Progr. Mater. Sci. 12 97 (1963).
- 5. R. W. Kraft, "Controlled Eutectics," J. Metals, 18(2) 192-7 (1966).
- H. W. Kerr and W. C. Winegard, "The Structure of the Tin-Lead-Cadmium Eutectic," J. Inst. Metals, 93 63-64 (1964).
- J. D. Hunt, "Development in Eutectics," J. Cryst. Growth, 3,4 82 1968.
- F. Durand, Bull. Soc. Fr. Mineral. Crystallogr., 92 571 (1969).
- 9. L. M. Hogan, R. W. Kraft and F. D. Lemkey, <u>Advances</u> <u>in Materials Research Vol. 5</u>, (H. Herman, ed.), Wiley (Interscience), New York, 1970.
- E. Scheil, "Uber die Eutektische Kustallisation,"
   Z. Metallkunde, 45 298-309, 1954.
- L. M. Hogan, "The Solidification of Binary Eutectic Alloys," J. Aust. Inst. Metals, 6(4) 279-288 (1961).
- K. A. Jackson, "The Dendrite-Eutectic Transition in Sn-Pb Alloys," Trans. Met. Soc. AIME, 242(7) 1275-79 (1968).
- 13. K. A. Jackson and J. D. Hunt, "Lamellar and Rod Eutectic Growth," Trans. Met. Soc. AIME, 236(8) 1129-42 (1966).

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- 14. J. D. Hunt and K. A. Jackson, "The Dendrite-Eutectic Transition," Trans. Met. Soc. AIME, 239(6) 864-67 (1967).
- V. A. Filonenko, "On Phase Orientation in Composition Materials," Phys. Metals. Metallogr. (USSR), 29(3) 641-44 (1970).
- V. A. Filonenko, "Relation Between Entropies of Fusion of Components and Structure of Binary Eutectics," Zh. Fiz. Khim., 44(5) 1163-66 (1970).
- 17. R. H. Hopkins and R. W. Kraft, Trans. TMS-AIME, 242 1627 (1968).
- H. W. Weart and D. J. Mack, "Eutectic Solidification Structures," Trans. TMS-AIME 212(10) 664-70 (1958).
- N. M. Rumball, "Cellular Growth in Eutectic Systems," Metallurgia, 78(465) 141-45 (1968).
- 20. V. I. Aleksandrov, et al., "Melting Refractory Dielectrics by Direct High Frequency Heating in a Cold Container," Izv. Akad. Nauk SSSR, Neorg. Mater., 9(2) 236-8 1973.
- D. Viechnicki and F. Schmid, "Eutectic Solidification in the System Al<sub>2</sub>O<sub>3</sub>/Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>," J. Mat. Sci., 4 84-88 (1969).
- 22. F. Schmid and D. Viechnicki, "Oriented Eutectic Microstructures in the System Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>," J. Mat. Sci., 5 470-73 (1970).
- M. H. Leipold and J. L. Taylor, "Ultra-High Frequency Induction-Heating Furnace," Technical Report No. 32-32 NASA Contract No. NASw-6, 1961.
- 24. M. Perez Y Jorba and R. Collongues, "Sur Le Chauffage Et La Fusion Sans Creuset Par Induction Haute Frequence de Quelques Oxydes Refractaires," Rev. Hautes Temper. et Refract., 1 21-25 (1964).
- 25. M. E. Packer and M. J. Murray, "A Floating Zone Furnace for Melting Refractory Metals and Metal-like Compounds," J. Sci. Instrum., 5(3) 246-8 (1972).
- 26. F. W. Crossman and A. S. Yue, "Unidirectionally Solidified Ti-TiB and Ti-Ti\_Si, Eutectic Composites," Met. Trans., 2(6) 1545-55 (1971).

- 27. J. S. Haggerty, et al., "Preparation and Characterization of High Quality Single Crystal Refractory Metal Borides and Carbides," Air Force Materials Laboratory Technical Report AFML-TR-68-228, 1968.
- D. Venable and T. P. Kinn, "Radio Frequency Heating," <u>Industrial Electronics Reference Book</u>, John Wiley and Sons, Inc., 1948, 348.
- D. N. Hill, "Internal Zone Melting of Refractory Oxides Using Induced Eddy-Current Heating," M. S. Thesis, Georgia Institute of Technology, 1969.
- 30. C. A. Tudbury, <u>Basics of Induction Heating</u>, Vol. I, John F. Ryder Publisher, Inc., 1960.
- 31. B. Gayet, et al., "Melting UO<sub>2</sub> By High Frequency Induction," Fuel Element Symposium, Worcester, Mass., Nov. 5-6, 1963.
- 32. A. T. Chapman and G. W. Clark, "Growth of UO<sub>2</sub> Single Crystals Using the Floating Zone Technique,"<sup>2</sup>J. Amer. Ceram. Soc., 48(9) 493-95 (1965).
- 33. A. T. Chapman, et al., "UO<sub>2</sub>-W Cermets Produced by Unidirectional Solidification," J. Amer. Ceram. Soc. 53(1) 60-61 (1970).
- 34. M. D. Watson, et al., "Solidification Behavior of Stabilized ZrO<sub>2</sub>-W," J. Amer. Ceram. Soc., 53(2) 112-13 (1970).
- 35. T. A. Johnson and J. F. Benzel, "Unidirectional Solidification of Stabilized Hf0<sub>2</sub>-W," J. Amer. Ceram. Soc., 56(4) 234-35 (1973).
- 36. A. T. Chapman, et al., "Melt-Grown Oxide-Metal Composites," Final Technical Report (No. 5), ARPA Order No. 1637 and Contract DAAHO1-70-C-1157, School of Ceramic Engineering, Georgia Institute of Technology, December, 1972.
- 37. R. P. Nelson and J. J. Rasmussen, "Composite Solidification in the Systems: Cr<sub>2</sub>O<sub>3</sub>-Mo, Cr<sub>2</sub>O<sub>3</sub>-Re, Cr<sub>2</sub>O<sub>3</sub>-W, and MgO-W," J. Amer. Ceram. Soc. 53 527 (1970).
- 38. V. N. Vigodorovich, et al., "Use of Zone Melting with A Temperature Gradient for Physical Chemistry Research," Zavod. Lab., 36(11) 1350-54 (1970).

- 39. Ch. V. Kopetskii and V. A. Marchenko, "Shape of the Crystallization Front During Crucible-Free Zonal Melting," Prib. Tekh. Eksp. 5 231-33 (1971).
- 40. A. T. Chapman, et al., "Unidirectional Solidification Behavior in Refractory Oxide-Metal Systems," J. Cryst. Growth, 13-14 765-771 (1972).
- P. E. Hart, "Observations on Oxide-Metal Eutectic Systems," Proc. Conf. In Situ Composites, National Academy of Sciences, Washington, D. C., 1973, 119-128.
- 42. H. T. Anderson and B. J. Wuensch, "CeO<sub>2</sub>-Y<sub>2</sub>O Solid Solutions," J. Amer. Ceram. Soc., 56(5) 285-86 (1973).
- J. D. McCullough and J. D. Britton, "X-Ray Studies of Rare Earth Oxide Systems: II," J. Amer. Ceram. Soc., 74(20) 5225-27 (1952).
- 44. G. Brauer and H. Gradinger, "Anomalous Mixed Crystals of the Fluorite Lattice Type," Naturwissenschaften, 38(24) 559-60 (1951).
- 45. D. J. M. Bevan, et al., <u>Rare Earth Research, Vol. 3</u>, Science Publishers, Inc., New York, 1965, 441-68.
- 46. G. V. S. Rao, et al., "Electrical Conduction in Binary Oxide Systems of the Type M'02-M"203," Indian Journal of Chemistry, 9(3) 242-46 (1971).
- 47. R. C. Anderson, "Thoria and Yttria," <u>High Temperature</u> <u>Oxides, Part III</u>, (A. M. Alper, ed.), <u>Academic Press</u>, <u>1970</u>, 1-16.
- A. I. Lenov, et al., "The Chemistry of Cerium in Oxide Systems," Chemistry of High-Temperature Materials, (N. A. Toropov, ed.), Consultants Bureau, New York, 1969, 99-103.
- 49. D. J. M. Bevan and J. Kordis, "Oxygen Dissociation Pressures and Phase Relationships in the System CeO<sub>2</sub>-Ce<sub>2</sub>O<sub>3</sub> at High Temperatures," J. Inorg. Nucl. Chem., 26(9) 1509 (1964).
- 50. W. A. Weyl and E. C. Marboe, <u>The Constitution of</u> <u>Glasses</u>, Interscience Publishers, New York, 1962, pp. 203-218.

- 51. R. E. Latta and R. E. Fryxell, "Determination of Solidus-Liquidus Temperatures in UO<sub>2</sub>, Systems (-0.5<x <0.20)," J. of Nucl. Matl., 35 195-210 (1970).</p>
- 52. D. R. Stull, et al., <u>JANAF Thermochemical Tables</u>, National Bureau of Standards, Institute of Applied Technology, August, 1965, dist. CFSTI.
- 53. C. E. Wicks and F. E. Block, <u>Thermodynamic Properties</u> of 65 Elements--Their Oxides, <u>Halides</u>, <u>Carbides</u>, <u>and</u> <u>Nitrides</u>, <u>Bulletin</u> 605, <u>Bureau</u> of <u>Mines</u>, <u>Washington</u>, <u>U. S. Govt</u>. Print. Off., 1963.