

CeO₂-Mo COMPOSITES PRODUCED BY
UNIDIRECTIONAL SOLIDIFICATION

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CeO₂-Mo COMPOSITES PRODUCED BY
UNIDIRECTIONAL SOLIDIFICATION

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SUMMARY

Eutectic structures in the CeO_2 -Mo system were unidirectionally solidified using the internal molten zone technique utilizing radio frequency induction heating. The composites consisted of molybdenum fibers and platelets in an oxide matrix. Investigations into the effects of sample composition, growth rate, and growth atmosphere on the solidification behavior of the CeO_2 -Mo system were studied. Finally, studies into the solubility of molybdenum in molten ceria lead to the investigation of the stoichiometry changes in pure ceria under certain atmospheric conditions.

CHAPTER I

INTRODUCTION

The floating zone method of unidirectional solidification of eutectic alloys has received considerable attention in recent years. Investigations have resulted in growing oriented fibers and platelets of a conducting metal in a semiconductor or insulator with high electrical resistance. Composites of UO_2 -W were the first oxide-metal composites unidirectionally solidified using the floating zone method. The eutectic structures produced in the UO_2 -W system were suitable for high field electron emission devices. Oxide-metal composites are envisioned to have potential applications to mechanical and structural systems as well as further magnetic and electronic applications.

The investigation of the CeO_2 -Mo system was undertaken for several reasons.

1. Previous studies proved that a stable internal molten zone could be established in CeO_2 by radio frequency induction heating.

2. With proper stoichiometry control, CeO_2 is considered a possible host for a variety of low melting metals compared to Mo and W due to its lower melting point.

The purpose of this study was to investigate the eutectic structures formed in the CeO_2 -Mo system by

unidirectional solidification. To accomplish this objective it was necessary to determine the effects of compositional variables, growth atmospheres, growth rates, and stoichiometry changes of pure ceria.

CHAPTER II

SURVEY OF LITERATURE

This chapter is a review of the literature related to the topic of unidirectional solidification of $\text{CeO}_2\text{-Mo}$. The use of induction heating in the internal molten zone technique is briefly explained. A description of eutectic structures, the systems previously studied, and the coupled zone theory are reviewed. A brief explanation of stoichiometry changes in ceria is also included.

Induction Heating

Induction heating is a method for the heating of electrically conducting materials. Crystalline samples of refractory metal oxides,¹⁻⁵ carbides, and borides⁶⁻⁸ have been prepared by various modifications of the induction heating technique. This method of heating is clean, fast, repeatable, and easily automated. Leatherman and Stutz⁹ give several advantages of induction heating:

1. There is no contact required between the work load and the heat source.
2. Very high temperatures can be reached.
3. Heating is rapid.
4. Control of processing and production is simplified.

5. Higher efficiency than many other methods may be achieved.

6. Heat generation can be restricted to a surface zone of the work piece.

7. Heating may be restricted to localized areas.

8. Vacuum or controlled atmospheres may be easily used.

Induction heating is also useful because it allows precise heating and cooling rate control, mixing of the melt in radial and vertical directions by convection currents due to thermal gradients, and formation of a stable and reproducible molten zone.

Radio frequency induction heating is accomplished¹⁰⁻¹¹ by placing a conductive material in an alternating magnetic field produced by energizing a copper coil with alternating current. The magnetic field induces an electromotive force in the material and forms eddy currents. The magnitude of the eddy currents depends on the magnitude of the induced voltage and the impedance of the material. The induced electromotive force produced by the eddy currents results in I^2R heating.

The distribution of the current in a conductor by an alternating magnetic field is given in the following equation:

$$\nabla^2 \bar{J} = j8\pi\mu f \sigma \times 10^{-3} \bar{J}$$

where $\vec{J}$ is the vector current density (amps/cm²), μ is the permeability of the conductor material, σ is the electrical conductivity of the material (ohm cm⁻¹), f is the frequency (Hertz), and j is $\sqrt{-1}$. This equation shows that the current density decreases exponentially from the surface of the conductor to its interior when subjected to an alternating current. This is known as the induction heating "skin effect."

A solid cylindrical specimen¹² will absorb power from an alternating magnetic field in relation to the ratio of the radius to the skin depth. The skin depth is defined as the depth below the surface where current density is reduced to $1/e$ or approximately 37% of the surface density. The ratio of the radius of the work piece to the skin depth must exceed four or five to achieve sufficient heating in the piece. The skin depth δ (cm) is related to the frequency (Hertz) and the electrical conductivity σ (ohm cm)⁻¹ by the equation

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

The operating frequency of commercial rf generators (3-5 megahertz) is high enough for the melting of metals. However, it is not high enough for an adequate skin effect in insulating (low σ) oxide materials. The frequency is also limited by other considerations. Above a frequency of 30 MHz, the current is very difficult to contain on the surface

of the copper tubing. In addition, arcing between the turns of the coils and to the specimen as well as increased ionization of gases further limit the 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.

Induction Melting of Oxides and Oxide-Metal Mixtures

A number of refractory metal oxides have been melted by induction melting devices. Hill¹¹ successfully initiated molten zones in pellets of CeO_2 , TiO_2 , $\text{Ca}_{.1}\text{Zr}_{.9}\text{O}_{1.9}$, Cr_2O_3 , and BaTiO_3 using from 6 to 30 MHz fields. During the investigation of melt-grown oxide-metal composites, Chapman *et al.*¹⁴ melted a number of refractory oxide compounds including: $\text{NiO}:\text{TiO}_2$, TiO_{2-x} , $\text{Cr}_2\text{O}_3 + 40 \text{ wt. } \% \text{ ZrO}_2$, and $\text{ZnO} + 20 \text{ wt. } \% \text{ Nb}_2\text{O}_5$. Chapman and Clark¹⁵ 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 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 the thermal gradients.

The magnitude of the thermal conductivity played an

important role in the induction melting of oxides. Due to the extensive cooling by surface radiation and the inherent low value of the thermal conductivity of most oxides¹³ the outer part of the material was kept solid, the center being melted. The oxides acted as their own crucible and contamination was avoided.

Chapman and co-workers¹⁴ used the furnace and growth apparatus shown in Figures 1 and 2. In this technique uniaxially or isostatically pressed rods of the oxide-metal mixture were sintered inside rf heated molybdenum tubes in the desired atmosphere (N_2 , H_2/N_2 , H_2/H_2O , CO/CO_2) to densify and preheat the material. The molybdenum tube heaters were separated when the temperature had increased sufficiently to allow direct coupling to the oxides. This exposed the pellet to an rf field of 3 to 30 MHz depending on the material to be melted. The increased temperature, electrical conductivity, and resistance heating resulted in the melting of the interior of the pellet. By slowly lowering the pellet through the rf field the molten zone was moved upward and unidirectional solidification was achieved.

Chapman and co-workers¹⁴ also developed and produced melt-grown oxide-metal composites for high field electron emission testing. Using induction melting and unidirectional solidification a number of refractory oxide-metal composites (UO_2 -W, UO_2 -Ta, $HfO_2(Y_2O_3)$ -W, $ZrO_2(Y_2O_3)$ -W, $Y_2O_3(CeO_2)$ -W or Mo , $Gd_2O_3(CeO_2)$ -W or Mo , $Nd_2O_3(CeO_2)$ -W or Mo , and

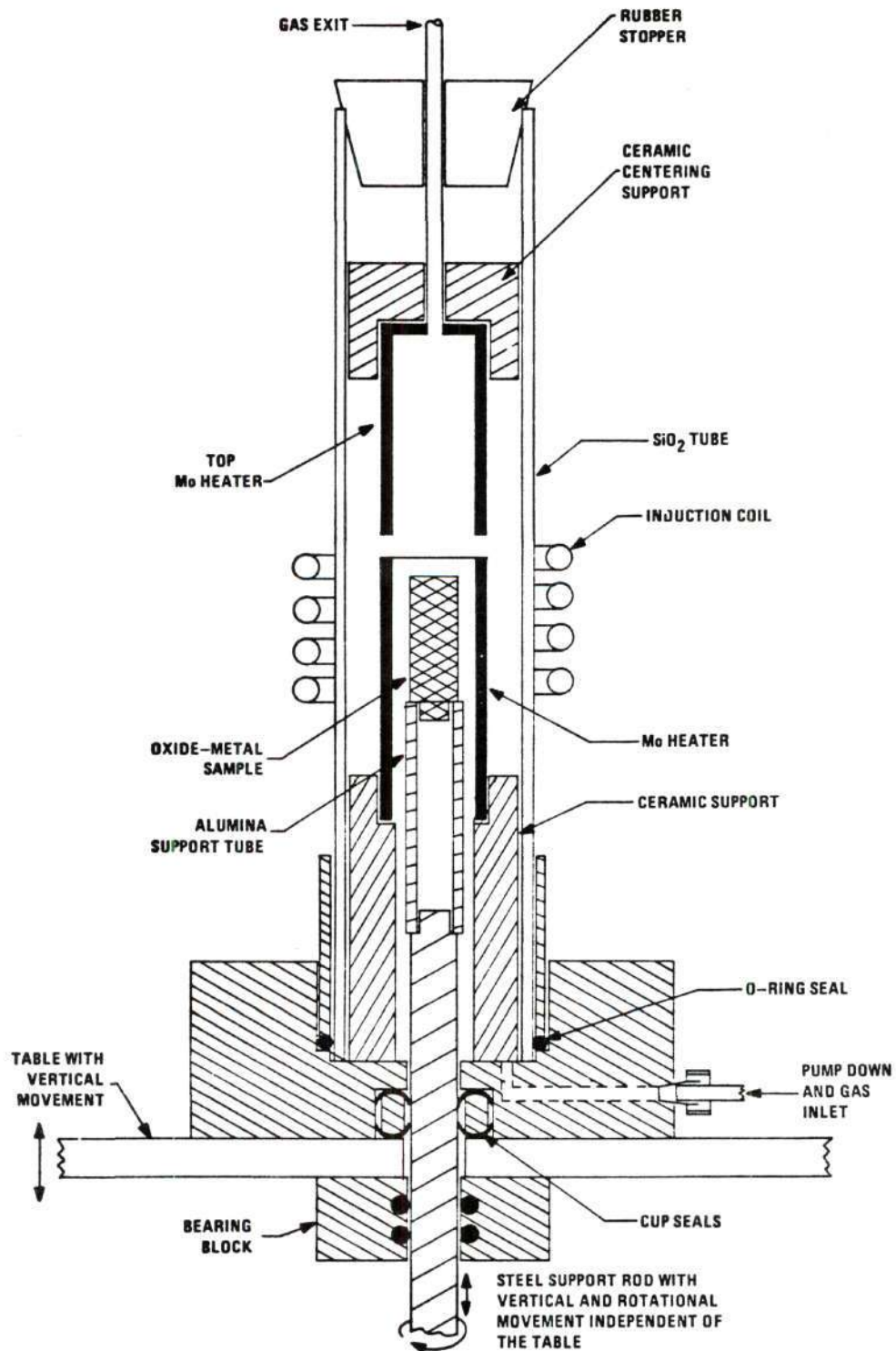


Figure 1. Schematic Diagram of the Facility for the Growth of Oxide-Metal Composites.

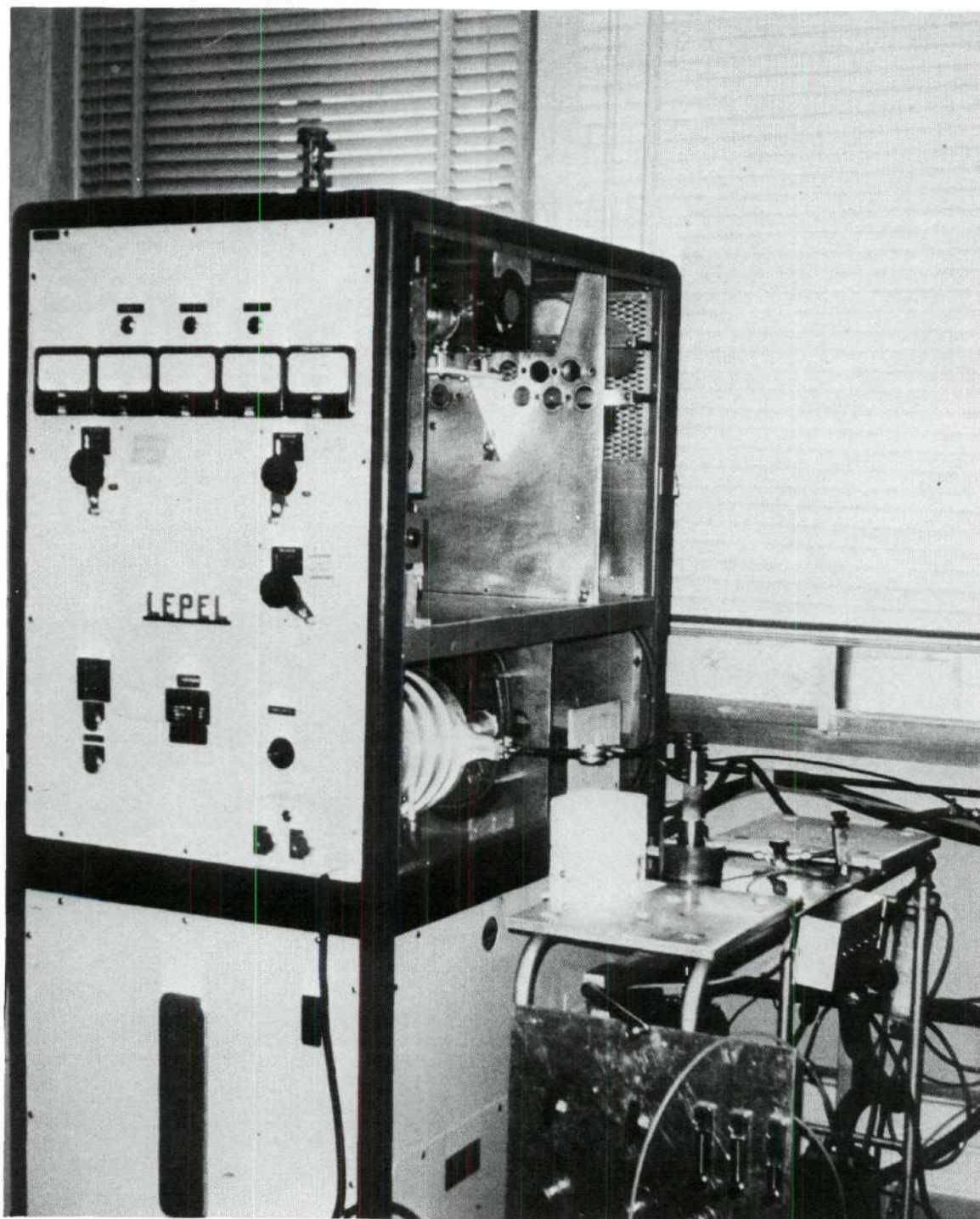


Figure 2. Overall View of the Dual Frequency of Generator and Composite Growth Equipment.

$\text{La}_2\text{O}_3(\text{CeO}_2)\text{-W or Mo}$) were produced. This team of investigators also established some of the parameters that influence composite growth (Table 1).

Table 1. Parameters Influencing Composite Growth in Refractory Oxide-Metal Systems after Chapman et al.¹⁴

-
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
-

Eutectic Structures

Scheil¹⁶ developed a classification of eutectics based on solidification. The structures are divided into

three classes: (a) normal, (b) anomalous, and (c) degenerate. Structures that are of highly ordered nature such as lamellar and fiber structures are classified as normal. In an anomalous eutectic the phases are still closely intermingled but there is less regularity. Degenerate eutectics have a minimum association of phases. Since normal structures are the most important they are described in more detail below.

Tiller¹⁷ and Hogan¹⁸ presented the characteristics of the normal eutectic structure. The phases of a normal eutectic solidify simultaneously in a close physical association. The solid phases grow into the liquid by movement of a uniform front which may be almost planar, the lamellae or fibers solidify parallel to the growth direction and normal to the liquid-solid interface. The lamellae or fibers are uniformly spaced for given growth conditions. As the solidification rate increases the spacing between the fibers and/or lamellae will decrease.

The eutectic structure does not necessarily occur at the eutectic composition given by the phase diagram. Under certain freezing conditions the eutectic structure may be found at compositions greatly different from the equilibrium composition.

The School of Ceramic Engineering at the Georgia Institute of Technology¹⁴ and the Oak Ridge National Laboratory Metals and Ceramic Division conducted

investigations of oxide-metal systems using the floating zone technique. Eutectic structures of aligned metal fibers in a continuous oxide matrix were observed in the following oxide-metal systems: $\text{UO}_2\text{-W}$,¹⁹⁻²² $\text{HfO}_2(\text{Y}_2\text{O}_3)\text{-W}$,^{23,24} $\text{ZrO}_2(\text{Y}_2\text{O}_3)\text{-W}$,²⁵⁻²⁷ and $\text{CeO}_2\text{-Mo}$.¹⁴ Oxide-metal eutectic were also observed in the following CeO_2 doped systems:¹⁴ $\text{Nd}_2\text{O}_3(\text{CeO}_2)\text{-Mo}$ or W , $\text{La}_2\text{O}_3(\text{CeO}_2)\text{-Mo}$ or W , $\text{Eu}_2\text{O}_3(\text{CeO}_2)\text{-Mo}$, $\text{Ho}_2\text{O}_3(\text{CeO}_2)\text{-Mo}$, and $\text{Gd}_2\text{O}_3(\text{CeO}_2)\text{-Mo}$ or W .

The $\text{UO}_2\text{-W}$ ¹⁹⁻²² system was the first system investigated and has received the most attention. Chapman *et al.*¹⁹ using a modified floating zone process melted UO_2 plus 5 to 15 wt. % W pressed rods to produce well ordered $\text{UO}_2\text{-W}$ structures with metallic lamellar and fiber arrays.

Stabilized $\text{ZrO}_2\text{-W}$ was successfully unidirectionally solidified by Watson *et al.*²⁶ Johnson and Benzel²⁴ produced $\text{HfO}_2(\text{Y}_2\text{O}_3)\text{-W}$ composites with fiber densities of $7.2 \times 10^7/\text{cm}^2$ and fiber diameters of 0.15 μm .

Coupled Zone Theory

This theory is explained in detail by both Watson²⁸ and Graves,³¹ therefore, only a review is presented here. The theory of coupled zone growth is based on a concept developed by Scheil.¹⁶ This concept later reviewed by Tiller¹⁷ and Hogan¹⁸ assumed that the solidification rate of any solid phase is proportional to the degree of supersaturation of the melt with respect to that phase. A

degree of supersaturation is necessary for growth to occur and the rate of solidification increases with increasing supersaturation. Supersaturation can be produced by a compositional change or by supercooling.

The coupled zone as defined by Brady²⁹ and named by Kofler³⁰ is a region below the eutectic temperature into which supercooling can lower the temperature of the liquid. In this region there is a compositional range from which eutectic structures can be solidified on either side of the equilibrium eutectic point (Figure 3). Solidification of the melt produces a normal eutectic structure.

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

Figure 3 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,

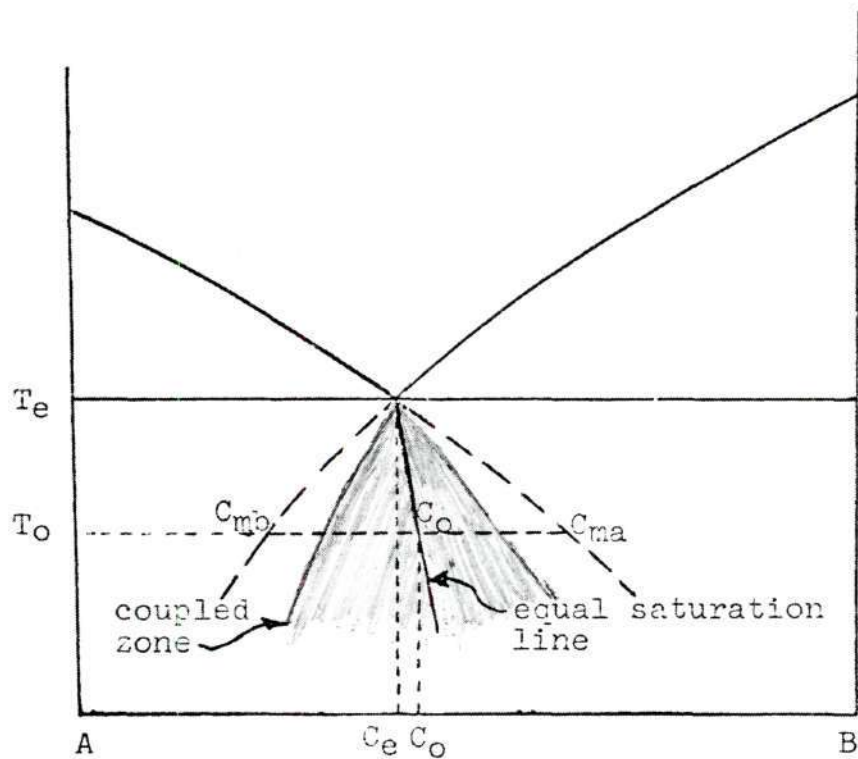


Figure 3. The Coupled Zone and Equal Saturation Line in a System in which the Extended Liquidus Lines are Roughly Symmetrical about the Eutectic Point. The Distance $C_{mb} - C_o$ Equals the Distance $C_{ma} - C_o$.²⁸

if a melt of composition C_e is supercooled to T_0 , 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.

Kofler³⁰ described two possible types of coupled regions as shown in Figures 3 and 4. In Figure 3 the coupled region is almost symmetrical so that a normal eutectic structure would be achieved. Alloys either side of C_e would solidify as pure eutectic if enough undercooling were achieved. Figure 4 represents a different situation which is typical of anomalous eutectic structures. The coupled zone is skewed toward the higher melting component instead of centered below the eutectic point. The skew is caused by the greater degree of supercooling of the liquid with the higher melting point. Due to the unequal undercooling even if the saturation of both phases is the same the solidification rates will be different. The inequality of solidification rates at equal supersaturation produces the displacement of the coupled zone to a region in which the rates are equal.

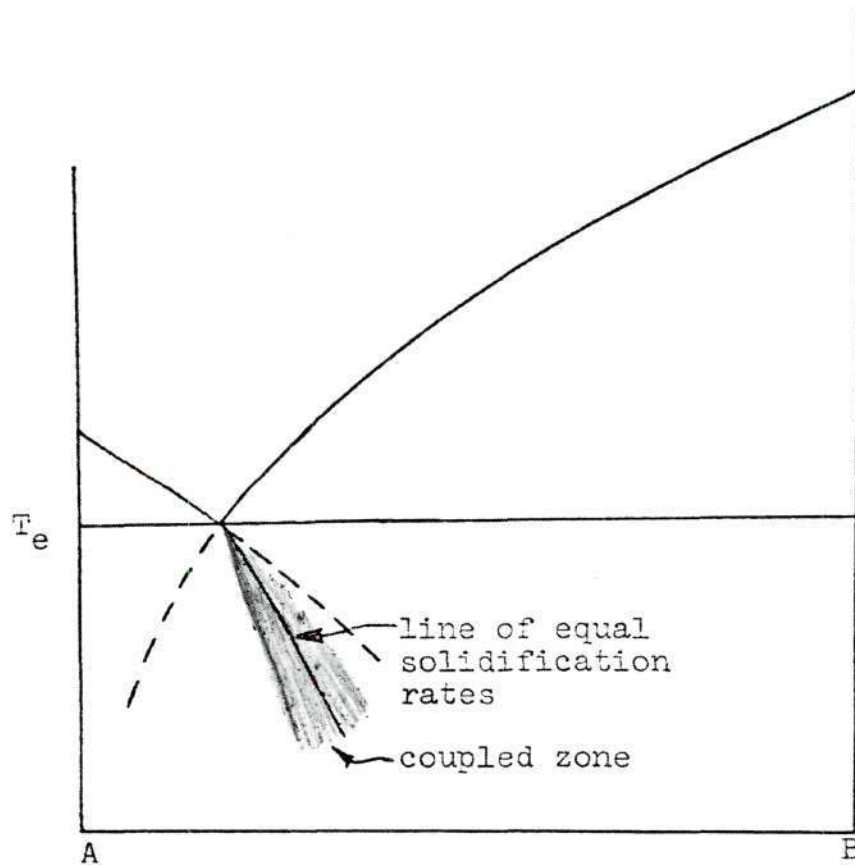


Figure 4. The Skewed Coupled Zone in Systems with Unsymmetrical Liquidus Lines.

Ceria

Ceria is one of the two principal oxides of cerium that is stable in air. It has a fluorite-type structure with an approximate melting point of $2340 \pm 25^\circ\text{C}$. The distinguishing feature of the cerium ion³² is the nature of its transition from the tetra- to tri-valent state. This dissociation of CeO_2 to Ce_2O_3 has been the subject of research by several different investigators. A review of their findings is presented here.

Rienacher and Birkenstaedt²³ investigated the reduction of CeO_2 at $250\text{--}350^\circ\text{C}$. They observed that CeO_2 was reduced as much as 12% in hydrogen at these temperatures and still showed only the x-ray diffraction lines of CeO_2 . It was also noted that the CeO_2 underwent a color change (yellowish-white to gray-blue) when reduced to Ce_2O_3 at 1250°C .

Sata and Yoshimura³⁴ made a similar study on the reduction of CeO_2 at 600 to 1700°C in hydrogen using thermogravimetric differential thermal analysis, dilatometric, and x-ray analytical methods. This investigation discussed the color changes that were prominent during reduction and that a departure from stoichiometry occurred and increased with temperature up to $\text{CeO}_{1.53}$ at 1700°C .

Bevan and Kordis³⁵ made a comprehensive study of the influence of oxygen pressure on the stoichiometry of CeO_2 - $\text{CeO}_{1.5}$ at temperatures of 636 to 1169°C . To establish

definite oxygen pressures, either CO/CO_2 , $\text{H}_2/\text{H}_2\text{O}$, or $\text{H}_2/\text{H}_2\text{O}-\text{Cr}/\text{Cr}_2\text{O}_3$ buffered mixtures were used as gaseous mediums brought to equilibrium with the heated ceria samples.

Figure 5 shows plots of $1/2 \log P_{\text{O}_2}$ (atm) against oxide composition for temperatures ranging from 636 to 1169°C. It is obvious that data from all three techniques of controlling oxygen potential agree well where comparison is possible.

Bevan and Kordis³⁵ believed that their data represented true equilibrium values, since the same data were observed for both oxidation and reduction when the experimental temperature was above 872°C. Some of the results at temperatures below 872°C were not equilibrium values, however, the authors were able to present an hypothesis based on experimental data that allowed the calculation of theoretical equilibrium data. The hypothesis was that the equilibrium values of the free energy ($1/2 RT \ln P_{\text{O}_2}$) in the range investigated varied linearly with temperature. Using this hypothesis it was possible to construct a phase diagram for the system CeO_x ($1.5 \leq x \leq 2.0$) (Figure 6). Using high temperature x-ray methods and tensimetric measurements with $\text{H}_2/\text{H}_2\text{O}$ atmospheres Brauer, Gingerich, and Holtschmidt^{36,37,38} agreed with this diagram. Fair agreement of this data was also reached by Kuznetsov, Belyi,

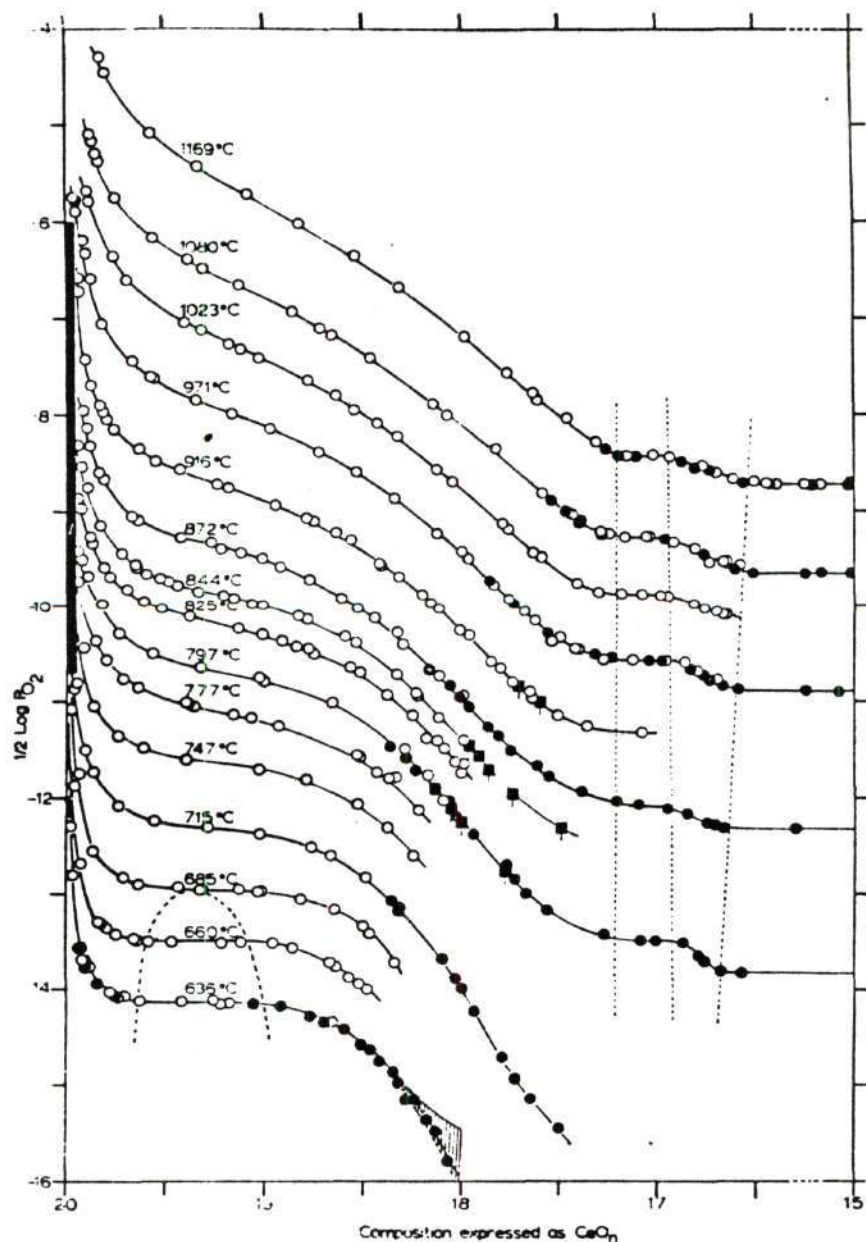


Figure 5. Equilibrium Oxygen Partial Pressure as a Function of Molten Ceria Composition for Temperatures of 636 to 1169°C.

- CO_2/CO
- $\text{H}_2\text{O}/\text{H}_2$
- $\text{H}_2\text{O}/\text{H}_2\text{-Cr/Cr}_2\text{O}_3$ Buffer

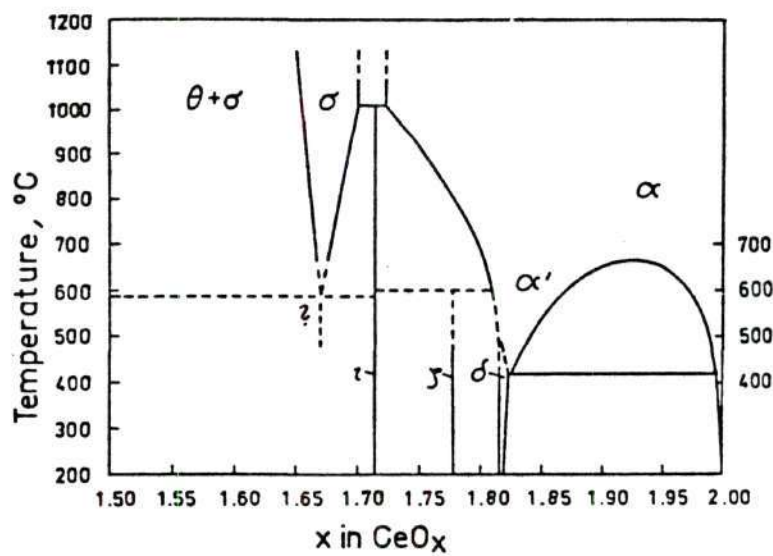


Figure 6. Phase Diagram for the System CeO_x ($1.5 < x < 2.0$) Derived and Constructed by Bevan and Kordis.³⁵

and Rezukhina³⁹ whose data were based mainly on electro-
motive force measurements.

CHAPTER III

PROCEDURE AND EQUIPMENT

This section will explain in detail the general procedure used for producing CeO_2 -Mo composites. The subjects explained in this section include: sample preparation, growth apparatus, stoichiometry changes, and sample examination. Due to the large number of variables that effect composite growth slight variations of the general procedure were sometimes necessary.

Sample Preparation

Samples inductionally melted were small cylinders 1.9 cm in diameter and about 3.5-4.5 cm long. Previous experiments showed this to be an ideal size for induction melting with the rf generator. Batches were prepared by weighing the required ingredients, i.e., CeO_2 powder (Fisher Chemical Co., 99.6% purity) and molybdenum powder (Teledyne Wah Chang, 99.9% purity), then mechanically mixing these powders with a mortar and pestal.

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. Powder was added to top off the die, and this was pressed to 5000 psi. The pressure

was released, raised to 5000 psi, and released.

Growth Apparatus

Green samples were placed in the apparatus previously shown in Figure 1 in the Survey of Literature, which permitted vertical translation of the sample, vertical positioning of molybdenum pre- and post-heaters (22 mm O.D., 1 mm wall thickness), and atmosphere control.

The sample was supported by an Al_2O_3 spacer fitted over a hardened steel rod extending through the table to a hydraulic cylinder used to lower the sample. A hydraulic cylinder rather than a mechanical system allowed smooth lowering, minimizing growth fluctuations caused by non-uniform lowering rate and provided a more stable liquid-solid solidification front. A porous Al_2O_3 spacer held the lower molybdenum shield in position around the pellet. An upper molybdenum tube controlled the shape of the rf field and limited the size of the growth zone in the pellet. All of these components were enclosed inside a 35 mm ID silica tube. The system was evacuated to 500 millitorr with a mechanical pump and controlled ratios of $\text{N}_2:\text{H}_2$, $\text{N}_2:\text{CO}/\text{CO}_2$, $\text{H}_2:\text{H}_2\text{O}$, and $\text{CO}:\text{CO}_2$ were passed through the system (entering at the bottom and exiting at the top) at rates between 400-500 cc/min.

A Lepel dual frequency rf generator (model T-10-3 MC-HW), operating at 3.6 MHz was used in all experiments.

Temperatures were optically measured with no correction for emissivity radiation losses due to the vitreous silica tube or to vapor deposits.

During preheat, rf powder was automatically controlled from room temperature to approximately 1500°C, which required about fifty minutes. Sintering occurred during this period.

After preheating, the sample was coupled directly to the rf field. Power was decreased about 20%, the preheat tube was quickly lowered out of the induction coil, and the power was increased until coupling occurred. After 10 to 30 seconds the interior of the pellet melted, causing a simultaneous decrease in the plate voltage and an increase in the plate current. On melting the power was quickly cut back to prevent the molten interior from melting through the outer skin.

After melting, the power input was stabilized, the lower molybdenum tube was raised inside the coil (about two turns), and the upper molybdenum tube was pushed down inside the coil over the pellet, leaving a fixed separation of 26 mm centered about the molten zone. Optimum placement of the Mo tube shields was based on experience.

Unidirectional solidification was achieved by lowering the pellet through the induction coil. Variations in the lowering rate were examined as one of the factors effecting composite growth. For experiments not concerned

with lowering rate, a rate approximately two centimeters per hour was used. After solidification, power was reduced slowly by the automatic power controller to minimize cracking caused by rapid thermal changes.

Stoichiometry Changes

To determine stoichiometry changes that occurred in pure CeO_2 during rf melting the same basic procedure was used with a few exceptions. The top molybdenum pre- and post-heater was not used to confine the molten zone and the pellet was not lowered. The pellet remained molten in the coupled zone until equilibrium was reached and the reaction between the CeO_2 and the atmosphere was completed. The schematic diagram (Figure 7) shows the flow meters used to control the inlet gases, and the aluminum oxide hygrometers used to monitor the H_2O content of both the inlet and exhaust gases when $\text{H}_2\text{O}/\text{H}_2$ mixtures were employed. Typical gas flow rates were between 400-500 cc/min.

Equal H_2O content at the inlet and outlet probes indicated the establishment of equilibrium and melting was continued an additional hour or two after reaching equilibrium. Samples were quenched by stopping the rf heating. Cooling below 1000°C was accomplished in 30 to 45 seconds. The samples usually remained molten between 3 to 8 hours.

Several experiments were performed in CO/CO_2 atmospheres to achieve a higher oxygen potential than available

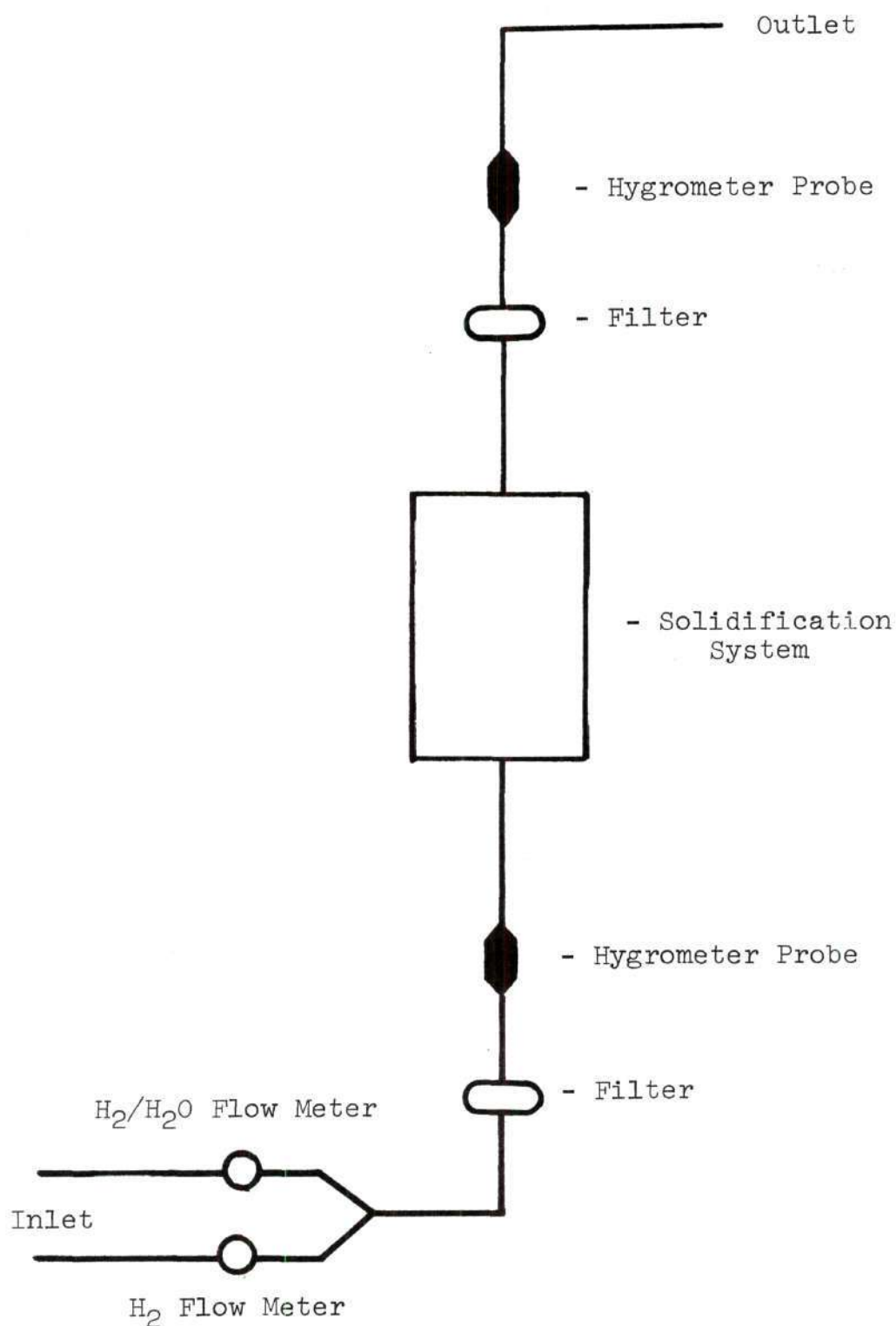


Figure 7. Schematic Diagram of Gas Mixture Inlet and Outlet Lines Showing the Placement of Hygrometer Probes.

with $\text{H}_2\text{O}/\text{H}_2$ using commercial tanks of CO and CO_2 . Different mixtures were achieved by the use of flow meters. In these runs the CeO_2 samples were initially heated in N_2 prior to melting. The N_2 atmosphere was replaced with the CO/ CO_2 atmosphere before coupling. Gas flow rates were approximately 500 cc/min.

After melting and quenching the CeO_{2-x} samples, they were crushed and the molten material (easily distinguished from the unmelted skin) was hand selected and the O/Ce ratio determined by ignition to CeO_2 (by heating for 24 hours at 700°C in air). Weight-gain studies were made of the fused materials. Two samples of each material were weighed and heated in the furnace. Any weight gain recorded was assumed to be due only to an increase in the oxygen content of the heated sample. Using this assumption it was possible to determine the oxygen-to-metal ratio of the ceria samples. The method used to calculate the oxygen-to-metal ratios is outlined in Appendix A.

Sample Examination

Sample examination was mostly done by metallographic techniques. Pellets were usually cut in half parallel to the lowering direction using a diamond saw. The samples were ground flat using SiC abrasive papers (180, 320, and 600 grit) and then polished on a nylon covered wheel with one micron diamond paste. Photomicrographs were taken with

a Reichert MeF metallograph equipped for dark field as well as normal bright field viewing. In dark field viewing the fibers slightly beneath the surface were visible while bright field viewing showed only surface features.

CHAPTER IV

RESULTS AND DISCUSSION

The results of this work fall broadly into three areas, each of which is dependent on the others yet distinct enough to be discussed separately. First, the effect of varying the CeO_2/Mo ratio was determined. Secondly, after the optimum CeO_2/Mo ratio was established this mixture was used to determine the effect of various growth atmosphere on CeO_2 -Mo composite structures. And lastly, as a consequence of the growth atmosphere studies, the stoichiometry changes in pure CeO_2 were investigated in various gas mixtures.

Effects of Oxide/Metal Ratio

Initial investigations studied the effect of molybdenum concentration from 2 to 20 wt. % on the CeO_2 -Mo eutectic structure. Samples were analyzed for the geometry of the molybdenum and the continuity of the metal phase. A summary of the results is presented in Table 2. A typical longitudinal section of a $\text{CeO}_2 + 10$ wt. % Mo structure with uniform geometry is shown in Figure 8. The transverse view of this sample ($\text{CeO}_2 + 10$ wt. % Mo) revealed that the composite contained both fibers and platelets (Figure 9). These photos show the uniformity of the microstructure that

Table 2. Effects of Varying the Molybdenum Content on the Unidirectionally Solidified CeO_2 -Mo Composites.*

Composition	Comments
CeO_2 + 2 wt. % Mo	Trace of molybdenum, no fiber or platelet growth, insufficient metal.
CeO_2 + 4 wt. % Mo	Bottom--no metal present Middle--trace of metal and oxide dendrites Top--Some fiber and platelet growth and areas of oxide dendrites.
CeO_2 + 6 wt. % Mo	Bottom--little growth, fibers and platelets Middle--some growth, fibers and platelets, some oxide dendrites Top--some continuous growth, mostly oxide dendrites.
CeO_2 + 8 wt. % Mo	Bottom--scattered growth, oxide dendrites Middle--increase in growth, oxide dendrites Top--areas of continuous growth, oxide dendrites.
CeO_2 + 10 wt. % Mo	Very good growth in the top of sample, bottom contained several areas of primary oxide.
CeO_2 + 13 wt. % Mo	Good growth, some excess metal present.
CeO_2 + 15 wt. % Mo	Globs of excess molybdenum, molybdenum dendrites.
CeO_2 + 20 wt. % Mo	Large globs of excess molybdenum, molybdenum dendrites.

*For all experiments the growth rate was 1.81 cm/hr and the growth atmosphere was 90 v/o N_2 + 10 v/o H_2 .

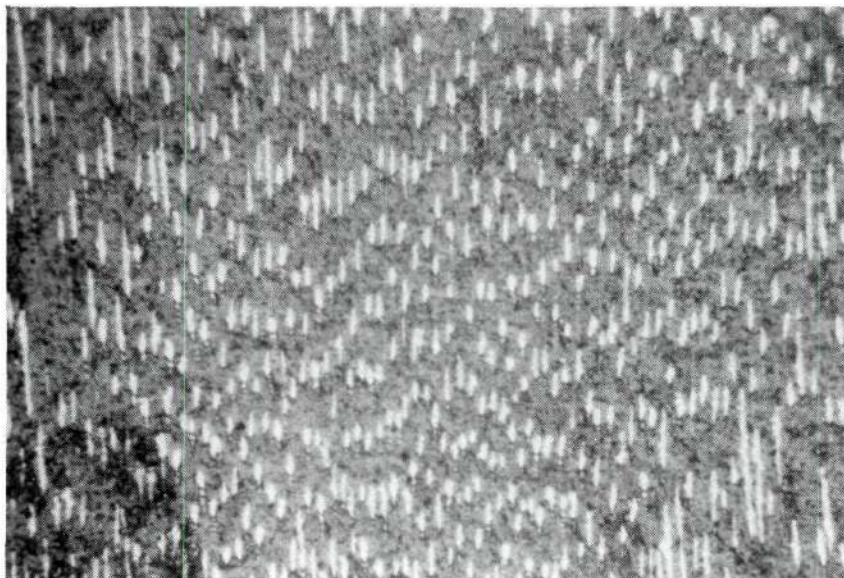


Figure 8. Longitudinal Section of $\text{CeO}_2 + 10 \text{ wt. \% Mo}$ Sample Unidirectionally Solidified. Bright Field, X1050.

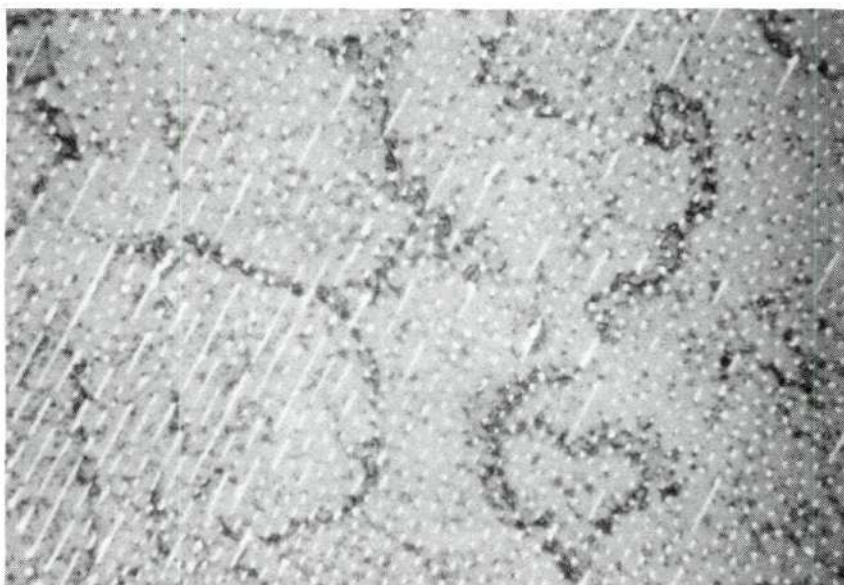


Figure 9. Transverse Section of $\text{CeO}_2 + 10 \text{ wt. \% Mo}$ Sample Unidirectionally Solidified. Bright Field, X1050.

is called "good composite growth" in Table 2 and in subsequent descriptions of composite growth.

Figures 10 and 11 show a transverse and longitudinal section, respectively, at approximately 600X, of compositions with less than 9 wt. % molybdenum concentration. It will be noted in the longitudinal section that there is ordered growth (fibers and platelets) in some areas while in others there are areas of oxide dendrites (primary oxide phase). The amount of primary oxide present decreased as the molybdenum concentration increased. Thorough examinations of all samples containing less than 9 wt. % molybdenum showed few or no fibers and/or platelets in the bottom of the sample, an increase in growth (fibers and platelets) in the middle, and still more growth in the top of the pellet. This seems to indicate that as the pellet was lowered through the rf zone the metal remained molten until it reached a concentration that allowed eutectic growth in the ceria matrix.

The formation of primary oxide was explained by Chapman et al.¹⁴ who state that the formation of primary oxide occurred because as the cooling of the oxide-rich melt proceeded, the primary excess phase solidified at a higher temperature than the eutectic temperature. Therefore, the remaining liquid moved down the liquidus line toward the eutectic composition. Since there was, at some later time, sufficient undercooling to initiate nucleation

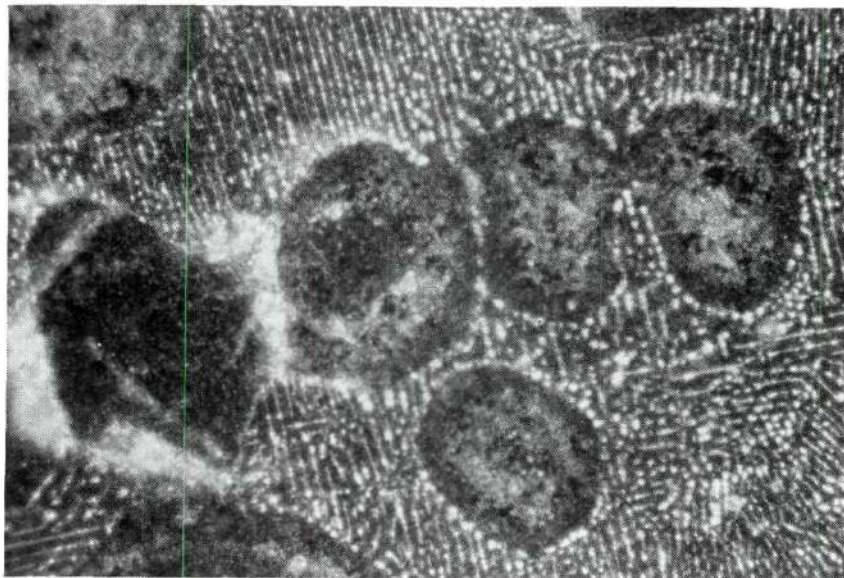


Figure 10. Transverse section of $\text{CeO}_2 + 8 \text{ wt. \% Mo}$ Sample Unidirectionally Solidified. Dark Field, X600.

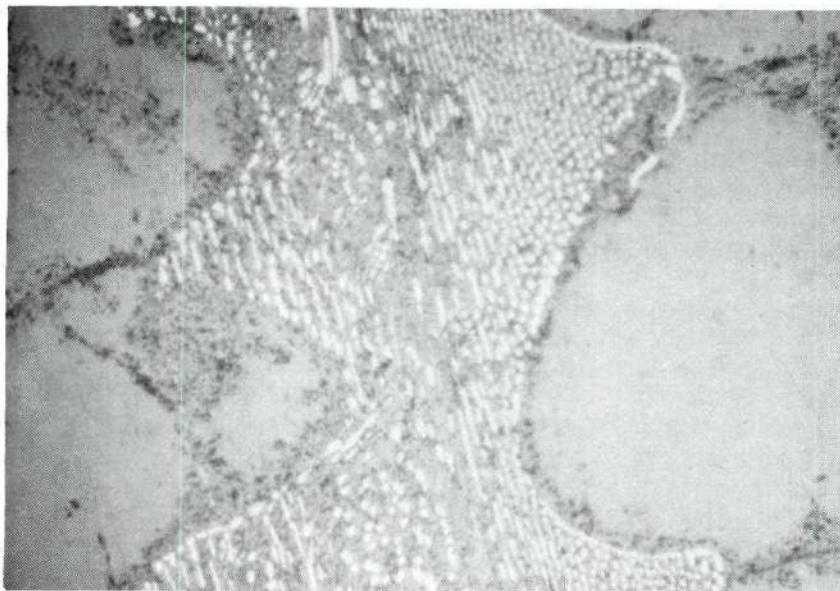


Figure 11. Longitudinal Section of $\text{CeO}_2 + 8 \text{ wt. \% Mo}$ Sample Unidirectionally Solidified. Bright Field, X600.

of the remaining melt, the resulting structure was primary oxide surrounded by an area of near eutectic composition. This explanation is analogous to the skewed coupled zone concept. Since the liquid was rich in oxide components and the coupled zone was skewed toward the molybdenum component which has a higher melting point, the oxide phase solidified at a faster rate than the eutectic structure. Primary oxide regions solidified extending into the liquid above the normally flat liquid-solid interface. The liquid between these primary oxide regions was depleted of the oxide components moving the liquid composition into the coupled region.

In the samples with 11 wt. % molybdenum or greater, the melt was apparently too far on the molybdenum-rich side of the eutectic to allow good composite growth. Figures 12 and 13 are photomicrographs of a $\text{CeO}_2 + 20 \text{ wt. \% Mo}$ sample. The microstructure remained much the same until the molybdenum concentration was reduced below 11 wt. % (as the melt was still metal-rich until reaching this composition).

Compositions containing around 90 wt. % $\text{CeO}_2 + 10 \text{ wt. \% Mo}$ were found to give consistently good growth over a wide range of conditions. This composition did not allow the area ahead of the solidification front to become depleted of molybdenum and yet did not contain so much molybdenum that metal dendrites would form. This ratio

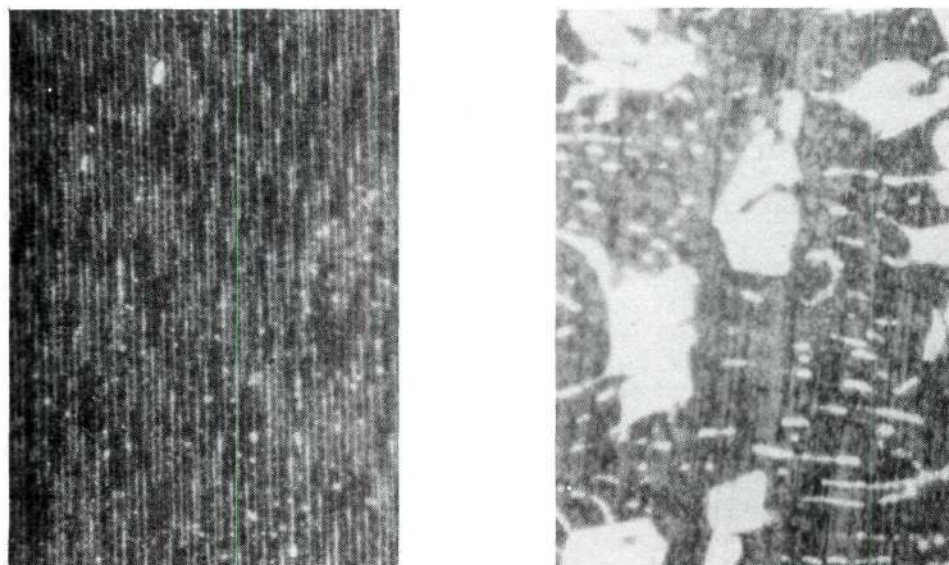


Figure 12. Longitudinal Section of $\text{CeO}_2 + 20 \text{ wt. \% MO}$ Samples Unidirectionally Solidified.

(a) Fiber Growth
Dark Field, X600

(b) Excess Metal
Bright Field,
X600

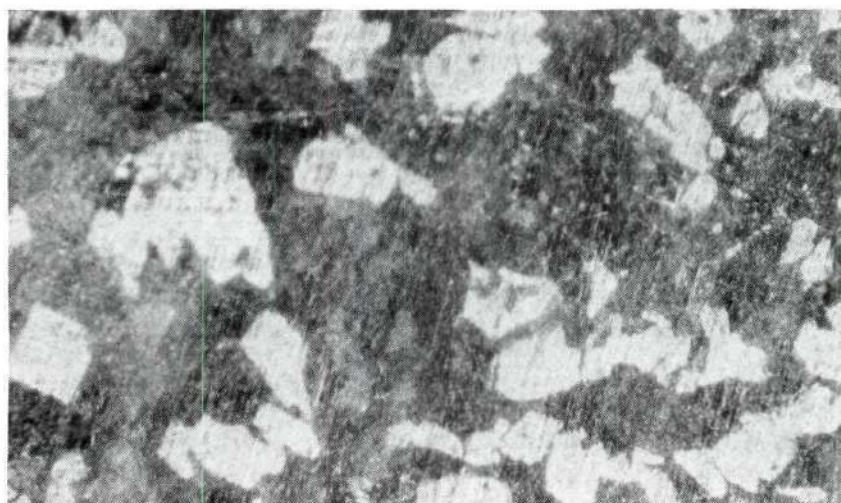


Figure 13. Transverse Section of $\text{CeO}_2 + 20 \text{ wt. \% Mo}$ Sample Unidirectionally Solidified Showing Molybdenum Dendrites. Bright Field, X600.

was used to explore the effect of growth rate on the composite structure.

Growth Rate

The influence of lowering rates on composite geometries was studied using CeO_2 + 10 wt. % Mo samples solidified in an atmosphere consisting of N_2 - 10 v/o H_2 (Table 3).

Table 3. Effect of Growth Rate on Unidirectionally Solidified CeO_2 + 10 wt. % Mo Composites*

Sample	Growth Rate (cm/hr)	Comments
27-17	2.93	Scattered growth platelets and fibers, large oxide voids.
27-26	3.00	Poor growth, large areas of primary oxide.
27-33	2.40	Scattered fibers and platelets, large areas of oxide dendrites.
27-34	1.51	Good growth, few areas of primary oxide phase.
27-35	1.00	Very good growth, very few areas of primary oxide phase.
27-36	1.00	Very good growth.
27-42	1.94	Good growth, a few areas of oxide dendrites.

*The growth atmosphere used for all samples was a 90 v/o N_2 - 10 v/o H_2 .

The lowering rates were varied from 1.0 to 3.0 cm/hr. At the slower growth rates, 1.0-1.94 cm/hr, the most uniform

and extensive composite geometries were achieved. A typical structure is shown in Figure 14. At the fast growth rates, 2 cm/hr and above, the occurrence of primary oxide areas (dendrites) increased (Figure 15).

Growth Atmosphere

Once the composition that produced the best samples was determined a study on the effect of growth atmosphere on eutectic structures was undertaken. The atmospheres used included ratios of $N_2:H_2$, $N_2:CO/CO_2$, and H_2/H_2O .

Most of the early composite growth in the CeO_2 -Mo system was performed in a $N_2:H_2$ atmosphere, typically containing approximately 10 v/o H_2 , using molybdenum pre- and post-heaters. Tables 2 and 3 give the various compositions and growth rates that were investigated in an N_2 - 10 v/o H_2 atmosphere. Some general observations can be made from this data. All of the samples solidified contained some primary oxide phase. Oxide dendrites (Figure 16) appeared most often at the bottom of the composite growth indicating that solidification started with an oxide-rich composition initially solidifying above the eutectic temperature. The majority of the metal usually appeared as ordered growth consisting of both fibers and platelets (Figures 17 and 18). While this indicated that there was some mutual solubility in the liquid between the molybdenum and ceria, there was too much solubility to produce only fibers.

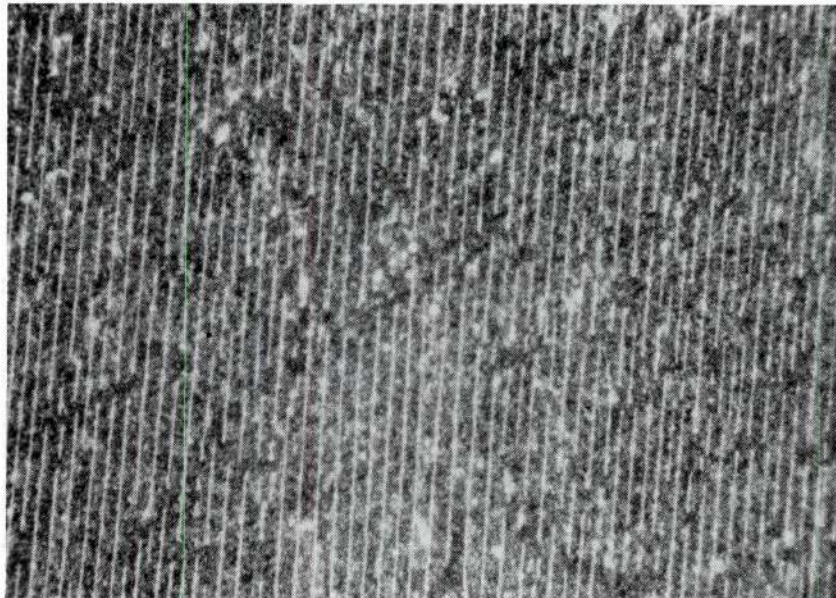


Figure 14. Longitudinal Section of $\text{CeO}_2 + 10 \text{ wt. } \% \text{ Mo}$ Sample Solidified in a $\text{N}_2 - 10 \text{ v/o } \text{H}_2$ Atmosphere. Growth Rate 1.5 cm/hr . Dark Field, $\times 600$.

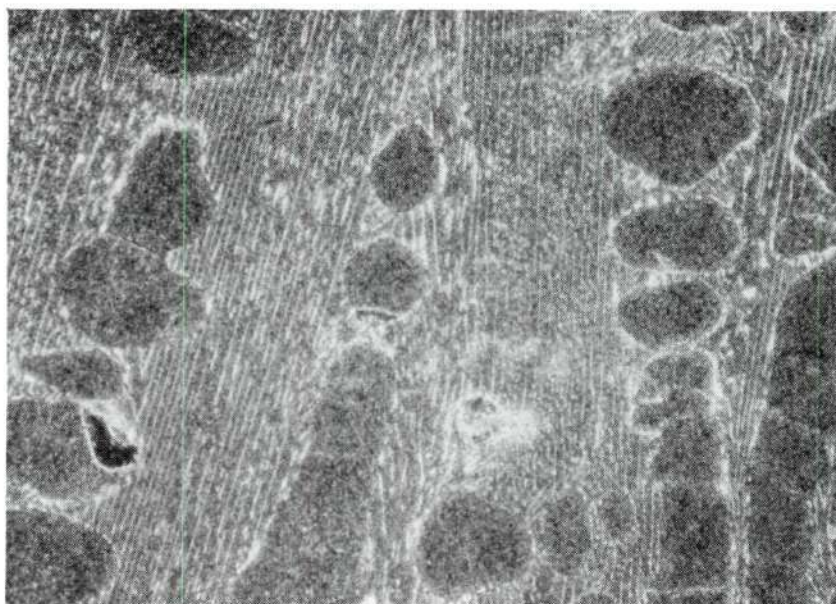


Figure 15. Longitudinal Section of $\text{CeO}_2 + 10 \text{ wt. } \% \text{ Mo}$ Sample (Displaying Oxide Dendrites) Solidified in a $\text{N}_2 - 10 \text{ v/o } \text{H}_2$ Atmosphere at 2.8 cm/hr . Dark Field, $\times 600$.

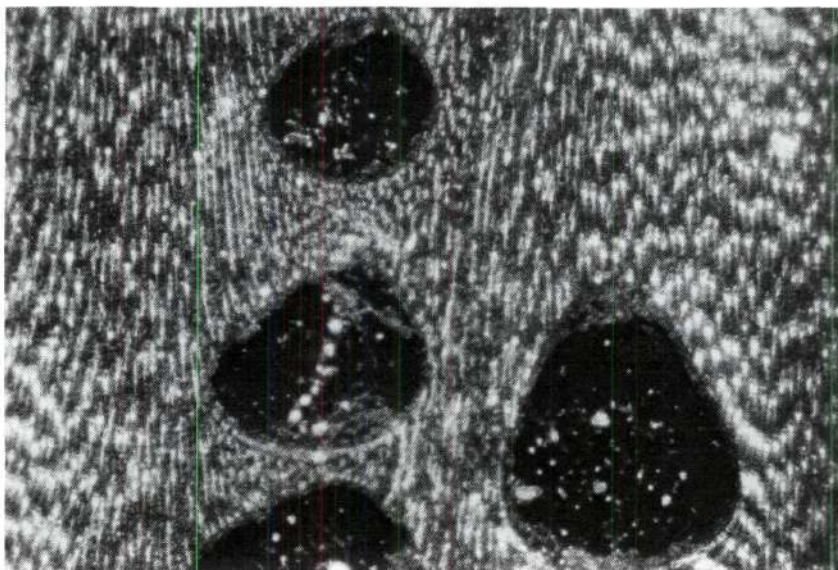


Figure 16. Longitudinal Section of $\text{CeO}_2 + 10 \text{ wt. } \% \text{ Mo}$ Sample Unidirectionally Solidified in a $\text{N}_2 - 10 \text{ v/o } \text{H}_2$ Atmosphere Showing Oxide Dendrites. Dark Field, X600.

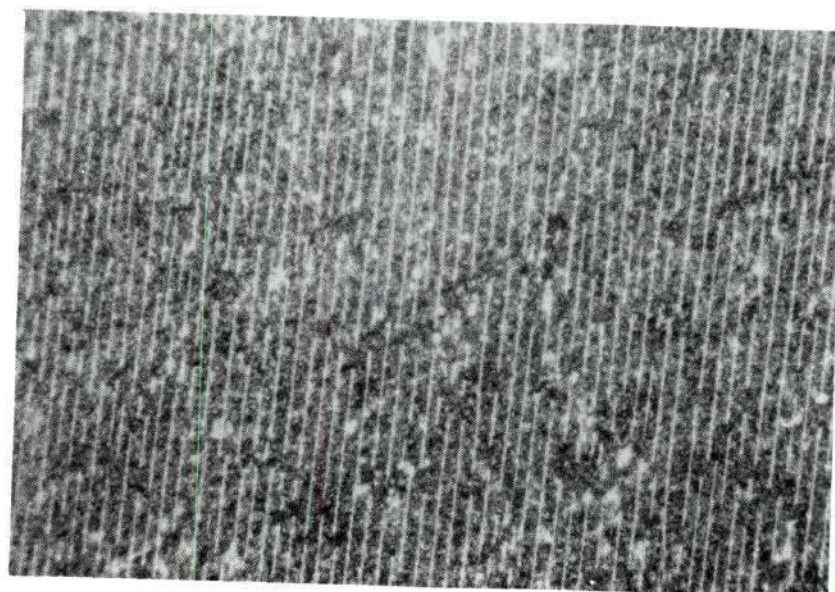


Figure 17. Longitudinal Section of $\text{CeO}_2 + 10 \text{ wt. } \% \text{ Mo}$ Sample Unidirectionally Solidified in a $\text{N}_2 - 10 \text{ v/o } \text{H}_2$ Atmosphere. Dark Field, X600.

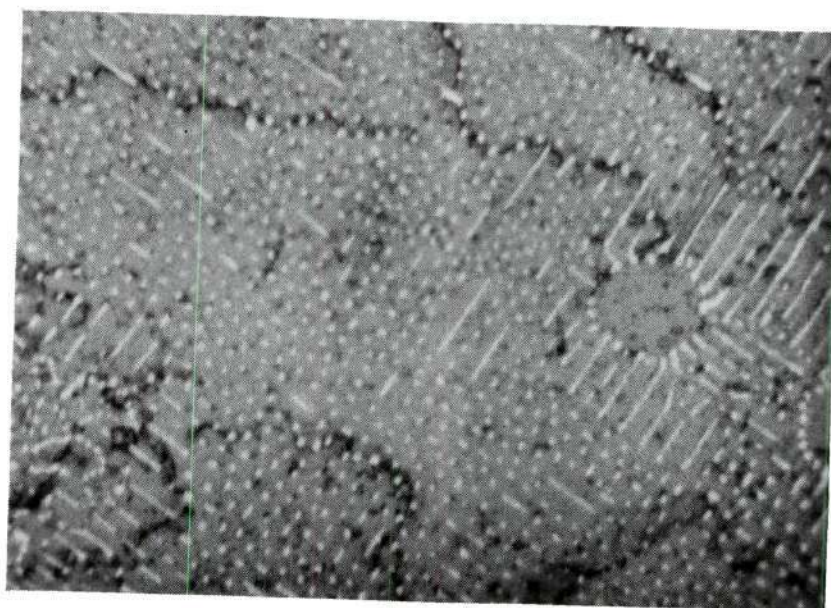


Figure 18. Transverse Section of $\text{CeO}_2 + 10 \text{ wt. } \% \text{ Mo}$ Sample Unidirectionally Solidified in a $\text{N}_2 - 10 \text{ v/o } \text{H}_2$ Atmosphere. Bright Field, X1050.

In an effort to determine if the atmosphere was a dominating factor for fiber growth several samples were solidified in a 100% N_2 atmosphere and several in a pure H_2 atmosphere. The samples from the 100% N_2 atmosphere were very similar to those produced in the N_2 - 10 v/o H_2 atmosphere. Figures 19 and 20 are typical of the composite growth formed in a CeO_2 + 10 wt. % Mo sample solidified in a 100% N_2 atmosphere. While there was some continuous fiber and platelet growth most of the samples contained oxide dendrites.

The samples solidified in a 100% H_2 contained almost exclusively fiber growth and Figure 21 shows the continuous geometry that was achieved in this atmosphere. This type of geometry was typical of the entire length of the composite growth. The transverse of a CeO_2 + 9 wt. % Mo shows that the composite growth was completely fibrous (Figure 22), although the fibers were not as uniform in size and distribution as has been observed in other oxide-metal eutectic structures.¹⁴

Composite growth differences in the N_2 and H_2 atmospheres indicated that there was a reaction between the oxide and the H_2 atmosphere that effected eutectic structure and solubility of molybdenum. This lead to the investigation of the effect that the atmosphere had on the stoichiometry of ceria. This will be discussed in the next section.

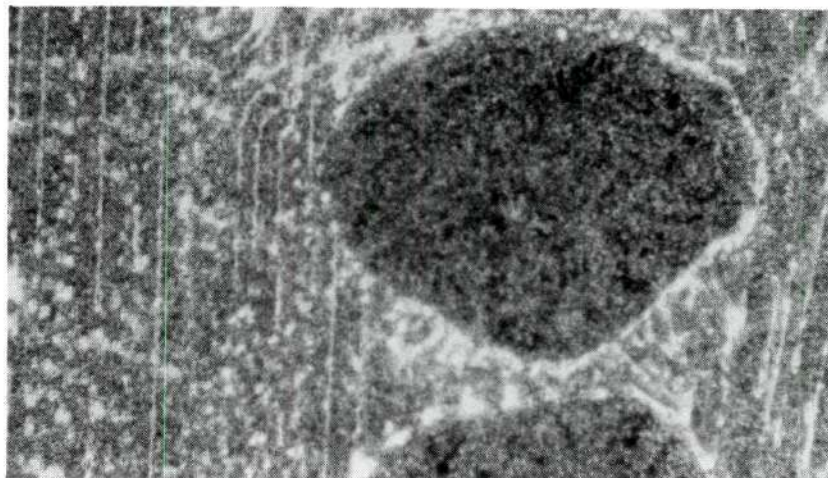


Figure 19. Longitudinal Section of $\text{CeO}_2 + 10 \text{ wt. } \% \text{ Mo}$ Sample Solidified in a 100% N_2 Atmosphere. Bright Field, X600.

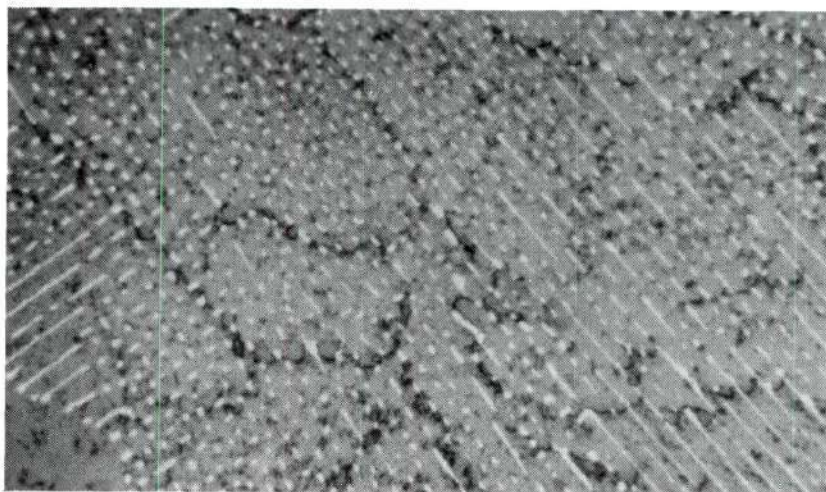


Figure 20. Transverse Section of $\text{CeO}_2 + 10 \text{ wt. } \% \text{ Mo}$ Sample Solidified in a 100% N_2 Atmosphere. Bright Field, X1050.

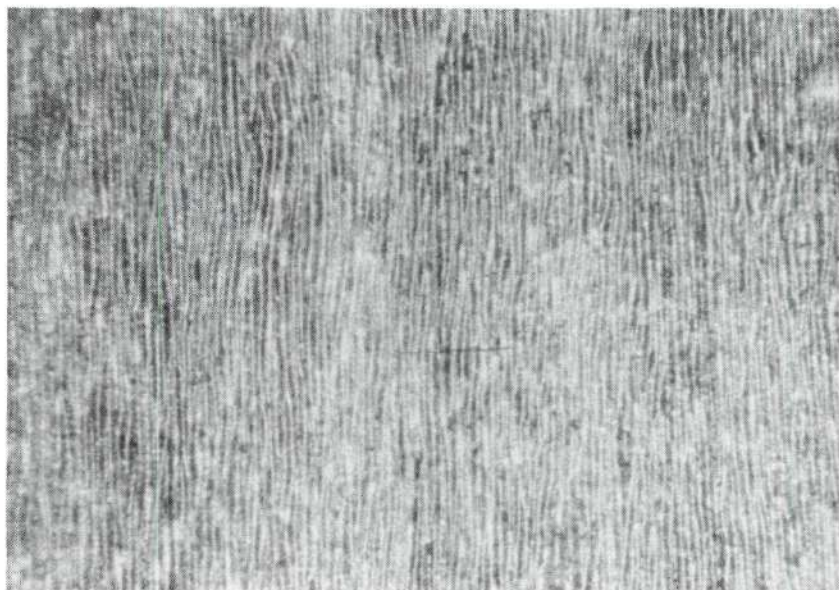


Figure 21. Longitudinal Section of $\text{CeO}_2 + 9 \text{ wt. } \%$ Mo Sample Unidirectionally Solidified in a 100% H_2 Atmosphere. Bright Field, X600.

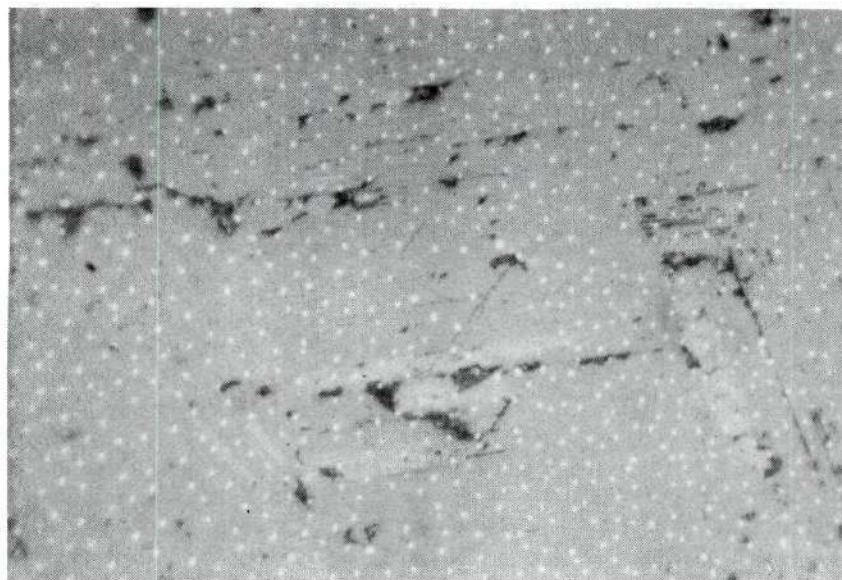


Figure 22. Transverse Section of $\text{CeO}_2 + 9 \text{ wt. } \%$ Mo Sample Unidirectionally Solidified in a 100% H_2 Atmosphere. Bright Field, X600.

In studying growth atmospheres some work was done in the $N_2:CO/CO_2$ atmospheres. Samples were solidified in atmospheres of $N_2 - 10$ v/o CO/CO_2 and $N_2 - 20$ v/o CO/CO_2 . (The CO/CO_2 used was 1 v/o CO_2 .) Figure 23 is typical of all composites produced in a $N_2:CO/CO_2$ atmosphere. There appeared to be limited solubility between the CeO_2 and molybdenum in these atmospheres. In This case as in the pure H_2 atmosphere it was thought that the stoichiometry of the oxide was being effected by the growth atmosphere. This will be discussed in the next section.

The last growth atmosphere studied varied ratios of H_2/H_2O . The ratios ranged from 5 to 15 v/o H_2O and 95 to 85 v/o H_2 . These atmospheres were studied more for stoichiometry effects than actual composite growth. However, these atmospheres also produced continuous fiber growth. All samples grown in an H_2/H_2O atmosphere had the geometry shown in Figures 24 and 25. Here as in the 100% H_2 atmosphere all the metal growth was present in the form of fibers. The fibers as seen in Figure 25 were nonuniform in size and distribution. Comparison of Figures 22 and 25 suggests that the fibers produced in the H_2/H_2O atmospheres were smaller in diameter and greater in number than those found in pure H_2 . Another effect of the addition of water vapor to the H_2 was the formation of molybdenum dendrites in the sample (Figure 26). It seemed that increasing the water vapor content of the H_2 atmosphere effected the

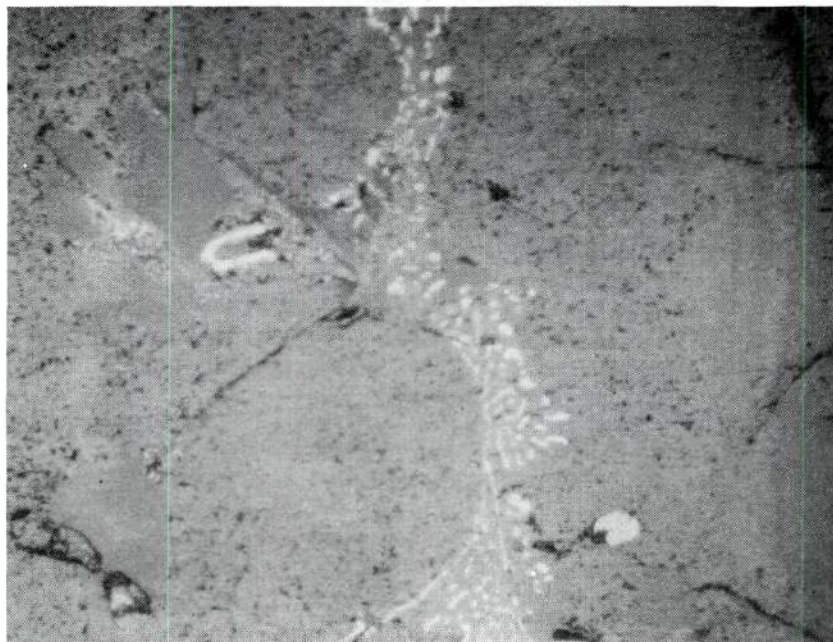


Figure 23. Longitudinal Section of a $\text{CeO}_2 + 10 \text{ wt. \% Mo}$ Sample Solidified in a $\text{N}_2 - 10 \text{ v/o CO/CO}_2$ Atmosphere. Bright Field, X600.

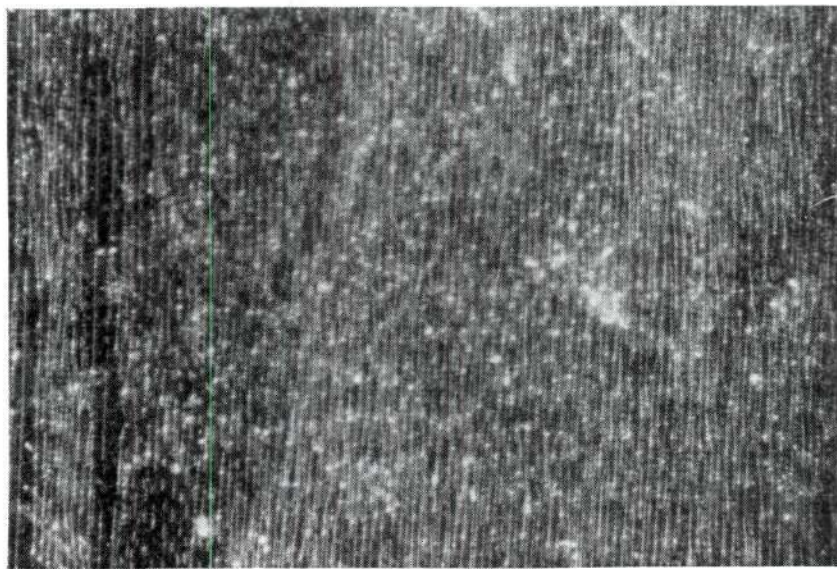


Figure 24. Longitudinal Section of a $\text{CeO}_2 + 9 \text{ wt. \% Mo}$ Sample Unidirectionally Solidified in a $\text{H}_2 - 10 \text{ v/o H}_2\text{O}$ Atmosphere. Dark Field, X600.

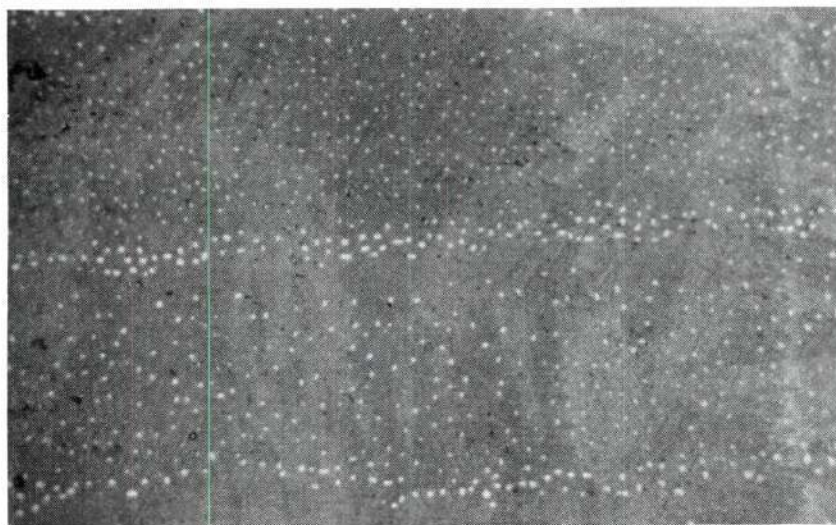


Figure 25. Transverse Section of a $\text{CeO}_2 + 9 \text{ wt. \% Mo}$ Sample Unidirectionally Solidified in a $\text{H}_2 - 10 \text{ v/o H}_2\text{O}$ Atmosphere. Bright Field, X600.

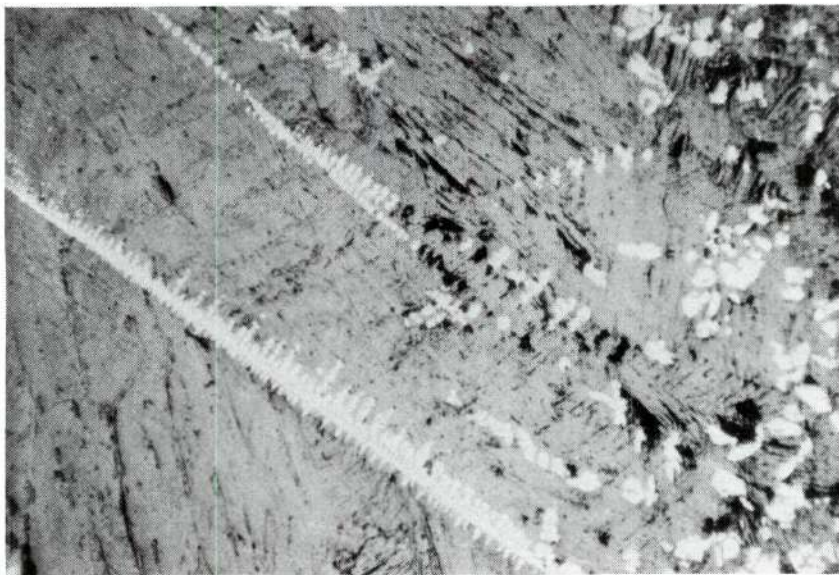


Figure 26. Transverse Section of $\text{CeO}_2 + 9 \text{ wt. \% Mo}$ Sample Unidirectionally Solidified in a $\text{H}_2 - 10 \text{ v/o H}_2\text{O}$ Atmosphere Showing Molybdenum Dendrites and Excess Molybdenum Globs. Bright Field, X50.

molybdenum solubility in ceria such that molybdenum dendrites and large globs of excess molybdenum form. This indicated that there was a definite relationship between the oxygen potential and the molybdenum solubility. A study was undertaken to investigate the effect oxygen potential had on the stoichiometry of ceria. This is discussed in the next section.

Stoichiometry Changes

This section describes a series of pure ceria melting experiments that were run to determine the stoichiometry changes of ceria in various atmospheres (H_2/H_2O and CO/CO_2). An effort was also made to correlate the stoichiometry changes of pure ceria with the composite structures produced by unidirectional solidification. A compilation of the experimental data including the gas mixtures used, the O/Ce ratios of the molten material, and the calculated oxygen pressures of the different gas mixtures at $2613^\circ K^{40}$ (estimated temperature of the molten CeO_2) are given in Table 4. The temperature $2613^\circ K$ is simply the melting point of CeO_2 ($2340^\circ C$) plus $273^\circ C$ to convert to $^\circ K$. Although there was no way to adequately measure the temperature of the molten ceria and it was known that the temperature would vary with changes in oxygen pressure it was assumed that the temperature of the liquid did not significantly vary. The calculated oxygen pressures were obtained

Table 4. Oxygen Partial Pressure and Composition
Data for Molten Ceria at 2613°K

Experiment No.	PPM H ₂ O in H ₂	Log P _{O₂} (atmosphere)	Oxygen to Cerium (O/Ce) Ratio*
27-60	250	-11.59	1.500 1.503
27-61	2000	- 9.39	1.534 1.535
27-62	4000	- 8.80	1.548 1.551
	PPM CO ₂ in CO ₂		
27-56	52,600	- 4.94	1.761 1.765
27-52	111,000	- 4.29	1.802 1.813
27-53	250,000	- 3.58	1.978 1.984

*Calculated as shown in Appendix A.

from the following equations used by Bevan and Kordis³⁵ in their study on the oxygen pressure equilibria in ceria.

$$\frac{1}{2} \log P_{O_2} = -\log K_1 + \log (P_{H_2O}/P_{H_2})$$

$$\frac{1}{2} \log P_{O_2} = -\log K_2 + \log (P_{CO_2}/P_{CO})$$

The values of K_1 and K_2 , the equilibrium constants were obtained from the JANAF Thermochemical Tables.⁴¹

The data presented in Table 4 are plotted in Figure 27 and show considerable scatter. A computer was used to determine the best linear fit for the relationship between $\log P_{O_2}$ and O/Ce ratio of the molten oxide at a temperature of 2613°K. This linear fit is also plotted in Figure 27 and is given by the equation

$$\log P_{O_2} = 15.52 (O/Ce) - 33.51$$

It is believed that the oxygen pressures obtained in this investigation are true equilibrium values. The method used to insure equilibrium conditions was described in Chapter III.

By using the equations of $\log P_{O_2}$ of Bevan and Kordis,³⁵ it was possible to compare the data of this investigation for equilibria oxygen pressure with their data. Figure 28 is a plot of $\frac{1}{2} \log P_{O_2}$ versus O/Ce generated by Bevan and Kordis. Their data is for oxide compositions for temperatures ranging from 636 to 1169°C. The oxygen-to-cerium (O/Ce) ratios obtained at 2340°C (2613°K) are plotted in Figure 28.

The plots of $\frac{1}{2} \log P_{O_2}$ and O/Ce ratios at various temperatures can be seen to flatten out into an almost linear relationship as the temperature increases. Bevan and Kordis used this fact to draw the hypothesis that the free energy ($\frac{1}{2} RT \ln P_{O_2}$) varied linearly with temperature.

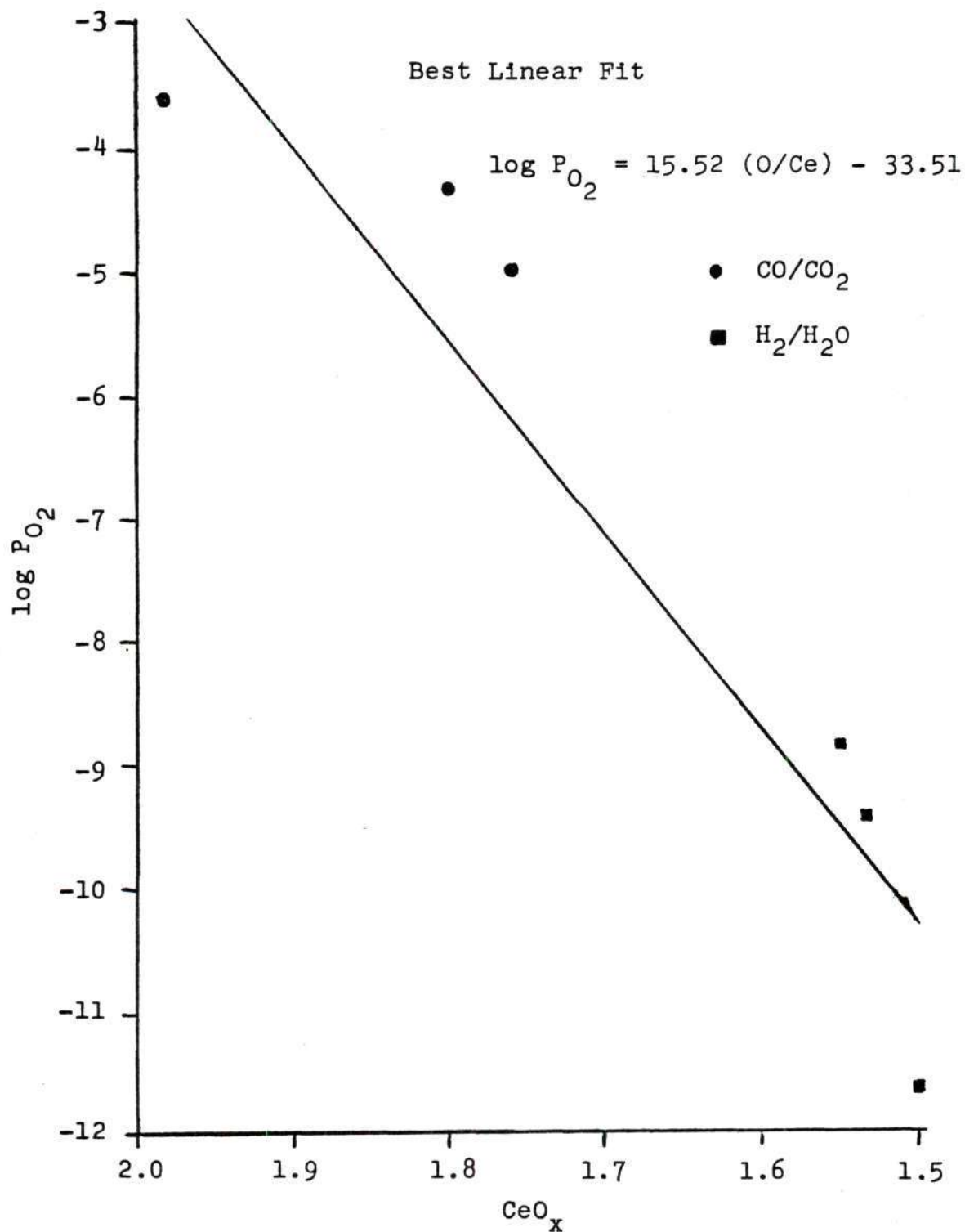


Figure 27. Plot of Log P_{O2} vs. CeO_x (1.5 ≤ x ≤ 2.0) for Molten Ceria at 2613°K.

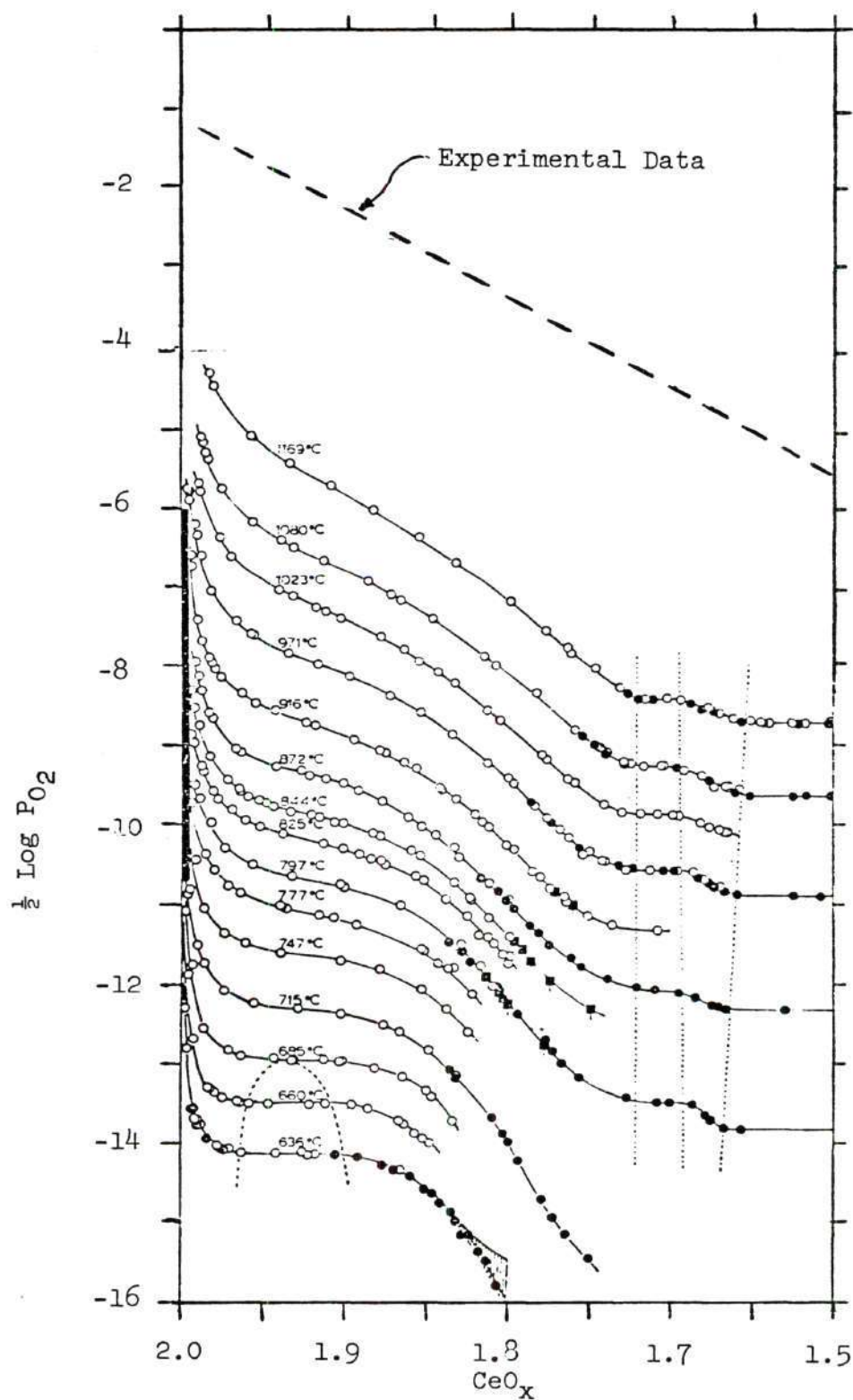


Figure 28. Plot of $\frac{1}{2} \log P_{O_2}$ vs. O/Ce Ratios at 636 to 1169°C Generated by Bevan and Kordis and Experimental Data at 2340°C.

They then constructed the phase diagram for the system CeO_x ($1.5 \leq x \leq 2.0$). The experimental data of this investigation has the same general slope that the data of Bevan and Kordis have. It is therefore safe to assume that the stoichiometry underwent changes during composite growth.

The effect that growth atmosphere had on composite growth varied with the ceria stoichiometry. In the $\text{H}_2/\text{H}_2\text{O}$ atmospheres, including 100% H_2 , the stoichiometry of the ceria varied from $\text{CeO}_{1.5}$ to $\text{CeO}_{1.551}$. It was in this range of ceria compositions that the best composite growth was developed. In pure H_2 ($\text{CeO}_{1.5}$) there was very good fiber growth with no oxide or molybdenum dendrites present, while at the upper limit of the range (H_2 - 15 v/o H_2O atmosphere, $\text{CeO}_{1.551}$) there was an abundance of molybdenum dendrites. This suggests that the stoichiometry of the ceria effects the solubility of the molybdenum.

In the systems containing CO/CO_2 as an atmosphere there was limited composite growth (Figure 23). In these atmospheres the ceria stoichiometry was found to range from $\text{CeO}_{1.7607}$ (CO - 5 v/o CO_2) to $\text{CeO}_{1.9777}$ (CO - 20 v/o CO_2). Since there was no ordered growth in this range it appeared that the solubility of the molybdenum in the liquid was greatly reduced. Apparently this gas mixture (CO/CO_2) had an upper limit that was lower than 5 v/o CO_2 . This behavior has been observed during the growth of $\text{UO}_2 + \text{W}^{14}$ although

the reactions that eliminated eutectic growth under these conditions are unknown. Excessive vaporization of molybdenum as molybdenum oxides was possibly a major contribution to this behavior, since the resultant oxide-metal structure was almost depleted of molybdenum.

CHAPTER V

CONCLUSIONS

1. The internal molten zone technique can be used to melt and unidirectionally solidify CeO_2 -Mo pellets.
2. The composition $\text{CeO}_2 + 10 \text{ wt. \% Mo}$ produced uniform composite geometry in a $\text{N}_2 - 10 \text{ v/o H}_2$ atmosphere.
3. Low growth rates ($1.0 - 1.5 \text{ cm/hr}$) produced the most uniform composite geometries.
4. High growth rates (2.0 cm/hr and above) increased the occurrence of primary oxide phase areas.
5. An all fibrous geometry was obtained in a 100% H_2 atmosphere when a $\text{CeO}_2 + 9 \text{ wt. \% Mo}$ sample was unidirectionally solidified.
6. The composite structure produced by unidirectionally solidifying $\text{CeO}_2 + 9 \text{ wt. \% Mo}$ samples in $\text{H}_2/\text{H}_2\text{O}$ atmospheres contained good continuous fibrous growth and molybdenum dendrites.
7. Composites solidified in a $\text{N}_2:\text{CO}/\text{CO}_2$ atmosphere were almost completely void of any metal content.
8. Comparison of the O/Ce ratio of the molten ceria after quenching with the calculated oxygen pressures of the different gas mixtures (at a temperature of 2613°K) indicated a linear relationship of

$$\log P_{O_2} \text{ (atmos)} = 15.52 (O/Ce) - 33.51 .$$

9. Composite growth and uniform eutectic structures were dependent on stoichiometry of ceria in the system CeO_2 -Mo. The most uniform growth was obtained in the range $CeO_{1.50} - CeO_{1.551}$.

CHAPTER VI

RECOMMENDATIONS

Some of the investigations required for the characterization of CeO_2 -metal systems for composite growth are outlined below.

1. The relationship between growth rate and fiber density and diameter should be determined.
2. The reasons for non-uniform fiber diameter and distribution should be studied.
3. Chemical etching of the oxide matrix and metal fibers should be explored.
4. The effect that O/Ce ratio has on molybdenum solubility should be explored.

APPENDIX A

STOICHIOMETRY CALCULATIONS AND
WEIGHT-GAIN DATA

The weight-gain data listed in Table 5 were used to calculate the oxygen-to-metal ratios in the specimens using the equation below:

$$R = \frac{W_I - (W_F/M_{MO}) M_M}{M_O (W_F/M_{MO})}$$

where R = oxygen-to-metal ratio in sample

W_I = weight of sample in grams prior to heat treatment

W_F = weight of sample in grams after heat treatment

M_{MO} = molecular weight of stoichiometric oxide in grams/gm. mol. wt.

M_M = molecular weight of metal in grams/gm. mol. wt.

M_O = molecular weight of oxygen in grams/gm. mol. wt.

Table 5. Weight-Gain Data and Oxygen-to-Metal Ratios of Fused Samples

Sample	Atmosphere	Initial Weight (gm)	Final Weight (gm)	Oxygen-to-Metal Ratio
27-56	CO - 5 v/o CO ₂	2.4312	2.4865	1.761 1.765
27-52	CO - 10 v/o CO ₂	2.9124	2.9669	1.802 1.813
27-63	CO - 20 v/o CO ₂	1.9738 1.4062	1.9779 1.4082	1.977 1.985
27-60	H ₂ - 5 v/o H ₂ O	2.2956 2.4479	2.4071 2.5672	1.503 1.500
27-61	H ₂ - 10 v/o H ₂ O	1.4764 1.269	1.5431 1.3271	1.535 1.534
27-62	H ₂ - 15 v/o H ₂ O	1.5714 1.5504	1.6400 1.6184	1.551 1.548

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