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INVESTIGATION OF THE GROWTH OF DIRECTIONALLY SOLIDIFIED EUTECTICS WITH POTENTIAL AS ELECTRON EMITTERS

FINAL TECHNICAL REPORT

(Period: 1 April 1975 to 3 September 1976)

Project Director: James F. Benzel

Principal Investigators: A.T. Chapman and J.K. Cochran

This work was performed for the Jet Propulsion Laboratory California Institute of Technology sponsored by the National Aeronautics and Space Administration Under Contract NAS7–100

JPL Contract Number 954193

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ABSTRACT

Oxide-metal cold cathode emitters are potential replacements for thermionic emitters. Examples of potential users are: electron sources for high energy gas pulsed lasers, electron guns for high resolution TV cameras and electron guns for "instant-on" TV sets. At the present time current densities over 10 amps/cm^2, noise levels of less than 1% and lifetimes greatly in excess of 3000 hours are achievable. There are indications that a large market for oxide-metal field emitters could develop over the next ten years.

Continued analysis of the expected solidification behavior of oxide-metal eutectics in space indicates that the advantages previously reported (Ref. 24) for space processing are still relevant. The data obtained from solidification experiments performed in space tend to confirm these projected advantages.

A technique for rf melting small diameter oxide-metal rods to their surfaces was developed. However, because of experimental difficulties further work in this area was terminated in favor of accelerating the construction of a verticle axis solar furnace. The construction of a solar furnace has been completed and it has been tested after a preliminary alignment of the heliostat mirrors.

After final alignment, the solar furnace will be used for directional solidification experiments designed to simulate space conditions.

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I. INTRODUCTION

This document represents the final report of a study performed for the Jet Propulsion Laboratory, California Institute of Technology on the "Growth of Directionally Solidified Eutectics with Potential as Electron Emitters," carried out under National Aeronautics and Space Administration Contract NAS7-100. The objectives of this program were: 1) to continue evaluating the advantages of processing unidirectionally solidified oxide-metal composites in space, 2) to develop techniques for melting small diameter oxide-metal eutectic rods to the specimen surface, 3) to determine the improvement in yield achievable by extending the floating zone to the surface of oxide-metal solidification rods, 4) to construct a solar-heating facility suitable for directional solidification studies, 5) to evaluate vaporization of oxide-metal composite systems in the molten state, 6) to begin determining the amount of improvement to be expected in oxide-metal composites grown in the absence of turbulent convection, 7) to re-evaluate the economic advantage of processing oxide-metal composites in space and 8) to up-date potential market volume projections for oxide-metal composites.

This type composite typically contains 10-50 x 10^6 metal fibers/cm^2 with the fibers aligned parallel to their growth direction in an oxide matrix. Variation of the growth rate allows the diameters of the metal fibers to be controlled between 0.1 and 1μm.

Currently the major potential uses of this type oxide-metal composite are electronic in nature, with various types of high field electron emitters being the most promising. Typical examples are: electron source for high energy gas pulsed lasers, electron gun for high resolution TV cameras and electron guns for "instant-on" TV sets that do not use any power when turned off. At the present time current densities over 10 amps/cm^2, noise levels of less than 1 percent and lifetime greatly in excess of 3000 hours are achievable. Another demonstrated application is the use of oxide-metal composites to produce low voltage electron guns. The low voltage emitter relies on a very short anode-to-cathode spacing to achieve the required electric field at low potentials. Emission from this type diode has been achieved with anode-to-cathode potentials of less than 15 volts.

For these types of applications, it should be borne in mind that the emitter operates at ambient temperature and therefore does not require a heater. In addition, isolation transformers and associated hardware which are a major consideration in terms of the cost of many present day systems are also not required in equivalent field effect emitter systems. These facts should allow significant weight reductions in field and portable equipment.

II. BACKGROUND

Cermet composites consisting of an oxide matrix containing millions of less than one micrometer diameter metal fibers per square centimeter have been grown from near eutectic compositions by various unidirectional solidification techniques (Refs. 1-3). The largest and most uniformly ordered oxide-metal composites reported to date have been grown using an internal floating zone technique (Refs. 1, 4-9) utilizing direct rf eddy current heating. The main advantages of this technique are that the molten zone is self-contained by an unmelted sample skin which eliminates the contamination and containment problems associated with other techniques, and that the liquid-solid interface is well defined because of the steep temperature gradients inherent in this technique. Its major drawbacks are that only relatively small samples can be grown, that only a limited number of refractory oxides have high enough elevated temperature electrical conductivity to support eddy current heating and also have melting points that are sufficiently high, so that the radiant energy lost from the sample surface is great enough to prevent melting through to the surface.

Previous publications (Refs. 7 and 8) have described in detail the internal floating zone technique employed to grow oxide-metal composites. A brief description of this growth technique is being included here as it provides valuable background information for evaluating the prospects of growing this type of composite in the low-g environment of space.

The samples from which composite structures are unidirectionally solidified are fabricated by dry mixing the desired proportions of high purity - 325 mesh oxide and metal powders. This mixture is then pressed into a cylindrical rod 1.9 centimeters in diameter by about 3.8 centimeters in length. These rods are sintered inside an inductively heated molybdenum preheat tube (Figure 1) using a radio frequency (rf) generator. A dynamic atmosphere of either H_2, N_2, H_2 - N_2 or CO-CO_2 passes through the quartz atmosphere containment tube to provide the neutral or reducing environment necessary to prevent the oxidation of the metal powder in the rod and molybdenum preheat tube. Typically preheat temperatures between 1500°C (UO_2-W) and 2000°C (stabilized HfO_2-W) are required to sinter the sample rods and to increase their electrical conductivity high enough to allow their direct heating by the rf field when the molybdenum preheater tube is quickly lowered out of the rf field and the generator's output immediately maximized. The resulting resistance heating and simultaneous increase of electrical conductivity of the rod act to raise the rod's temperature until the interior of the rod melts. Melting is detected by an increase in plate current and a simultaneous decrease in the plate voltage of the rf generator. At this point the power settings of the rf generator must be quickly decreased to prevent the internal molten zone from melting through the wall of the

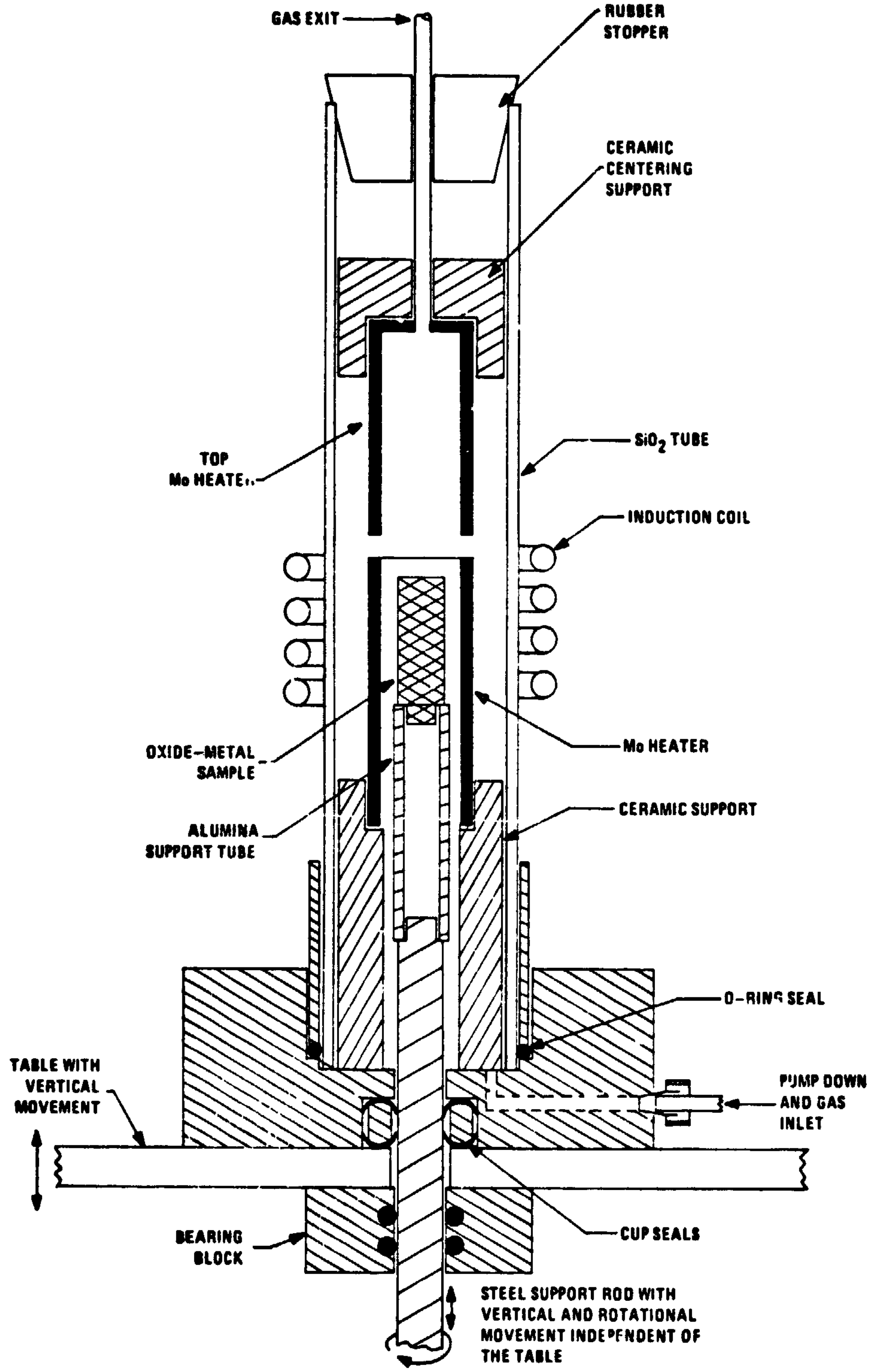
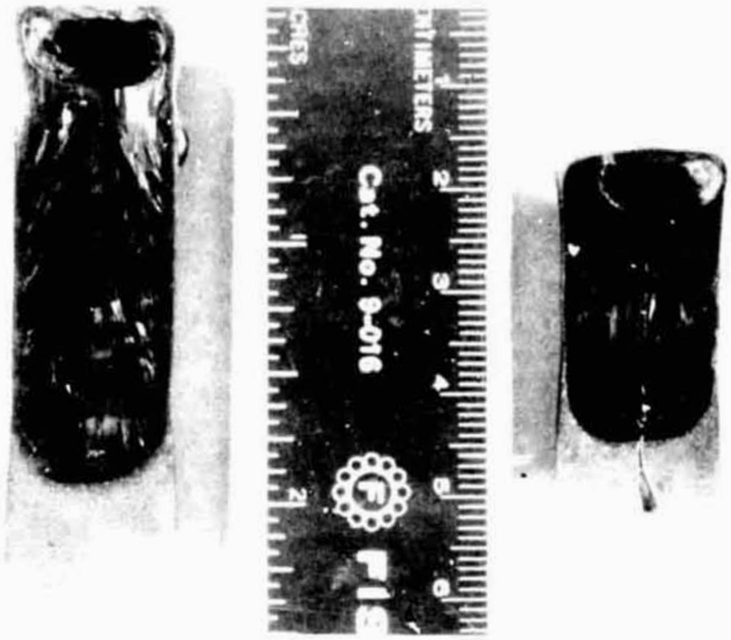


FIGURE 1. Schematic Diagram of the Facility for the Growth of Oxide-Metal Composites.

rod (Figure 2a). The high radiant heat loss from the surface of the rod and the relatively low thermal conductivity of the oxide-metal mixture produce a sufficient thermal gradient across the skin of the rod (Figure 2b) to maintain a surface temperature ($\approx$1900^{o}C) well below the melting point of the oxide-metal eutectic.

Unidirectional solidification is achieved by moving the molten zone upward through the rod by slowly lowering the rod. A cavity forms over the molten zone as it moves because of the difference in density between the porous sintered rod and the nearly void-free liquid and solidified composite. During the lowering of the rod the oxide-metal mixture melts at the roof of the cavity, runs down the interior wall of the pallet into the molten pool and is then unidirectionally solidified at the bottom of the molten zone. When a smaller thermal gradient between the molten zone and the solidified portion of the rod is desired to prevent thermal cracking, the rod is lowered into the molybdenum tube which has been repositioned in the lower turns of the induction coil so as to act as a heater ($\approx$1500^{o}C). After the rod has been lowered several centimeters, the cavity becomes too large to allow melting above it, at which time the rod decouples from the rf field and the remaining liquid solidifies. The molybdenum tube is then raised further to radiantly heat the entire length of the rod and control the rate of sample cooling.



a) Gd_2O_3-CeO_2-Mo Samples

b) UO_2-W Sample (4X)

FIGURE 2. Low Magnification Photographs Showing Unmelted Composite Skin.

Ordered eutectic growth has been reported in the following refractory oxide-metal systems: UO_2-W (Ref. 1); UO_2-Ta (Ref. 6); stabilized ZrO_2-W (Ref. 4); stabilized HfO_2-W (Ref. 5); Cr_2O_3-Mo, Cr_2O_3-Re, Cr_2O_3-W, MgO-W (Ref. 2); rare earth sesqueoxide (Gd_2O_3, La_2O_3, Nd_2O_3, Er_2O_3, or Ho_2O_3)-CeO_2-(Mo or W) Refs. 10 and 11); CeO_2-(Mo or W) (Ref. 12); and Y_2O_3-(Y or W), Ta_2O_5-Ta, ZrO_2-(Zr r W), HfO_2-Hf, $Al_2O_3(Cr_2O_3)$-W, Al_2O_3-$ZrO_2(Y_2O_3)$-W, (Gd_2O_3 or Y_2O_3)-CeO_2-Ta, Y_2O_3-CeO_2-Y, Cr_2O_3-Al_2O_3-Cr (Ref. 13). Typical composite morphologies are shown in Figures 3 and 4.

It should also be noted that several oxide-oxide systems have also been successfully unidirectionally solidified, for example (CaO, MgO, SrO and BaO)-UO_2 (Refs. 14 and 15); CaO-NiO, Al_2O_3-NiO (Ref. 16); MgO-Mg Al_2C_4 (Ref. 17); Al_2O_3-$Y_2Al_5O_{12}$ (Ref. 18); ZrO_2-Y_2O_3 (Ref. 19); ZrO_2-MgO (Ref. 20); $BaTiO_3$-$CoFe_2O_4$, Al_2O_3-$ZrO_2(Y_2O_3)$, (Ref. 21); piezomagnetic spinel-piezoelectric perovskite eutectics in the Fe-Co-Ti-Ba-O system (Ref. 22); and $BaNb_2O_6$-Sr Nb_2O_6 (Ref. 23).

In our previous report (Ref. 24) we identified seven potential areas in which the growth of oxide-metal composites should be improved by processing in space. These were:

1. Growth of larger oxide-metal composites
2. Elimination of grain boundaries
3. Elimination of colony boundaries
4. Elimination of impurity segregation
5. Elimination of banding (discontinuous fibers)

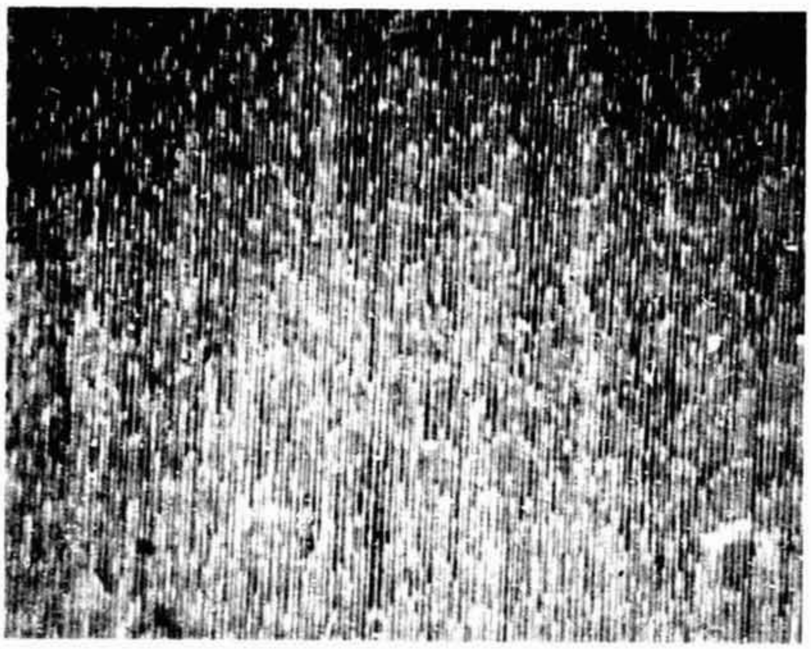


FIGURE 3. Longitudinal Crossection of ZrO_2-Y_2O_3-W Composite (Dark Field, 600X).

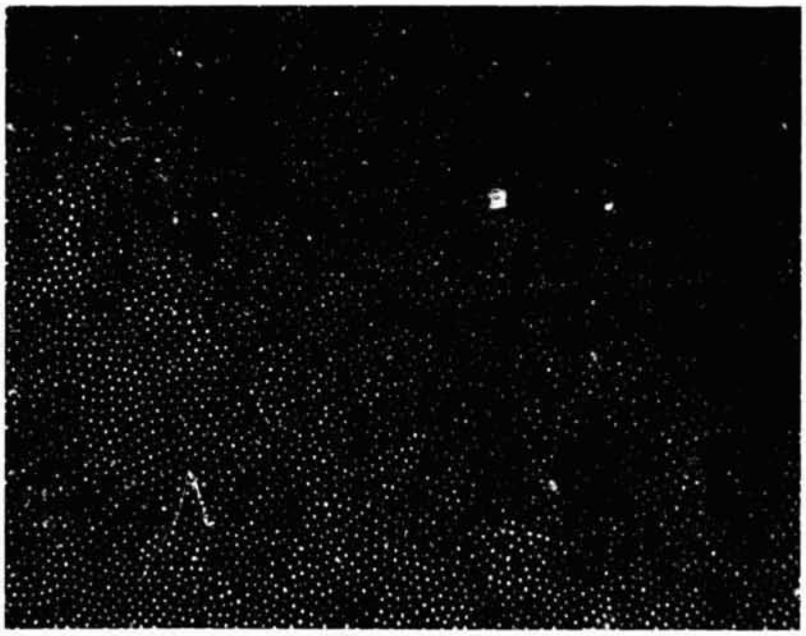


FIGURE 4. Transverse Crossection of ZrO_2 - Y_2O_3 -W Composite (Dark Field, 600X).

6. Growth of off-eutectic compositions

7. Growth of low melting point eutectic composites

In addition it was concluded that a large market for oxide-metal high field emitters would develop over a ten year period and that space processing of these devices would be economically cost effective.

III. TECHNICAL DISCUSSION

This section is subdivided into eight subsections: A) Advantages of Processing Unidirectionally Solidified Oxide-Metal Composites in Space, B) Effect of Melting Small Diameter Oxide-Metal Eutectic Rods to Their Surface, C) Estimation of the Improvement in Yield From Oxide-Metal Composites Melted to the Surface, D) Construction of a Solar-Furnace Facility for Directional Solidification Studies, E) Evaluation of Vaporization of Oxide-Metal Systems in the Molten State, F) Effect of Growing Eutectic Composites in the Absence of Turbulent Convection, G) Evaluation of the Economic Advantage of Processing Oxide-Metal Composites in Space and H) Market Volume Projections for Oxide-Metal Composites. These subsections cover areas pertinent to simulating growth conditions similar to those in space and to assessing the feasibility of producing unidirectionally solidified oxide-metal composites in the weightless environment of space.

A. Advantages of Processing Unidirectionally Solidified Oxide-Metal Composites In Space.

Even though we often refer to the zero-g conditions in orbiting space craft,it is apparent that absolute zero-g exists only under ideal conditions and that in fact production operations would be subject to low-g levels (Ref.25) depending on the orbital characteristics of the vehicle and their specific locations in relation to the center of gravity of the vehicle. However, the gravity levels are very low, for example at 8.7 feet away from the center of mass of the vehicle the gravity field is six orders of magnitude less than on earth.

If the material being processed is mechanically connected to the vehicle any accelerations caused by engine operations, astronaut motion, etc. would produce artificial gravity forces. An example of this was observed when ring-shaped grooves (Ref. 26) were produced in an indium antimonide crystal, grown on Skylab 4, by disturbances from very low thrust attitude control maneuvers of the space craft. Throughout the remainder of this report the following assumptions will be made: 1) that the gravity forces acting on matter in an orbiting manufacturing facility are so low that the environment can be assumed to be equivalent to zero-g, and 2) that, if necessary, techniques can be devised for preventing artificial accelerations from disturbing the manufacturing process.

The most apparent effect of a zero-g environment upon matter is the absence of relative mass acceleration. This eliminates the need for support of liquids and precludes the relative motion of fluids due to buoyancy effects or thermal convection. Although there are other lower order effects that the absence of gravity might allow to be useful in some processes, it appears that any improvement in the growth of oxide-metal composites in space will have to be the result of the low-g environment.

Seven primary areas in which improvements should be made by processing oxide-metal eutectic composites in space (Ref. 25) were previously identified. These are:

1. Growth of larger oxide-metal composites
2. Elimination of grain boundaries
3. Elimination of colony boundaries
4. Elimination of impurity segregation
5. Elimination of banding (discontinuous fibers)
6. Growth of off-eutectic compositions
7. Growth of low melting point eutectic composites

A summary of the experimental and theoretical information dealing with each of these areas, which has become available since the last report (Ref. 25), is presented below:

1) Growth of Larger Oxide-Metal Composites

During the past year internal floating zone techniques for growing UO_2-W composite pellets 32 mm in diameter (Figure 5) have been developed. Removal of the unmelted polycrystalline containment skin reduces the useable cross section to about 2 cm in diameter. This size is approaching the maximum composite diameter that can be achieved with a 10 kW rf generator. It should be noted, however, that solidification of pure UO_2 from green pellets as large as 7 cm in diameter has been reported (Ref. 27).

Figure 5. Large Diameter UO_2-W Composites Grown by the Internal Floating Zone Technique.

This was achieved by an rf internal melting technique similar to ours.

It is not known if the liquid-solid interface would remain planar (this condition is necessary for ordered composite structures to be grown but is not required for the growth of single crystals) if the internal molten zone of oxide-metal pellets was this large. However, the fact that UO_2 pellets of this size have been internally melted and the fact that we have been able to double the maximum growth diameter of UO_2-W composites suggests that by using a more powerful rf generator it might be possible to increase the maximum growth diameter in this system to 5-7 cm.

Recent calculations and computer simulations (Refs. 28 and 29) based on floating zone melting of silicon in space have reaffirmed that counter rotation of the crystal and feed-stock are required to provide a planar solid-liquid interface. For large diameter crystals heated from the surface it was found that the maximum allowable rotational rates varied from 24.35 RPM for a diameter of 7.6 cm to 1.15 RPM for a diameter of 60.8cm. The acceleration generated would be small enough not to create circulation currents great enough to adversely affect impurity distribution or crystal perfection. For example, if a crystal 5 cm in diameter were rotated at a rate of 20 RPM the acceleration field generated would be about 0.01g. The effect of rotating cylindrical liquid floating zones supported by two axially aligned circular discs (Ref. 30) were investigated on Skylab 4.

Based on these investigations it still appears that larger diameter oxide-metal composites can be grown in space than on earth.

2) Elimination of Grain Boundaries

There is considerable confusion existing in the literature concerning the structures of eutectic specimens. This is largely due to the fact that the subgrain (colony) structure is easily mistaken for the grain structure. For this reason a discussion of both grain and colony structures has been included in this subsection.

Weart and Mack (Ref. 31) defined the three structures produced during the eutectic solidification as the grain structure, the colony structure, and the eutectic structure, with each being contained by the one preceding it . The grain structure is analogous to the polycrystalline structure of a single phase material where each grain grows from a single nucleus. A broader interpretation is needed for eutectics because of the presence of two phases in each grain. Since in most eutectics one phase is dispersed in a matrix of the other, a grain may be taken to be that region in which the matrix phase is monocrystalline.

The colony structure is a subgrain structure whose units consist of phase particles arranged in a characteristic pattern. This pattern is a consequence of the shape of the solid-liquid interface during solidification. Colonies are distinguished by phase particle arrangement and not by differences in crystallographic orientation of the matrix as in the case of grains.

When viewed perpendicular to the growth direction it is very difficult, if not impossible, to distinguish between a grain and a colony boundary. However, when cross sections taken parallel to the growth direction are examined the substructure can easily be differentiated from the grain structure.

The fact that any form of liquid motion tends to increase the number of the nuclei formed (Ref. 32), suggests that the absence of thermal convection in space should allow the growth of composites containing fewer grain boundaries.

Several of the investigations carried out on Skylab missions (Refs. 33-35) may indicate that the decrease in convection currents resulted in fewer grains being present in directionally solidified specimens than were observed in identically earth processed specimens. A space grown $In_{0.3}Ga_{0.7}Sb$ sample (Ref. 33) appears to have contained slightly fewer grains. Another alloy in this system ($In_{0.1}Ga_{0.9}Sb$) did not show this effect. However, it was observed that grain boundaries present in the space grown specimens were much harder to detect and that there were fewer twin boundaries in the space samples.

3) Elimination of Colony Boundaries

As discussed earlier, the morphology of oxide-metal colonies normally consists of a regular rod arrangement in the middle of the colony. At the edge of the colony cell the fibers no longer are parallel to the growth direction but curve outward and in some cases may even be perpendicular to the growth direction. The colony boundary area is a highly disordered area between two colony cells.

The mechanism by which this type structure is formed can be visualized when the fact that the eutectic structure always grows normal to the liquid-solid interface (Ref. 36) is taken into account. Numerous investigators (Ref. 37-40) have shown that the liquid-solid interface during colony formation is not planar but is cellular with the middle of the cells penetrating into the liquid (Figure 6) with the edges of the cells lagging behind the center of the cells. As these domed shaped cells advance during unidirectional solidification the trace of the solidification path in the center remains parallel to the growth direction but the solidification path curves outward as the edge of the cell is approached so that the direction of solidification can remain perpendicular to the solid-liquid interface.

It is well known that when a multicomponent system is unidirectionally solidified, the solute distribution ahead of the liquid-solid interface does not remain uniform; instead, concentration gradients are

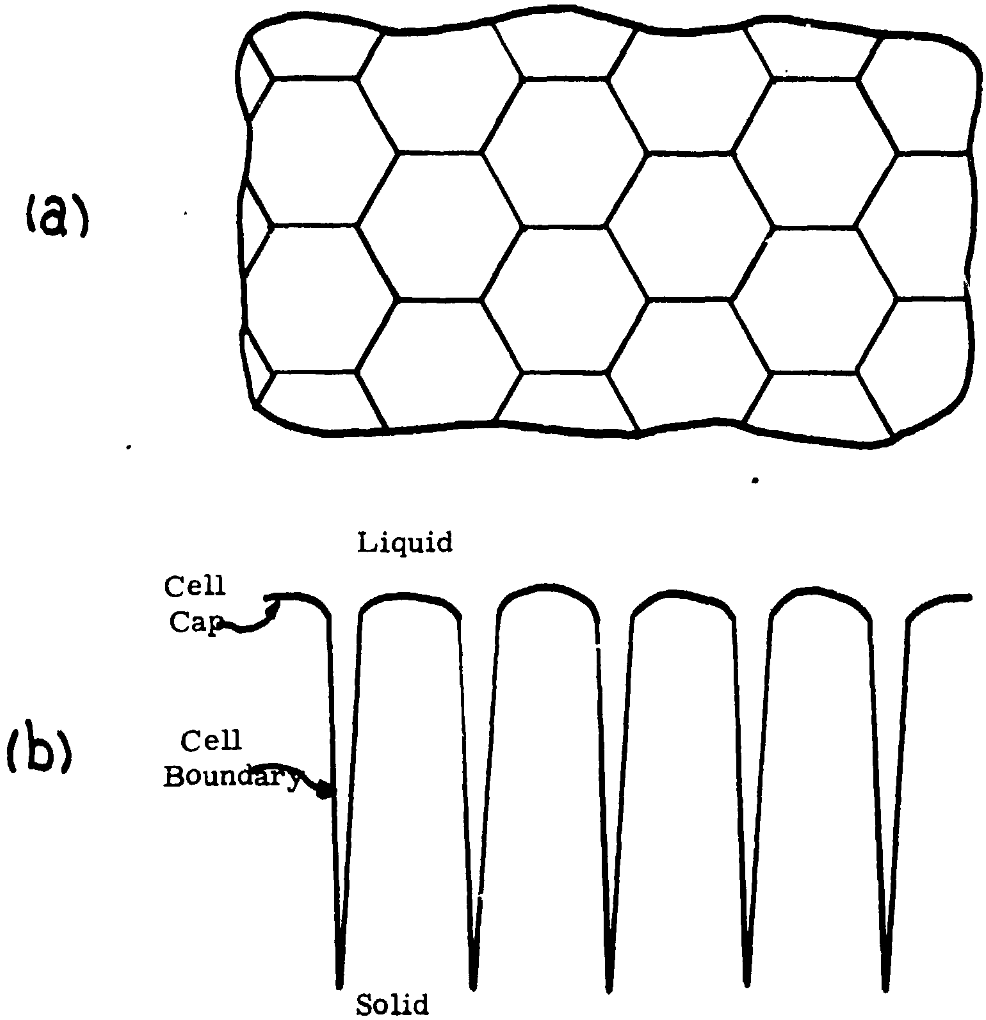


FIGURE 6. Illustration of Cell Structure: a) Perpendicular to Growth Direction and b) Parallel to Growth Direction.

formed which violate the conditions required for a planar interface. Examination of colony containing eutectics (Ref.41) has shown that impurities having solid/liquid distribution coefficients $k<1$ segregate to the colony boundaries and that impurities with $k>1$ segregate to the caps (centers) of the colonies. It should be noted that for both of these cases the liquid that freezes at the lower temperature is in the cell boundaries.

The earliest experiments demonstrating that thermal instability in fluids created a cellular flow pattern were done by Benard (Ref 42). If a horizontal layer of liquid is heated from below, a potentially unstable condition arises because the density of liquids decreases with increasing temperature. Due to the viscosity of the liquid, a critical temperature gradient must be exceeded before instability can set in. Once this occurs, a stationary cellular pattern consisting of a regular hexagonal pattern is established. The direction of flow is upwards at the center of the cells and downward at the walls of the cells. Convective flow also occurs when the solidification front travels in the horizontal direction.

In the theory of convective flow developed by Rayleigh (Ref.43) a dimensionless Rayleigh number was derived:

$$R = g\beta c\rho\theta\, h^3/\lambda\nu$$

where g is the acceleration due to gravity, θ is the effective temperature difference, h is the thickness of the liquid layer, and β, c, ρ, λ, and ν are respectively the coefficient of the thermal expansion, the specific heat, the density, the thermal conductivity, and the kenematic viscosity of the fluid. The critical value (Rc) for cellular convection is about 1700.

M. Hämäläinen (Ref. 44) has shown that the necessary conditions for the formation of the colony cell structure in alkali halide solid solutions is that there is convection in the melt at temperatures just above the freezing point and that constitutional supercooling due to the impurities takes place in the presence of these cells.

It is possible that the formation of cells by constitutional supercooling can take place in the presence of convection cells and that the distribution of impurities during solidification is due to the co-operation of these two mechanisms. Since the Rayleigh number equation has g in its numerator, convection cells due to unstable thermal convection will not exist under zero-g conditions. Thus it seems reasonable to predict that growth of eutectic composites in space can be accomplished without the formation of colony structures. This would allow much improved oxide-metal composites to be grown since electrical measurements indicate that only about 70% of the fibers are continuous through specimens one millimeter thick and that this is primarily because of non-parallel growth at the cell boundaries.

The decrease in fault density (Ref. 34) in Au-Cu eutectic samples and the increased optical transmission (Ref. 35) of NaCl-NaF eutectic samples grown in space is most likely the result of the elimination of colony boundaries due to the low-g environment.

4) Elimination of Impurity Segregation

The unstable thermal convection described in the preceding section has also been shown to be responsible for temperature fluctuations in the melt. The distribution of impurities (Ref.45) present in a directionally solidified crystal depend on the rate of solidification. When the speed of solidification is abruptly increased, an impurity striation of high solute concentration is formed in the solid; the reverse occurs when the speed is decreased abruptly. The thermal oscillations caused by unstable thermal convection have been demonstrated to cause impurity striations. It has been demonstrated that these striations can be eliminated by solidifying the melt in a magnetic field. Solidification under zero-g conditions has been shown to have a similar effect (Refs. 46-48) on a number of different systems. Six-fold reduction of macrosegregation and five-fold improvement in microsegregation were observed in space grown Gd doped Ge.

5) Elimination of Banding

Two types of banding have been observed in all unidirectionally solidified oxide-metal systems. Their common denominator is that a horizontal band of oxide containing either no fibers or very few fibers was solidified. None of the known reports on space processing of eutectics has described experimental results related to this problem.

6. Growth of Off-Eutectic Composites

Since the physical properties of composites are dependent upon the volume fraction of the fiber phase, it would be very useful to be able to vary this volume fraction. This would allow emitter geometries with larger pin spacings, which theoretical analysis indicates would increase the current density, to be grown.

At equilibrium conditions (zero growth rate) only the eutectic mixture can produce the eutectic structure without primary phase areas being formed. However, at finite growth rates equilibrium conditions do not exist and it has been shown in metal-metal systems (Refs. 49 and 50) that a range of compositions can be solidified with eutectic like structures.

Initially the conditions necessary for off-eutectic composite growth were established as:

a) Low growth rate

b) Steep thermal gradient

c) Essential absence of convection

More recent work (Refs. 51 and 52) indicates that off-eutectic growth can be accomplished even in the presence of considerable convection.

At the solid-liquid interface there will always be a layer of quiescent liquid in which diffusion is the only form of mass transport. A mass balance (Ref. 51) across this interface for the element present in excess of the eutectic then gives

$$\frac{d\overline{C_L}}{dZ} = -\frac{R}{D}\left(\overline{C_i} - \overline{C_s}\right)$$

where: R is the growth rate

D is the liquid diffusion coefficient

Z is the thickness of the quiescent liquid

$\overline{C_L}$ is the average concentration in the liquid

$\overline{C_i}$ is the average concentration in the liquid at the interface

$\overline{C_s}$ is the average concentration in the solid at the interface

This relationship holds with or without convection as long as the thickness of the diffusion controlled layer is greater than the lamellar (or rod) spacing in the solidifying material.

At steady state, C_i equals C_E, the eutectic composition, and C_s must equal the initial concentration of the alloy C_o. The above relation then becomes

$$\frac{dC_L}{dZ} = -\frac{R}{D}\left(C_E - C_o\right)$$

For a given alloy system, the parameters controlling the dendrite-composite transition are G (the temperature gradient), R, C_o and dC_L/dZ. This expression shows that the last two of these parameters (C_o and dC_L/dZ) are independent of the convective conditions. Therefore, except for extremely vigorous convection, the primary phase area-ordered composite transition in a given alloy should take place at about the same G and R for growth under convective or under non-convective conditions.

Attempts to grow ordered off-eutectic oxide-metal composites using the internal floating zone technique have been unsuccessful. It is assumed that the reason for this is that the very turbulent convection observed in the melt decreases the thickness of the diffusion controlled liquid zone to less than the spacing between rods, which makes the assumption on which the above equation is based invalid.

Yue and Voltmer (Ref. 47) concluded that the thickness of the solute boundary layer (Z, thickness of diffusion controlled liquid zone) was larger in the Gd doped Ge specimens solidified in space. This indicates that there is a high probability that off-eutectic oxide-metal composites could be successfully grown in space.

Two advantages to be gained from this are: 1) that the size and spacing of fibers could be modified and 2) that the metal volume fractions of systems which normally produce lamellar structures could be reduced so that rod type structures are produced.

7) Growth of Low Temperature Systems

When attempts are made to grow large diameter ($>$0.5cm) composites from lower temperature oxide-metal eutectic systems ($<$2000^{o}C) using the internal floating zone technique,the molten pool is lost due to melting of the containment skin. These systems could be melted in space without any difficulty. The resulting composites should have numerous applications, such as optical and magnetic devices, for which the high melting point systems are unsuitable.

B. Effect of Melting Small Diameter Oxide-Metal Rods to Their Surface

Oxide-metal composites currently grown by the internal floating zone technique have an unmelted polycrystalline containment skin that must be removed before the well ordered portion of the solidified rod can be used. A feasibility study (Ref. 24) identified seven primary areas in which improvements in the structure of oxide-metal composites could most likely be achieved by processing in space. In order to take advantage of these improvements, it is necessary for the floating zone to extend to the surface of the composite rod during unidirectional solidification. Thus, for experimental evaluation of the advantages of space processing using earth based simulation studies, composites must be melted to the surface.

Power sources under consideration for melting composites in space include rf coupling as used in the internal zone technique (least desirable), electron beam and solar energy supplied by parabolic mirrors. For these power sources to be used for earth based simulation of space conditions, small diameter rods ($\leq$0.5 cm diameter) must be used to allow surface tension to contain the liquid zone between the unmelted feed rod and the unidirectionally solidified composite rod. The purpose of this investigation was to demonstrate that rf coupling has the capability of inducing power sufficient to melt to the surface small diameter rods of the oxide-metal composites that are used for electronic applications. It must be remembered that all the oxide-metal composites that have usable geometries for electronic applications melt above 2000^{o}C and radiation losses are large for small rods at that temperature. This requires a large rf power input due to the large heat radiation and to a decreased coupling efficiency caused by the small rod diameter.

An apparatus specifically designed to couple to 0.6 cm diameter oxide-metal composite rods was constructed. The apparatus consisted of:

1. A molybdenum sample preheater tube; 0.75 cm ID x 0.96 cm OD x 7.5 cm in length. The tube was joined to a solid molybdenum rod of 0.6 cm dia to allow rapid removal of the preheater tube from the rf field via an O-ring vacuum feed through (during sample preheat, the Mo tube was positioned around the sample to act as an rf susceptor).

2. A quartz glass atmosphere containment tube (1.5 cm ID x 1.7 cm OD) surrounding the sample and preheater tube.

3. A four turn rf coil, fabricated from 0.64 cm diameter copper tubing. The rf coil was 1.9 cm ID and was positioned around the atmosphere containment tube.

The procedure for coupling trials consisted of preheating a composite composition to the desired temperature, quickly removing the Mo preheater from the rf field, and applying the maximum power available from a 10 kW rf generator. Three compositions were used in the coupling trials: (a) 84 w/o Y_2O_3 stabilized ZrO_2-16 w/o Mo, (b) 70 w/o Gd_2O_3-20 w/o CeO_2-10 w/o Mo, and (c) 65 w/o Gd_2O_3-20 w/o CeO_2-15 w/o Mo. All these compositions have produced good growth morphology when grown by the internal zone technique.

Seven attempts were made to couple to a 0.5 x 0.5 x 3.9 cm Y_2O_3 stabilized ZrO_2-W rod in a N_2-H_2 atmosphere. Sample preparation consisted of dry pressing 0.64 x 0.64 x 10 cm bars and vacuum firing to 1900°C for one hour with a resulting density of 89.1% of theoretical. Using a 4.8 MHz field, the sample rods were reheated to 1500, 1670, 1710, 1800, 1860, and 1900°C during the first six attempts to directly couple to the samples. Only at the two highest preheat temperatures did the rf field appear to be applying power to the sample as indicated by a slower cooling of the rod than had been observed at lower preheat temperatures. On the seventh attempt, the rf frequency was increased to 7.2 MHz. This experiment was terminated during preheat (1600^oC) when the field arced through the quartz tube.

Samples of the Gd_2O_3-CeO_2-Mo compositions were fabricated by isostatically pressing mixed powders in 3/8" tygon tubing and sintering in H_2 at 1400^oC. The 10 cm - long - rods were ground to 0.6 cm in diameter after sintering. Attempts were made to couple to the 70 w/o Gd_2O_3-20 w/o CeO_2-10 w/o Mo in a H_2-N_2 atmosphere using a 3.5 MHz field. Coupling directly to the rod was unsuccessful after preheating to 1520, 1625, 1720, 1770, and 1900^oC. The sample heated to 1900^oC appeared to have held temperature longer than those preheated to lower temperatures.

The Mo content of the second Gd_2O_3-CeO_2-Mo composition was increased to 15 w/o. After being preheated to 1850^oC, this composition coupled to the 3.8 MHz field and melted to the surface. Power applied at melting was 0.75 amperes and 6.3 KV. Unfortunately, the power could not be lowered fast enough to prevent spilling of the zone. The sample decoupled after spilling and cooled. The remaining solidified zone was ground and polished to a one micron diamond finish. Optical examination showed small regions of dendritic metal precipitates (Figure 7) indicating that some metal solution had occurred in the short time the rod was liquid.

Figure 7. Optical Micrographs of Molybdenum Dendrites in a Gd_2O_3-CeO_2 Matrix Produced by Melting a 0.64 cm Diameter Rod to the Surface (600X).

The successful coupling and melting to the surface of the small diameter oxide-metal composites showed that space simulation using rf melting is feasible. However, due to the effort and equipment required to maintain a stable molten zone and to unidirectionally solidify small diameter rods, it was decided to discontinue rf melting studies in favor of developing solar melting capabilities.

C. Determination of the Improvement in Yield Achievable by Extending the Floating Zone to the Surface of Oxide-Metal Composite Rods.

In addition to growing larger diameter oxide-metal composites in space, the yield per unit weight processed should also be improved considerably if the floating zone is extended to the surface of the solidification rod.

Oxide-metal composite systems grown at Georgia Tech utilizing the internal floating zone coupling technique all melt at 2000°C or higher. The surface of the sample remains solid and although this provides contamination free noncrucible melting, up to 50% of the sample volume (Figure 2) is lost due to the solid skin. For space processing, it would be desirable to increase the useable composite volume by melting to the surface in the gravity free environment. This would produce up to a 100% increase in efficiency compared to earth grown composites. The larger diameter UO_2-W composites grown during the past year have skins which occupy a smaller percentage of their cross-sectional areas (Figure 5) but considerable improvement in yield would still be realized by eliminating the skin.

In addition, unless energy were supplied by rf coupling, any other heating technique, either radiant or contact, would require melting to the surface. This consideration becomes most important should solar melting be used in space. For these reasons, it was desirable to know the degree of fiber uniformity to be expected near the surface of unidirectional solidified composite samples.

Our previous work (Ref. 24) on model systems ($NaCl$-$CaWO_4$ and NaCl-NaF) indicated that uniform eutectic morphologies could be obtained to at least within 30 to 40 μm of the surface of rods melted to their surfaces. Similar results (Refs. 53 and 54) have been obtained for three other systems. Pollock and Stormont (Ref. 53) grew LiF-CaF_2 and LiF-NaCl composites using edge-defined film-fed growth techniques. In the lamellar LiF-CaF_2 system, the lamellar structure appears to extend all the way to the surface. Lead-tin eutectic samples produced by zone melting (Ref. 54) films of the material with thickness between 10 and 75 μm were also observed to have a lamellar structure which extended completely through the solidified films.

We have been unable to confirm these results for oxide-metal systems because our solar furnace is just now becoming operational.

D. Construction of Solar-Heating Facility Suitable for Directional Solidification Studies

Unless directional solidification of eutectic composites is accomplished by direct rf coupling it is necessary to melt the specimens to their surface. The primary reason for wanting to grow this type composite in space is to eliminate turbulant convection of the liquid. Thus it is highly unlikely that rf melting techniques will be used in space because of the unavoidable rf stirring which would occur. This fact along with the problems we have encountered in melting small diameter oxide-metal rods to their surfaces by rf coupling suggested that a solar furnace melting system should be constructed.

Other advantages of using a solar heating technique are:

1. Conditions similar to those in space can be achieved in a solar furnace by incorporation of an acoustic positioning device and a magnetic field perpendicular to the growth direction to prevent turbulent convection.

2. Small diameter rods of oxide-metal compositions which melt at too low a temperature to be directionally solidified using the internal floating zone technique can be solidified in a solar furnace. This may allow the growth of composites containing nobel metal fibers in an oxide matrix which would be suitable for medical implants designed to create artificial sight for some blind people.

3. The use of solar melting requires very little electrical power. The limited power availability of

Space Shuttle may require that any large scale solidification of high melting point materials be accomplished using solar energy.

A vertical axis solar furnace was designed by personnel of the Georgia Tech Engineering Experiment Station. Their design was a modification of a horizontal axis solar furance designed for the School of Electrical Engineering which is turn was patterned after the eight small vertical axis solar furances located on the South side of the French solar furnace facility at Font-Romeu.

Our facility consists of: 1) a concentrating mirror and its support system, 2) a heliostat system, 3) an optical tracking and electronic control system and 4) a sample support and transport system. Each of these sub-systems is described below:

1. Concentrating Mirror and Support System

The concentrating mirror is a 1.524 meter diameter parabolic searchlight reflector (Figure 8) which is cantilevered (Figure 9) from the South side of the fourth floor of the Bunger Henry Building at Georgia Tech.

2. Heliostat System

The heliostat is a flat segmented mirror array (Figures 9 and 10) which is 3.01 meters square. Each of the 36 smaller back silvered mirrors which makes up the array is approximately 50 centimeters square and 5 mm thick.

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Figure 8. Parabolic Concentrating Mirror
and Support Frame

Figure 9. Vertical Axis Solar Furnace Facility

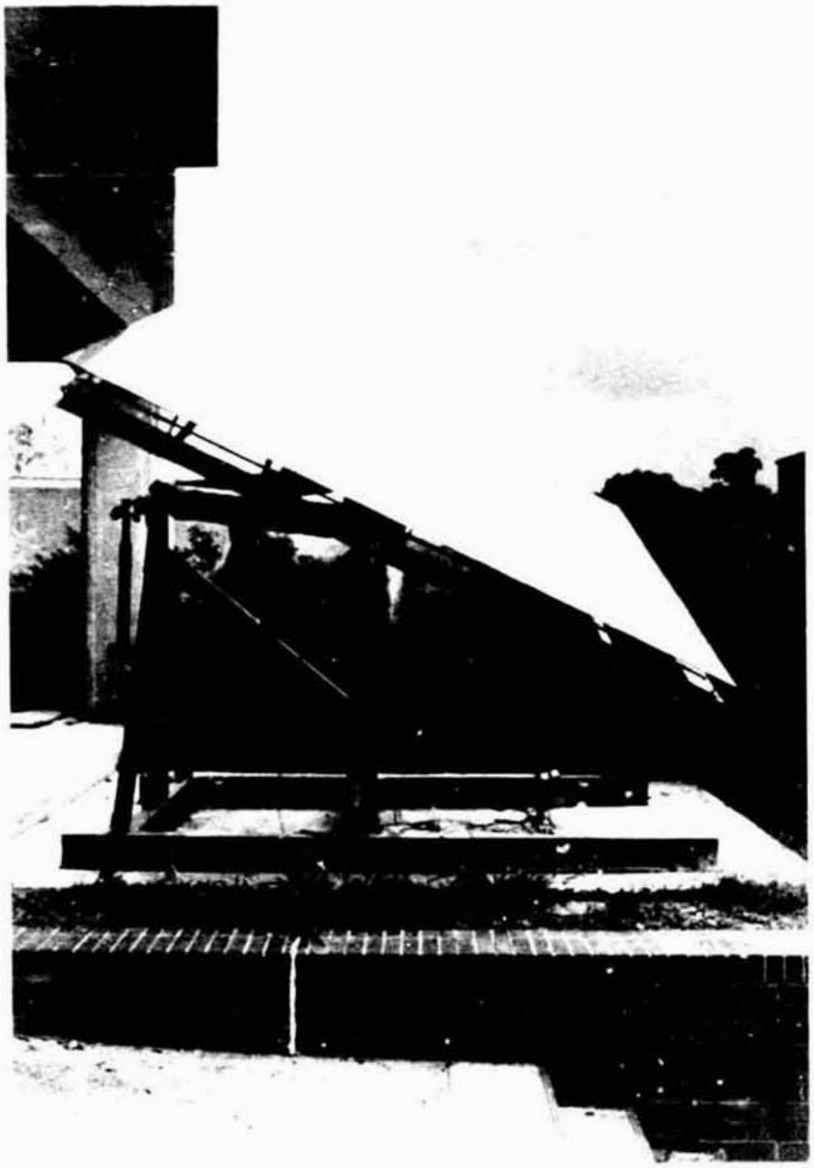

Figure 10. Heliostat (Segmented Mirror Array)

The function of the heliostat is to direct a beam of reflected solar energy parallel to the vertical into the concentrating mirror. This is accomplished by placing the heliostat directly below the concentrating mirror and then aiming it so that a normal to it bisects the angles between the incident solar energy and the vertical. The aiming process is accomplished by activating two electro-mechanical screw jacks which cause the mirror support frame to rotate about two axes at right angles to each other which pass through its center and are parallel to its edges.

Figure 11 shows the heliostat in its horizontal storage position. Figure 12 shows the backside of the heliostat after it has been rotated about both its X and Y axes.

The original mirror mountings (Figure 13) were aluminum brackets which contained a copper bronze spring and a set screw. The mirrors were each attached to the heliostat frame by three of these mounts (Figure 14). The individual mirrors were then to be aligned by moving the set screws and the springs were to hold the mirrors firmly in place.

Several problems were encountered with this mounting method: 1) there was not enough movement built into the system so that the mirrors could all be aligned in the same plane and 2) the stresses this system put on the mirrors (2.5 mm in thickness) either deformed them or occasionally broke them.

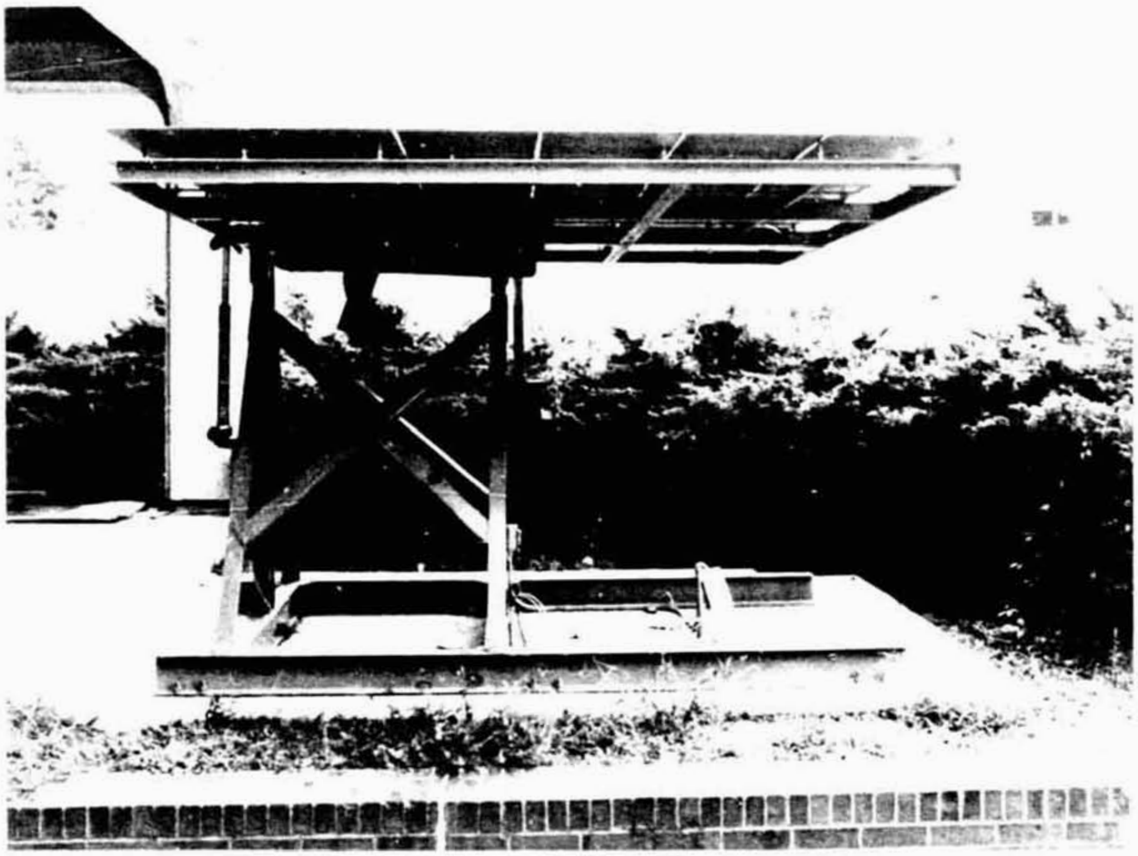

Figure 11. Heliostat in Storage Position: The X-Axis Screw Jack is Identified by an X and the Y Axis Screw Jack by a Y.

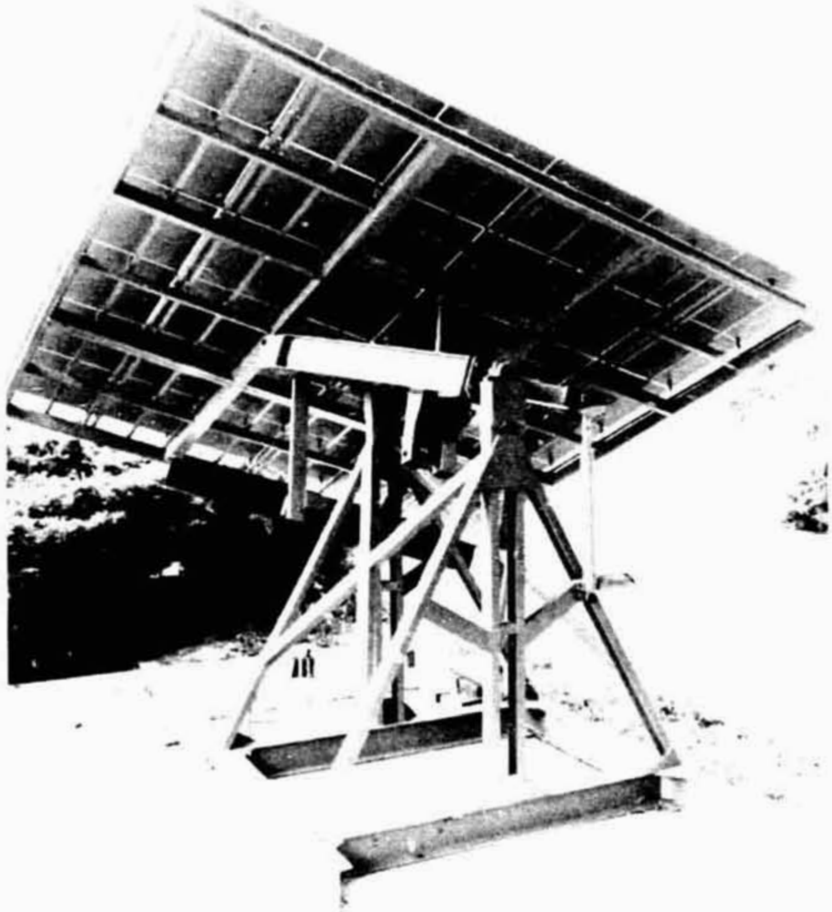

Figure 12. Rear View of Heliostats Showing Screw Jacks Partially Extended.

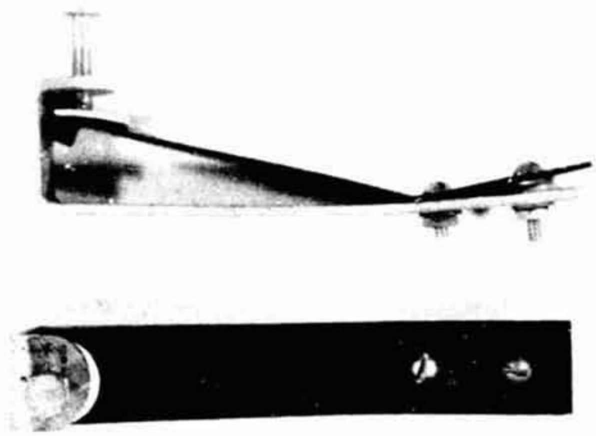

Figure 13. Original Mirror Mounting Brackets (0.5X).

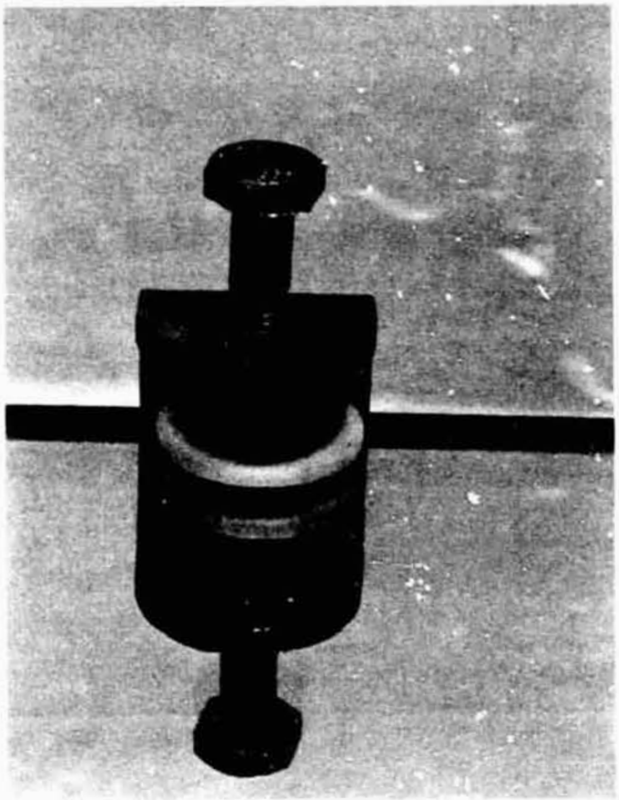

Figure 14. Original Mounting Bracket in Position on Mirror (1X).

Because of these problems a new stress-free mounting system was developed and thicker mirrors (5 mm) were purchased. The new mounting system was also attached to three points on each mirror (Figure 15). Figure 16 shows a closeup view of two of these mounts. Each mount consists of a ball joint which was directly attached to the heliostat frame. The threaded bolt end of the ball joint was screwed into the bottom end of a turnbuckle. The left handed bolt which was screwed into the upper end of the turnbuckle was silver soldered to a one inch washer which in turn was attached to the back of the mirror with an aluminum filled epoxy resin.

This system overcame all of the previous problems and in addition allowed the space between mirrors to be reduced from greater than 1/4 inch to less than 1/16 inch. Using a surveying level all of the mirrors were roughly aligned by placing the mirror surface directly over each mounting point in the same plane.

3. Optical Tracking System

Four photo diodes located at the focal point of a long focal length lens (101.6 cm) are the control elements that allow the heliostat to automatically track the sun so that a vertical beam of solar energy strikes the concentrating mirror. The optical tracking tube which contains these diodes can be seen extending below the concentrating mirror support frame in Figure 8.

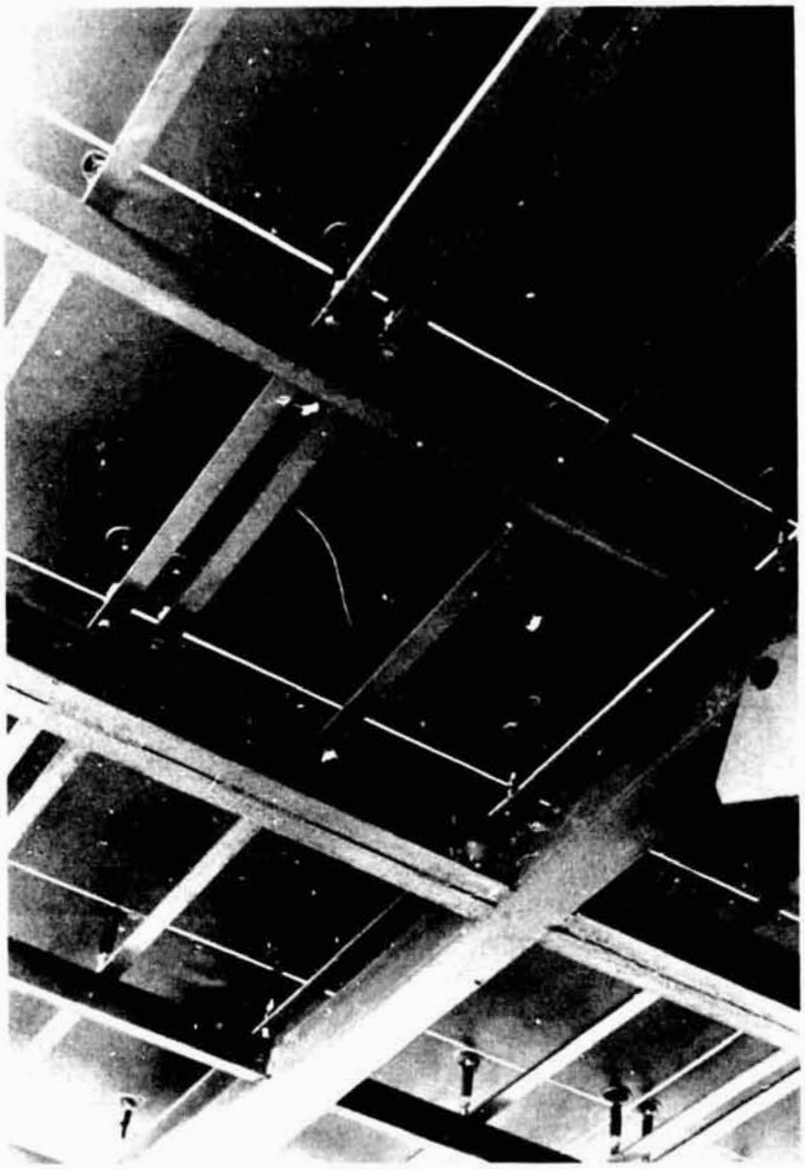

Figure 15. Mounting Arrangement for Improved Mirror Mounts.

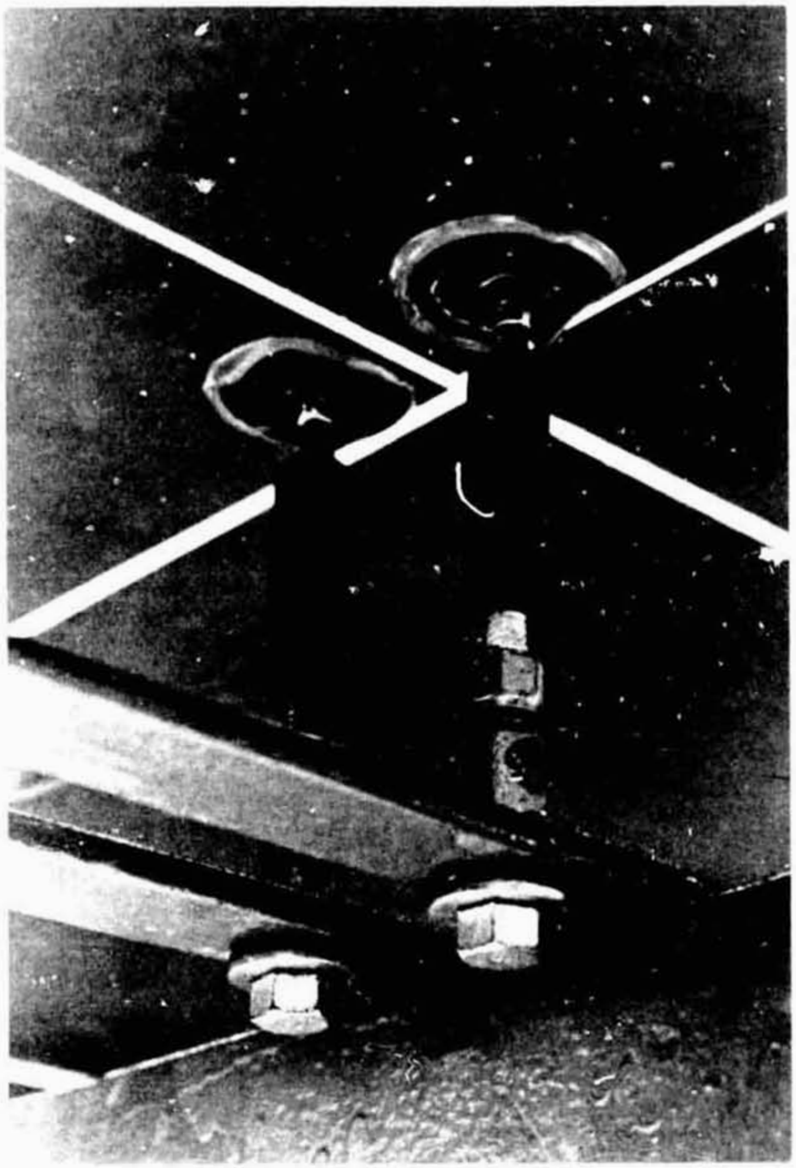

Figure 16. Close-up of Two of the Improved Mirror Mounts After Installation.

The photo diodes are arranged in two pairs with the axes of each pair aligned parallel to the X and Y axes of the heliostat. The focused image is subdivided into four segments by a baffle plate attached to the photo diode support plate. When the heliostat is correctly aimed each diode receives identical illumination and no correction signal is sent to the motor control system.

In order for the automatic tracking system to begin tracking it is necessary to use a manual electronic over-ride to correctly aim the heliostat. After this is accomplished and the system put on "automatic" the heliostat will remain aligned automatically.

4. Sample Support and Transport System

The sample support and transport system consists of a sample cart and rails on which to roll the cart into the focal area of the concentrating mirror. Figure 17 shows the cart in its set-up position. After the specimen (Figure 17) has been mounted an atmosphere chamber (Figure 18) can be put in place if required. After the set-up operation is completed the cart is rolled out on its rails and positioned in the focal area (Figure 19).

The screw jack is then locked into position (Figure 20) and the sample mounting table can then be translated in the X, Y and Z directions by applying power to the correct motor. There are two motors which can be utilized to operate the screw jack, one to rapidly raise the sample

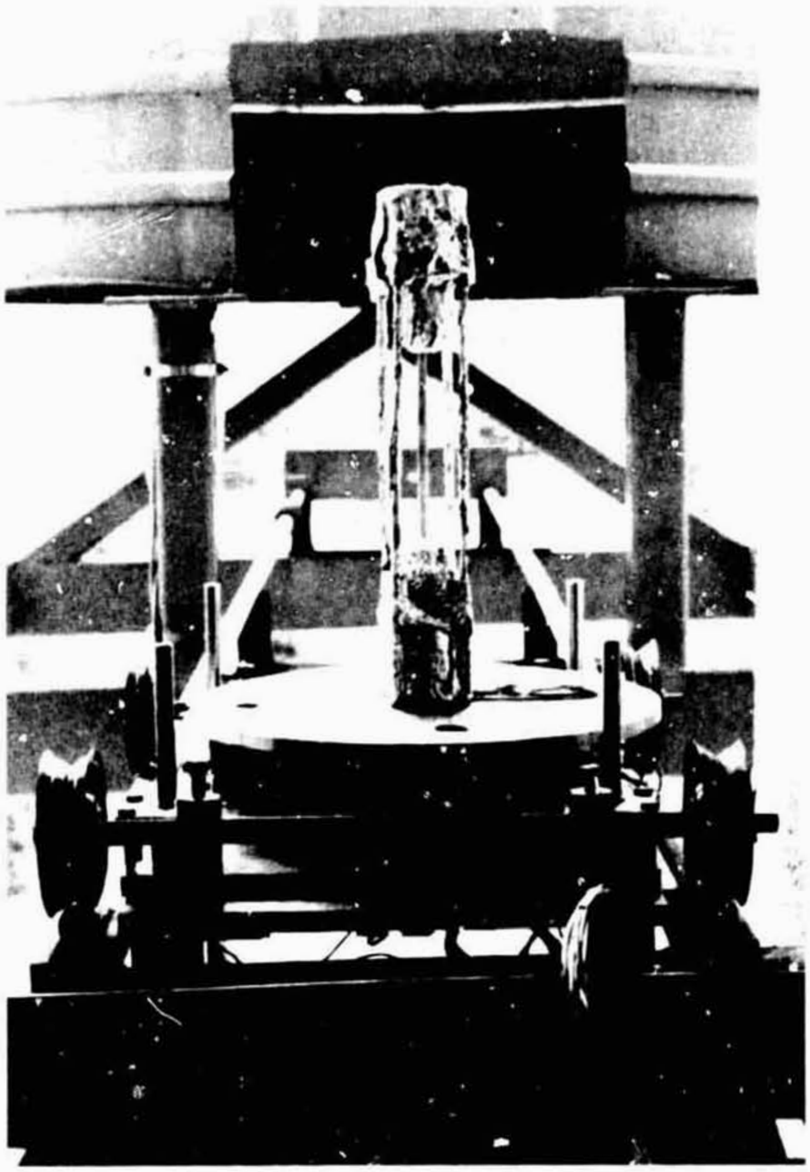

Figure 17. Sample Cart in Set-Up Position.

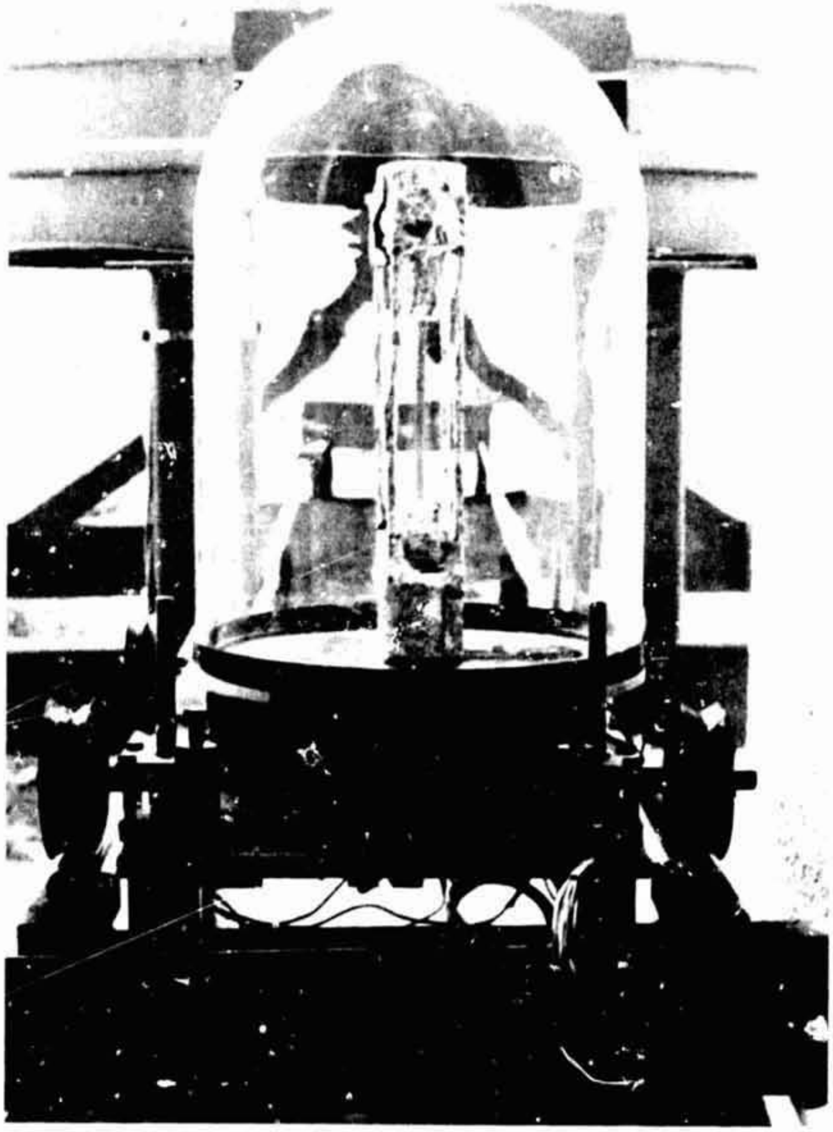

Figure 18. Sample Cart With Atmosphere Chamber in Place.

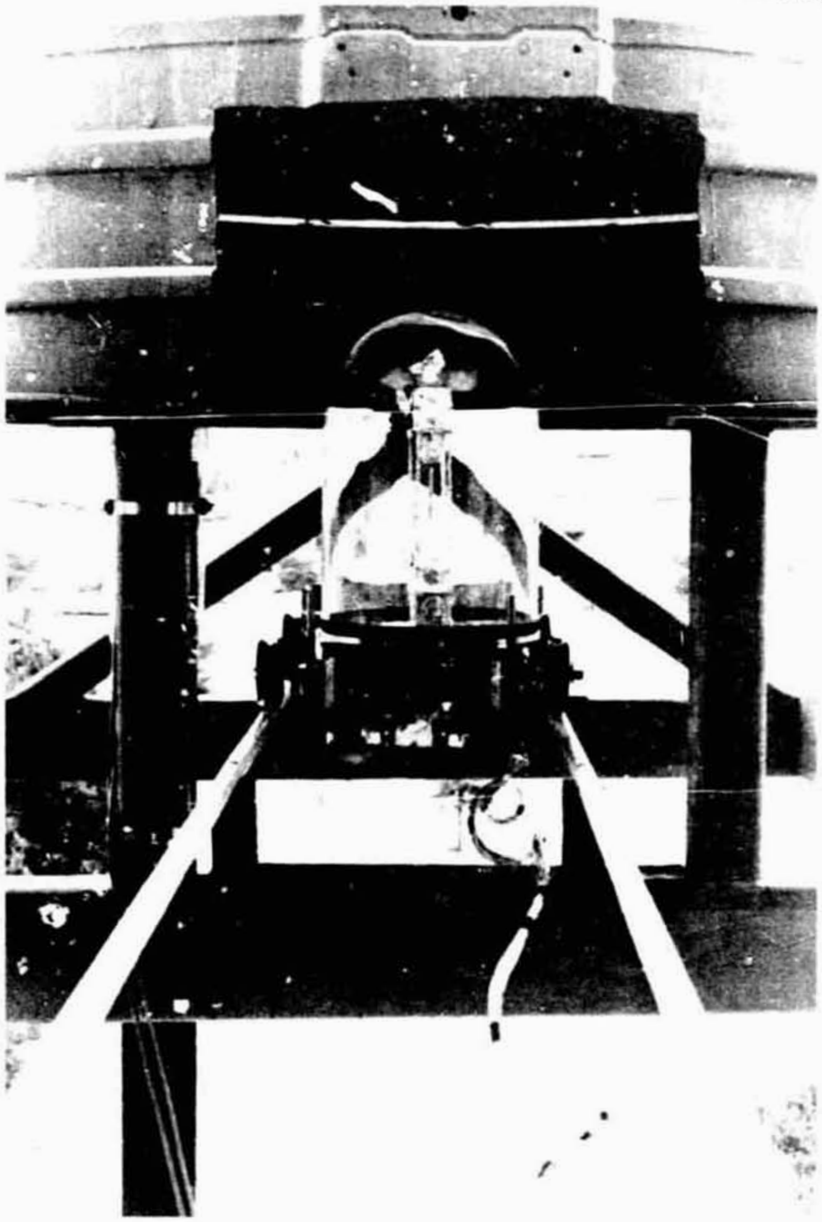

Figure 19. Sample Cart Positioned in Focal Area of Concentrating Mirror.

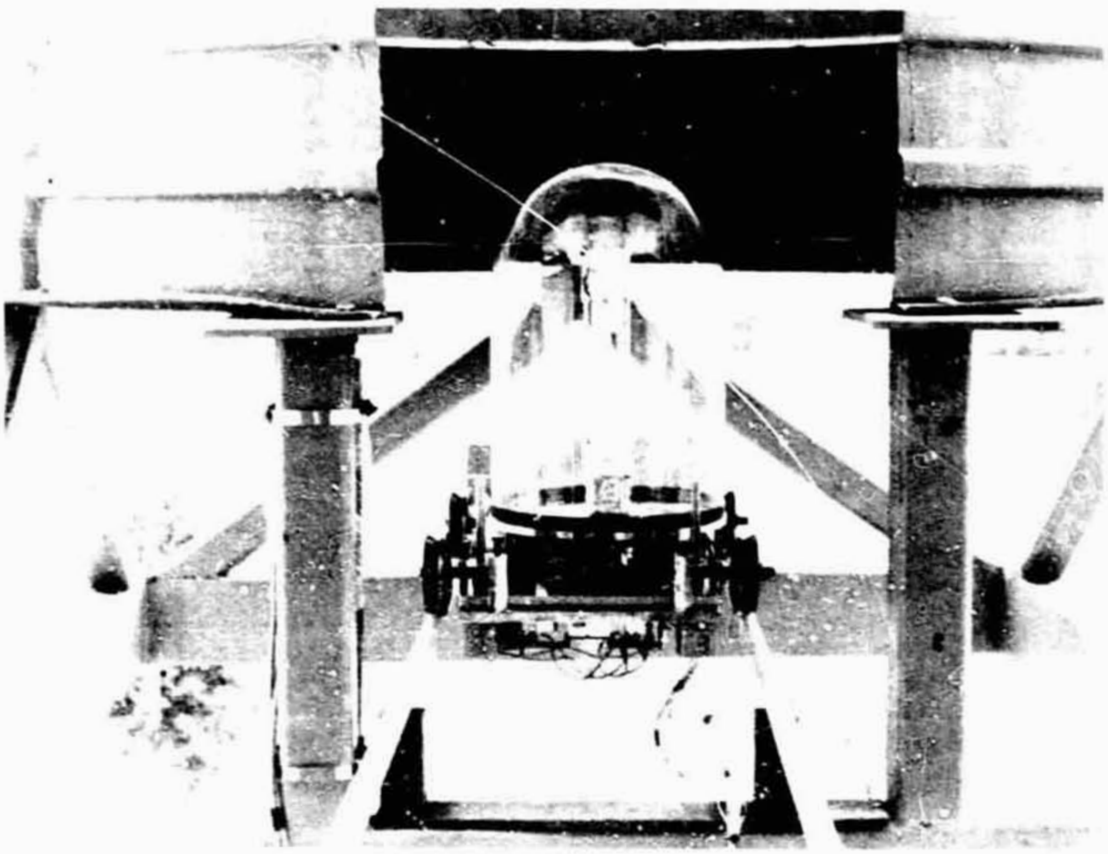

Figure 20. Sample Cart With Screw Jack Locked in Working Position.

to the desired position (Figure 21) and a second to lower the sample at a controlled rate during directional solidification experiments. An electronic clutch system is used to couple the correct motor to the screw jack drive.

A number of motors and gear boxes can be quickly interchanged prior to an experiment to adjust the controlled lowering speed. The range of lowering speeds available at this time is from 0.1 to 10 cm per hour.

In addition the sample can be rotated by two stepping motors. Before melting both motors will be run so the top and bottom of the sample rod are rotated in the same direction. However, after melting one of the stepping motors can be switched to rotate in the opposite direction so the top and bottom halves of the sample rod can be counter rotated.

After placing the sample to be melted in the correct position the heliostat is manually aligned and then placed in the automatic tracking mode to illuminate the specimen. Figure 22 shows an 8 mm diameter alumina rod being heated.

At the time these pictures were taken the focal spot striking a flat surface parallel to the sample suppo. ι table was approximately 6 cm in diameter. Because of this,the alumina rod could not be melted. However, a porcelain insulator (melting point 1200-1300^{o}C) was melted (Figure 23). After the heliostat mirrors are accurately

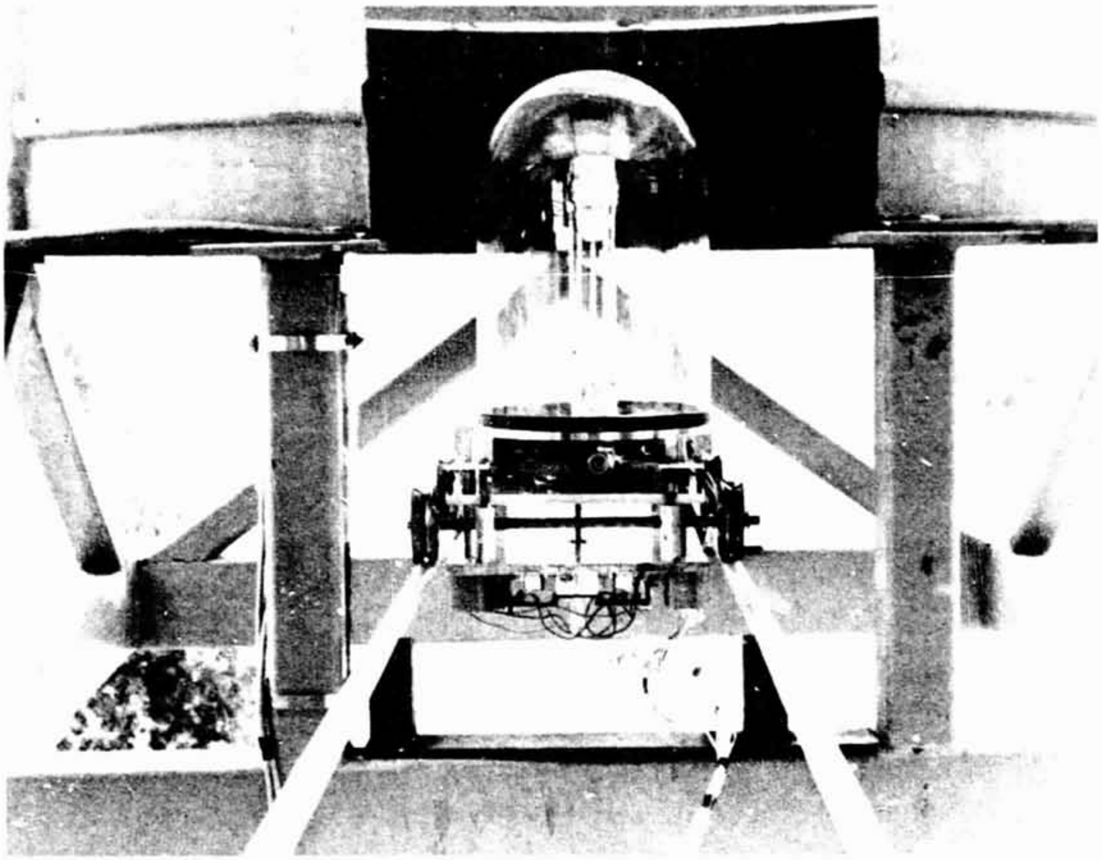

Figure 21. Sample Cart With Sample Support Table in Raised Position.

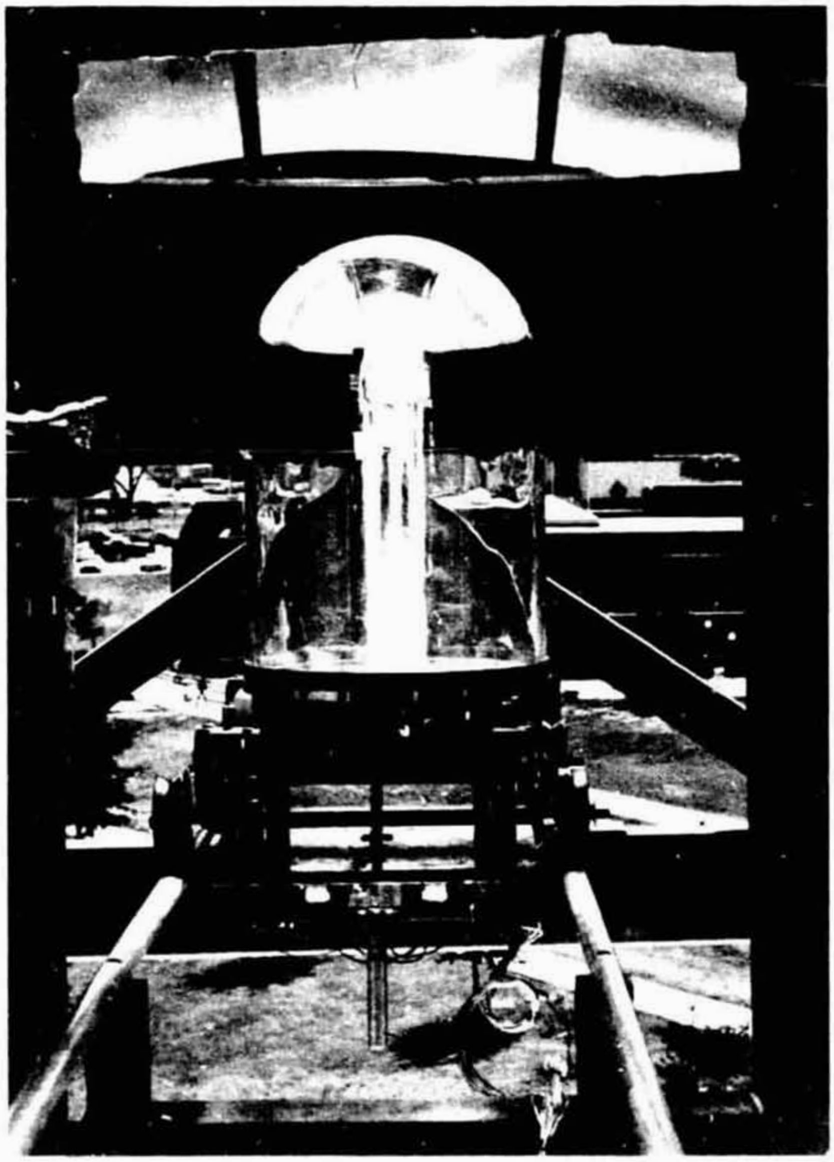

Figure 22. Alumina Rod Being Heated in the Solar Furance.

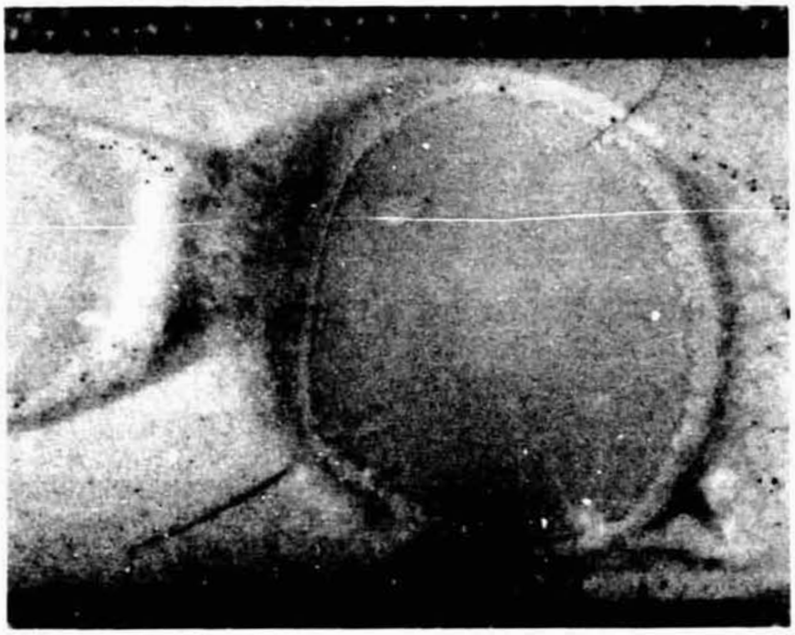

Figure 23. Porcelain Insulator Melted in Solar Furnace, With Heliostat Mirrors Roughly Aligned (8X)

aligned the focal spot diameter should be reduced to about 8 mm. This should allow us to easily melt materials considerable more refractory than alumina.

A summary of the design parameters and characteristics of the verticle axis solar furnace are listed in Table I.

Table I. Characteristics of Verticle Axis Solar Furnace.

<u>Heliostat</u>	
Type	Segmented
Number Mirrors	36
Mirror Size	50 cm x 50 cm
Total Mirror Area	9.06 m^2
<u>Concentrator</u>	
Configuration	Parabolic searchlight reflector
Diameter	1.524 m
Focal length	66 cm
Total Area	1.82 m^2
<u>Thermal Performance*</u>	
Total Thermal Power	1.4 KW (est.)
Thermal Efficiency	80% (est.)
Maximum Heat Flux **	2600w/cm^2 (est.)

* Based on insulation of 900 w/m^2.

** Assuming focal diameter of 8 mm.

E. Evaluation of the Vaporization of Oxide-Metal Composite Eutectics in the Molten State

The melting of oxide-metal rods to their surface in space should allow larger diameter composites to be grown. However, vaporization of the metal phase may become a problem since some vaporization of metal (Mo or W) occurs when oxide-metal composites are grown by the internal floating zone technique. We anticipated that this area would be experimentally investigated during this study. The delays encountered in getting the solar furnace operational have made this impossible. However, the small diameter Gd_2O_3-CeO_2-Mo rod that was melted to its surface by direct rf heating did not display any appreciable vaporization during the short period of time it was molten.

The fact that many of the oxide-metal eutectic systems that Hulse (Ref. 13) solidified using a floating zone technique did not vaporize excessively most likely indicates that this is not a major problem area. However, it may be necessary to control the loss of metal from some oxide-metal combinations melted to the surface by means of pressurized gas envelopes.

F. Effect of Growing Eutectic Composites in the Absence of Turbulent Convection

There had been considerable speculation that variations in surface tension due to thermal gradients would cause turbulent convection currents to occur in the float zone of samples melted in space. Skylab results (Refs. 46 and 47) indicate that: 1) surface tension driven convection is small in comparison to gravity driven convection and 2) surface tension effects in space remain localized on the surface and do not affect growth or segregation in the bulk of the crystal.

If these conditions also hold for oxide-metal eutectic systems this should allow us to take advantage of the improvement predicted, in Section III (A), for space processing.

We expect to be able to simulate low convection conditions in our solar furnace by applying a magnetic field to the floating zone.

G. Evaluation of the Economic Advantage of Processing Oxide-Metal Composites in Space

It is extremely difficult to assess the economic advantage of producing a material in space that is not currently being utilized in a commercial application. However, if larger composites can be grown in space by extending the floating zone across the entire sample, it should increase the volume by useful composite by at least thirty percent. The elimination of structural imperfections such as grain boundaries, colony boundaries and bands by space processing would also increase the value of samples grown in space by allowing the area of emitters to be reduced because of the higher resulting current densities.

However, the most important consideration may be that it now seems that there is a good chance that by growing off-eutectic composites in space we could produce emitter pin arrays which are much closer to the theoretical optimum than we can on earth. It thus may be necessary to grow this type emitter structure in space in order for the potential market to even develop.

H. Market Volume Projections for Oxide-Metal Composites

In our previous report (Ref. 24) it was concluded that a large market (≈$20,000,000) for oxide-metal emitters was likely to develop over the next ten years. The fact that the operating parameters for this type of emitter have been improved considerably during the past 23 months indicates that this projection may be closer to realization. A brief summary of these improvements are listed in Table I.

Table II. Summary of the Improvements in Oxide-Metal Emitter Properties

Property	November 1974	October 1976
Current Density	1 amp/cm^2	10 amps/cm^2
Noise Level	$<$ 2%	$<$ 1%
Demonstrated Life Time	$>$1000 hours	$>$3000 hours

In addition a cooperative evaluation program has been initiated in conjunction with one of the larger manufacturers of thermionic emitters. This program is evaluating the possible replacement of the standard dispenser cathode with a field emitter in selected types of microwave tubes.

Samples of oxide-metal composites have been furnished to: 1) Interactive Radiation, Inc.; 2) U.S. Army Electronics Command; 3) Microwave Associates; 4) RCA Laboratories; 5) U.S. Army Missile Command and 6) Exxon Corporation, for evaluation in electronic and other type applications.

The possibility that sponsorship for the development of low voltage emitters will be available in the near future also should increase the probability of commercial production of oxide-metal composite electronic devices.

IV. SUMMARY AND CONCLUSIONS

In the two years since our original Report (Ref. 24) a number of experiments have been performed in space. The results obtained from several of these investigations seem to substantiate our earlier conclusion that larger and more perfect oxide-metal composite structures could be grown under zero-g conditions. The observation of decreased impurity segregation coupled with the fact that surface tension convection appears to be confined primarily to the surface of the floating zone most likely indicates that oxide-metal composites containing few or no colony boundaries can be grown in space. It also is likely that the number of grain boundaries in these materials could also be decreased by space processing.

Possibly the most significant result related to growing oxide-metal composites in zero-g is that it appears that the thickness of the diffusion controlled liquid zone is larger in space than on earth. If this is true it means there is a high probability that ordered off-eutectic oxide-metal structures could be produced in space. This would allow us to grow composites containing emitter pin arrays much closer to what theory predicts would maximize current density for this type emitter.

The solar furnace which has been constructed appears to be capable of directionally solidifying small diameter oxide-metal composites after its heliostat mirrors are precisely aligned. This facility should then be quite useful in simulating low-g growth experiments.

It still appears that a large market for oxide-metal high field emitters will develop by 1985. Significant improvement in the performance of this type emitter has been achieved during the last two years.

V. RECOMMENDATIONS

The large potential market for oxide-metal high field emitters and expected economic advantages to be gained by zero-g processing indicate that investigation of the manufacturing or oxide-metal composites in space should be continued. Some of the areas that should be given high priorities are:

1. Techniques for unidirectionally solidifying small diameter oxide-metal rods using our vertical axis solar furnace should be developed.

2. It should be determined if solar furance heat flux can be controlled well enough to prevent power fluctuation banding in oxide-metal composite.

3. The amount of improvement that can be expected in high temperature oxide-metal composites grown in the absence of turbulent convection should be evaluated. Unidirectional solidification of small-diameter rods with a magnetic field applied perpendicularly to the growth direction should allow this to be accomplished using our solar furnace.

4. An acoustic positioning device should be incorporated into the solar furnace system so that in conjunction with a magnetic field (see 3 above) conditions very similar to those in space would be available to study the solidification of spheres as large as 2 cm in diameter.

5. The extent of the vaporization problem when oxide-metal rods are melted to their surfaces should be determined and, if necessary, the effect of high pressure inert gas atmospheres on reducing the rate of vaporization can be evaluated.

6. Small diameter rods of oxide-metal composite compositions which melt at too low a temperature to be directionally solidified using the internal floating zone technique should be grown in the solar furnace. Composites containing noble metal fibers apparently would be suitable for medical implants designed to create artificial sight.

7. The solar furnace should be used to investigate the feasibility of growing beta alumina in space. Beta alumina is not a true eutectic but does exhibit a layered structure similar to a lamellar eutectic. Because of the difficulties of growing single crystals of this material under terrestrial conditions it has been suggested (Ref. 55) that it is a good candidate for space manufacturing.

VI. NEW TECHNOLOGY

Due to the limited experimental effort of this study, no reportable items of new technology were developed.

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