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YTTRIUM VANADATE: POLARIZER MATERIALS

G. A. Keig, et al

Union Carbide Corporation

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YTTRIUM VANADATE POLARIZER MATERIALS

INTERIM TECHNICAL REPORT

Contract No. DAAB07-72-C-0022

by

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SUMMARY

This program sponsored by the U. S. Army Electronics Command under Contract No. DAAB07-72-C-0022 is directed towards the development of a growth method for the production of high quality YVO_4 single crystals. These crystals will be fabricated into polarizing prisms for use with laser systems, and other applications requiring the use of polarized light.

During the first quarter the crucible and furnace for carrying out crystal growth have been designed and tested. Some initial runs were made to test the concept of maintaining melt stoichiometry by forming it within a sealed crucible. These runs were hindered by weld problems associated with the alloying of Iridium with Vanadium metal formed by the reduction of the YVO_4 melt. Changes in welding techniques and furnace design will be made to alleviate this problem.

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1.0 INTRODUCTION

Yttrium Vanadate, YVO_4, has been identified as an attractive single crystal material for use as a polarizer material. It exhibits a large, positive birefringence, a high refractive index, good transmission in the IR, and good fabrication properties. Investigations of laser damage resistance when compared to natural calcite demonstrates a higher damage threshold. Polarizer design studies have taken advantage of these specific properties and result in polarizer configurations which can out perform natural calcite by an increase in beam splitting efficiency, a reduction in air-gap reflection losses, and an increase in laser power handling capability for air-gap designs depending upon the specific design selected.

The objective of this contract effort is to establish a crystal growth method which will permit the fabrication of polarizer prisms from large diameter, high-quality YVO_4 crystals for use in laser systems. Specific goals are to obtain YVO_4 crystals approximately 3/4" diameter by 6" long of at least two crystallographic orientations and to fabricate demonstration polarizing prisms from such material.

The growth method chosen utilizes a sealed crucible containing a charge which is subsequently melted and cooled under programmed conditions in a controlled atmosphere furnace. Initial and modified crucible designs are discussed along with the results of experimental runs executed in the period covered by the report.

2.0 TECHNICAL BACKGROUND

Growth of single crystals of YVO_4 have been attempted through solidification from either a fluxed or a near-stoichiometric melt. The flux method has the advantage of lower melting points. The single crystals obtained, however, are small, relatively poor quality samples and are achieved through very slow growth rates.[1, 2, 3] The growth from stoichiometric melts has been attempted using the Czochralski,[4, 5] Float Zone,[6] and Verneuil[7] methods. Of these the Czochralski method has been the most successful and has yielded good quality doped and undoped crystals suitable for laser testing. It remained, however, somewhat erratic and difficult to control, and substantial doubt existed concerning its subsequent development to a reliable production method.

The basic problem lies with maintaining stoichiometry at the YVO_4 composition. Under conditions which will preserve an iridium crucible, the melt has a tendency to move its composition through a reaction which, in its most general form, can be given as:

$$YVO_4 \rightarrow YVO_{4-x} + \frac{xO_2}{2} \uparrow$$

This compositional change causes problems with establishing a set-point from which to grow the single crystals. In addition, the crystal reduces after growth due to a change in the valence state of the Vanadium ion from $V^{5+} \rightarrow V^{4+}$ and/or V^{3+}. The valence change, which comes about through holding the crystal at an elevated temperature in the growth atmosphere, gives a black coloration to the crystal. This, in turn, seriously affects the radiative heat flow through the crystal and introduces chromic control problems.

The method utilized in the present work attempts to maintain stoichiometry through forming the melt within a sealed crucible. A general description will be given of the process, and the progress reviewed. The bulk of the work to-date has been concerned with furnace design and calibration, along with the development of a method for successfully sealing the crucible. Some initial experiments have been conducted, in which a melt has been formed within the crucible.

3.0 GROWTH METHOD

The use of a sealed capsule to maintain the stoichiometry of a melt by preventing the volatilization of one or more of the compound species has been developed for a number of materials. Predominant in this regard is GaAs where growth is carried out in sealed quartz capsules and the stoichiometric composition is maintained through an overpressure of As above the melt.[8] This method represents the prime manufacturing process for polycrystalline III-V compounds and a large percentage of high quality single crystals. It has more recently been extended to cover a number of volatile, high-melting-point oxide materials, where growth is carried out in sealed refractory metal crucibles.[9]

The method requires that the volatilization of the unstable species proceeds to the point where a sufficient vapor pressure has been built up to suppress the forward reaction. Ideally, this would require an excess of the volatile species in the original composition so that equilibrium is established between a stoichiometric melt and the vapor. This can be calculated knowing the equilibrium overpressure at the melting point and the volume of the space filled by the vapor.

The decomposition is relatively straightforward for the compound semiconductors involving a transformation from the liquid to the gaseous state for one of the elements. With YVO_4, however, the situation is more complex, and breakdown of the constituent compounds occurs into reduced states. Thus, the Yttrium Vanadate melt can be considered as a $Y_2O_3:V_2O_5$ mixture with Y_2O_3 as the stable and V_2O_5 as the unstable compound.

The breakdown of V_2O_5 into the reduced vanadium oxide compounds can take place through the following reactions:

$$2V_2O_5 = 2V_2O_4 + O_2\,(g) \qquad (1)$$

$$2V_2O_4 = 2V_2O_3 + O_2\,(g) \qquad (2)$$

$$2V_2O_3 = 4VO + O_2\,(g) \qquad (3)$$

$$2VO = 2V + O_2\,(g) \qquad (4)$$

Data is available for the heat, free energy, and equilibrium oxygen pressure as a function of temperature, for the dissociation of these oxides.

All the reactions have positive free energies throughout the temperature range 298°K to 2000°K. Vanadium pentoxide dissociation is the most appreciable with calculated equilibrium oxygen pressure of ~0.8 atmosphere at 2000°K. It should be noted that, although the vanadium dioxide dissociation is relatively slow compared to the pentoxide at 2000°K, the oxygen pressure increases rapidly with temperature and starts to become significant at melt temperatures between 1850 and 1900°C.

To obtain some better feeling as to the equilibrium oxygen pressure for reactions (1) and (2) at temperature ($>$2000°K), the calculated data between 1000°K and 2000°K has been taken and a "least squares" best fit of a straight line to the data pairs (oxygen pressure-temperature) computed. Using this information, an extrapolation of oxygen pressure to temperatures between 1700°C and 2000°C has been made and is shown in Table I for dissociation of both the V_2O_5 and V_2O_4. These data can only represent an approximate value for the vapor pressure at the higher temperatures as the linear fit of log pO_2 against T is not a good one (log pO_2 against 1/T was also attempted with poorer result). They can, however, anticipate some of the experimental problems and indicate what is feasible.

At 1850°C the extrapolated equilibrium vapor pressure of oxygen is between 1.0 and 1.2 atmospheres for V_2O_5 dissociation to V_2O_4. This indicates that, provided the melt temperature is maintained at this level, the oxygen pressure necessary to maintain the melt composition can be contained in a properly sealed crucible. The dissociation of V_2O_4 will be of no consequence under these conditions, as the equilibrium oxygen vapor pressure can be shown to less than 5×10^{-2} atmospheres. This is not the case for open crucibles at 1850°C where oxygen pressures in the atmospheres above the melt cannot exceed 5×10^{-3} atmospheres if the iridium oxidation is to be controlled. In this case, the V_2O_4 dissociation reaction can proceed, and the pressure of both V^{4+} and V^{3+} ions would be anticipated in the melt.

In addition to the decomposition of the vanadium oxide, it is also necessary that the material chosen to contain the melt does not oxidize to build up an excess pressure of the metal oxide under the anticipated operating conditions. The equilibrium pressure of both iridium oxide and tungsten oxide has been calculated for one atmosphere oxygen pressure at 1810°C.

$2\ V_2O_5 = 2\ V_2O_4 + O_2\ (g)$ ....(1)

Temperature, °C	1600	1700	1800	1900	2000
O_2 Pressure, Atmos.		0.516	1.150	2.563	5.709

$2\ V_2O_4 = 2\ V_2O_3 + O_2\ (g)$ ....(2)

Temperature, °C	1600	1700	1800	1900	2000
O_2 Pressure, Atmos.		0.001324	0.0186	0.106	0.950

$Y = 3.479 \times 10^{-3}\ X - 7.151$ ....(1)

$Y = 9.521 \times 10^{-3}\ X - 21.633$ ....(2)

$Y = \log pO_2$ $\qquad$ $X = T^\circ K$

Table I. O_2 Pressure as a Function of Temperature for the Dissociation of V_2O_5 and V_2O_4

It is known that the volatile oxide of iridium above 1100°C is IrO_3, formed through the reaction:[10]

$$2Ir + 3O_2 \rightarrow 2IrO_3.$$

The partial pressure of IrO_3 can be given as a function of oxygen pressure through the expression:

$$p^2_{IrO_3} = K \times p^3_{O_2}$$

where K is the equilibrium constant which is related to the temperature through the equation:

$$\log_{10} K(mm) = \frac{2034}{T} - 7.346$$

A plot has been made in Figure 1 of the IrO_3 partial pressure in mm of Hg versus the centigrade temperature at one atmosphere pressure of pure oxygen. The IrO_3 partial pressure is shown to be approximately 1.5 mm Hg at the melt temperature of 1810°C; this clearly indicates the possibility of maintaining a stable melt within the sealed crucible without an excessive pressure build-up and/or erosion of the crucible walls.

The mechanical properties of iridium are superior to other refractory metals which might be used in this application except for tungsten. A similar calculation for tungsten shows that the equilibrium pressure for the oxide (WO_3) would be in excess of 40 atmospheres at the M. P. of yttrium orthovanadate, thus excluding its possible use. Table 2 shows the calculated results for both IrO_3 and WO_3.

The experimental work carried out for the contract seeks to develop the sealed crucible growth method into a practical working system capable of producing large-size, high-quality single crystals. The design of crucible and furnace is described along with an account of the experimental runs that have been conducted to date.

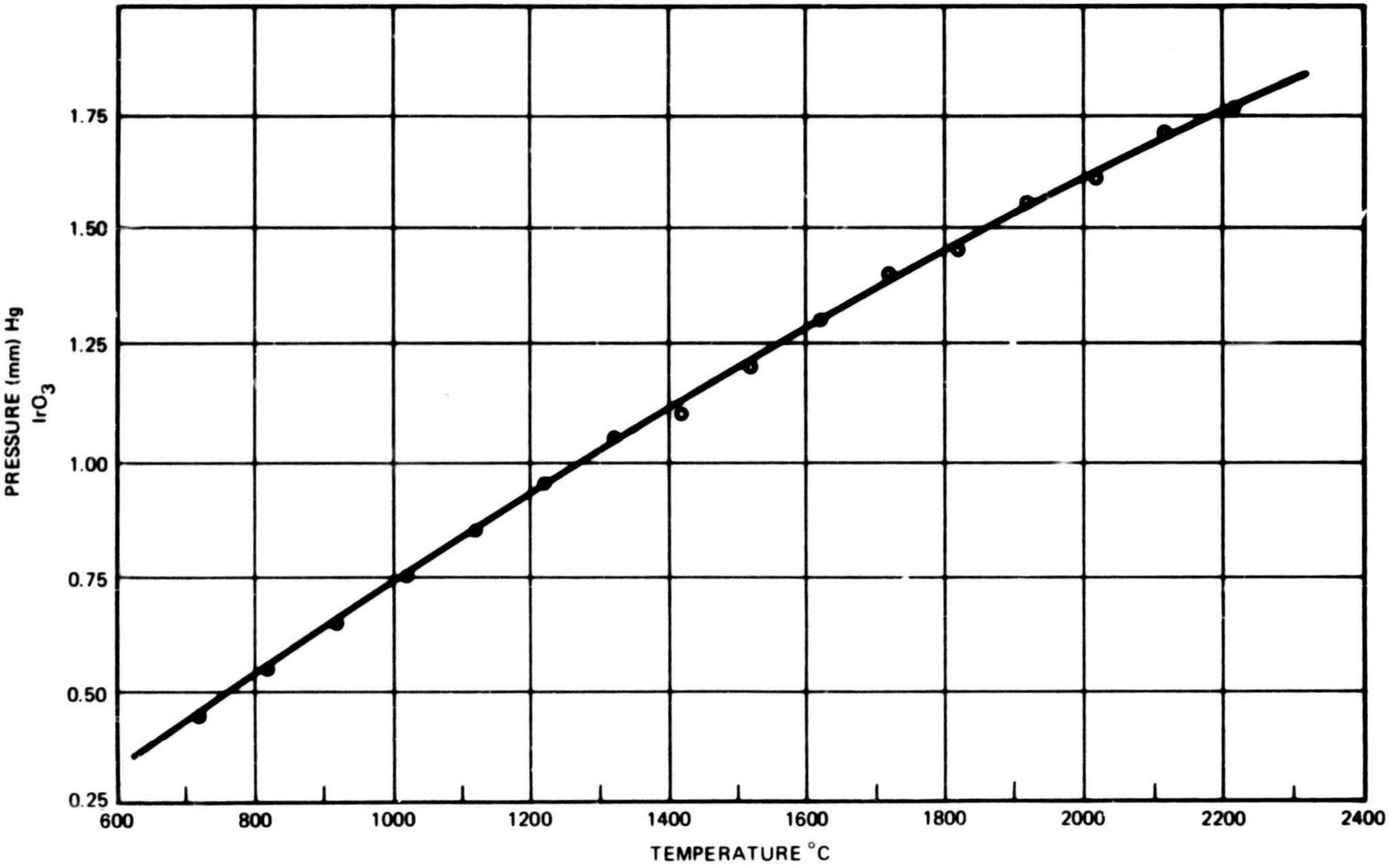

Figure 1. Partial Pressure of IrO_3 Plotted as a Function of Temperature for One Atmosphere Oxygen Overpressure

TEMPERATURE °K	PRESSURE IrO_3 mm. Hg.	PRESSURE WO_3 mm. Hg.
1.000E03	4.278E¯01	4.773E¯11
1.100E03	5.293E¯01	1.820E¯08
1.200E03	6.320E¯01	2.576E¯06
1.300E03	7.344E¯01	1.702E¯04
1.400E03	8.352E¯01	6.182E¯03
1.500E03	9.337E¯01	1.390E¯01
1.600E03	1.029E00	2.119E00
1.700E03	1.122E00	2.344E01
1.800E03	1.211E00	1.986E02
1.900E03	1.297E00	1.343E03
2.000E03	1.379E00	7.504E03
2.100E03	1.459E00	3.559E04
2.200E03	1.534E00	1.465E05
2.300E03	1.607E00	5.334E05
2.400E03	1.677E00	1.743E06
2.500E03	1.743E00	5.183E06

Table II. Vapor Pressure of IrO_3 and WO_3 at Equilibrium with One Atmosphere Oxygen in the Temperature Range 1000 to 2500°K

4.0 CRUCIBLE DESIGN

Initial experiments were conducted in roughly fabricated iridium crucibles to help establish parameters for a final design. The first test was run in such a crucible having a 1" diameter x 5" length with one end formed into a conical closure. In this case, some leakage occurred which was attributed to both fabrication and the previously-used iridium pieces from which it was constructed. The experiment was run in a zirconia-refractory lined furnace in a nitrogen atmosphere. Although the charge had not melted completely, the portion which did melt remained clean upon solidification; no attack was noted on the inner surfaces of the crucible.

Based upon this, a crucible was designed somewhat differently than originally planned in that the diameter was increased to 1" ID x 1-1/8" OD, taper was eliminated as being of no value to the upcoming experiments, and the overall length was changed to better fit the developed furnace configuration. The length was set at 4-1/2" of the 1-1/8" diameter body, the upper end was closed with a fusion-welded .090" thick disc, and the lower end fusion-welded to the large end of a 60° cone. The small end of the 60° cone terminated at its 1/4" diameter point where it was joined by fusion welding to a 1" long tube having an OD of 1/4" and ID of 3/16". The lower end of this tube was fusion-welded to a 1/4" diameter closure disc. See Figure 4 which shows the completed crucible before final closure.

Leak detection was accomplished using a Model MS9 Veeco leak detector at the various stages of assembly. The crucible was then cut off normal to the axis and 1/2" below the upper closure using a .015" thick rubber-bonded silicon carbide cut-off saw. This provided a smooth finish on the mating surfaces which were to be fusion butt-welded after charging with yttrium vanadate pellets.

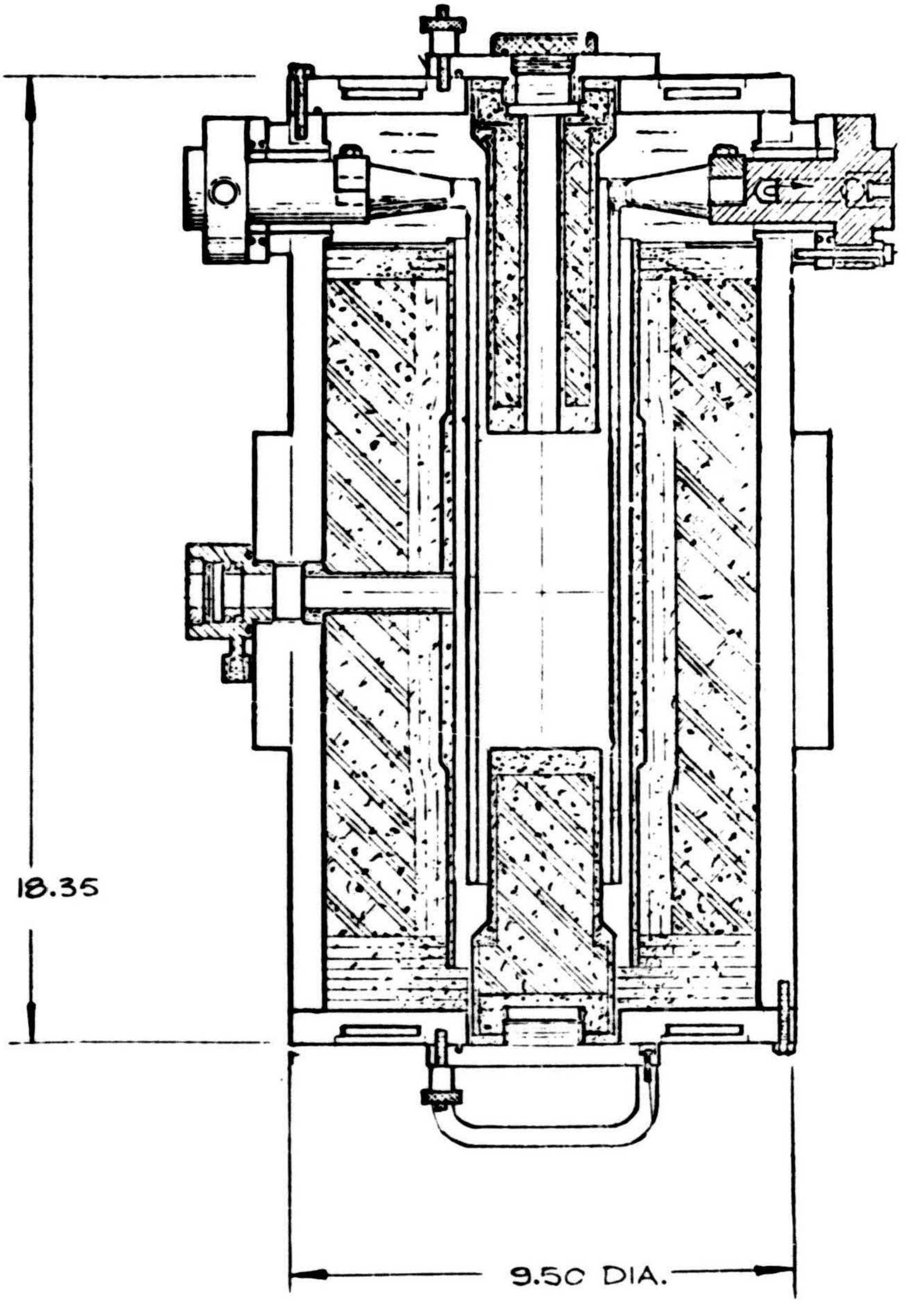

Figure 2. Standard Furnace Design according to Astro Industries

watt transducer output to an internal signal level established by the program set-point and makes necessary correction to the Loyola SCR control to null any signal difference. Line voltage variations are compensated in the same circuitry, automatically.

5.4 Gas Flow

As noted under 5.2 "Programming", the gas flow is programmed by the modified Datatrak and is stabilized for repeatability by a Conoflow Differential pressure regulator. Plant nitrogen distribution lines are connected to the flow control components through a pressure regulator which levels out plant demand excursions.

5.5 Recording

Each run is recorded on a six-point Model PBA 12 Rikadenki Kogyo recorder.

Traces recorded are:

- SCR output current which is sensed by a vacuum thermocouple across a shunt
- input gas pressure and back pressure of the lance cooling gas monitored by accessories to Statham load cells and a signal provided by Statham gold cells
- exit gas temperature measured with a chromel-alumel thermocouple
- gas temperature at the hot bulkhead measured by a W/6%Re versus W/26%Re thermocouple
- output of a Coloratio optical pyrometer sighting on the upper closure of the crucible

5.6 Testing and Calibration

Initial tests of the gas lance effectiveness were made prior to contract initiation, and resulted in some modification to the original proposed design. The final lance design, as shown in Figure 3, provides a temperature change on the upper crucible sighting spot of 40° downward from 1865°C during an increase in gas flow of 35 SCFH in the lance. A temperature gradient of about 40°C exists over the length of the crucible in the same temperature range. A program designed to increase the gas flow rate exponentially will provide a linear temperature rate change at any given point within the crucible. Thus, a uniform growth front velocity will be achieved. Other experiments have been run in an effort to simulate a filled crucible for a closer approach to actual conditions. These simulations have been helpful in arriving at the beginning parameters.

A switching problem interfered with program power initially and was corrected by using a more suitable relay. The original model relay had erratic resistance characteristics under essentially dry circuit conditions and produced unwanted excursions in the power.

Minor variations were noted in the gas flow using conventional regulation and it has proven to be due to pressure drop variations across the programmer valve. A Conoflow Differential Pressure Regulator was ordered and installed across the programmer valve to produce an acceptable gas program in subsequent runs.

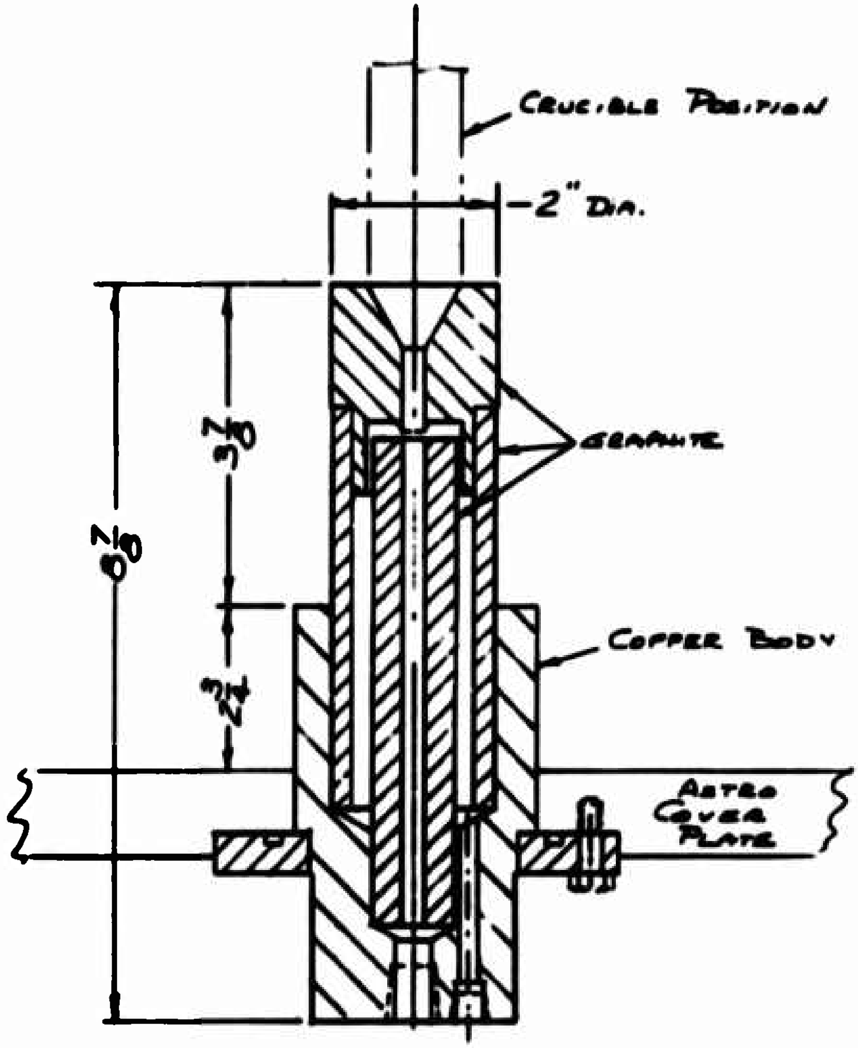

Figure 3. Gas Lance Modification for Astro Furnace

6.0 EXPERIMENTAL RESULTS

The experimental work is documented in a series of photographs contained in Figures 4 through 13 which show also the progressive use problems generated during the second and third furnace runs. Figure 4 shows the crucible after cutting from its original 18.5 cm body length. During further fabrication, the cover was rewelded to the 12.5 cm body length after charging with YVO_4 pellets. Run #1 was then made with the bottom tube open to furnace atmosphere purge with the stem in the stream of the gas lance jet of N_2. Furnace instability caused a premature shut down. The crucible was opened and recharged with new material after it was noted that melting had not occurred. For Run #2 the lower end was also sealed to form a pressure vessel. The furnace power was increased about 3% and resulted in upper surface melting of the charge. The run also showed the evidence of weld porosity and resultant leakage of some of the decomposed V_2O_5, which reduced to the metal vanadium in the furnace atmosphere and alloyed with the iridium. The section which was alloy contaminated (Figure 5) was necessarily removed and the original 6 cm length cut-off-end was rewelded to the remaining body diameter and a new cap fabricated for Run #3. After charging with YVO_4 pellets, the assembly was then sealed at the cap by electron beam weld at Solar Division of International Harvester Co.

Run #3 was made at a further power increase of 3%. During the run, a power excursion was apparent during switching from the power-ramp-up to power-hold for gas programming sequence and then again when switching from power-hold to power-ramp-down; these excursions were corrected by changing to a different model relay. The run was not seriously affected by the power excursion but a weld area leak did occur at the repair point which spilled a substantial amount of the charge again creating a destructive alloying which necessitated the retirement of the crucible. It was noted that the electron beam weld was clean and showed no evidence of failure. The crucible was opened by cutting through this weld. The metal at the weld was clean inside and outside the crucible. Figure 6 shows the crucible at this stage, and Figure 7 shows an enlargement of the leakage point. Figure 8 shows the leakage point approximately 180° from the one shown in Figure 7. Figure 9 shows the effect of the leaked compound on the crucible-graphite interface of the heat sink which resulted in the parting of a shallow layer of graphite from the sink and its attachment to the crucible cone. One additional fact observed on the crucible concerns the internal pressure developed during the run as evidenced by the bulge in crucible cap as shown in Figures 10 and 11; this could be the result of portions of the crucible being overheated into the 1900°C to 2000°C temperature range.

Figure 4. Original Iridium Crucible for YVO_4 Growth. Crucible is shown as-cut for refabrication.

Figure 5. Condition of Iridium Crucible After Run #2. Upper wall shows alloying effect.

Figure 6. Iridium Crucible After Run #3. Electron Beam Weld at top has been cut to open the crucible.

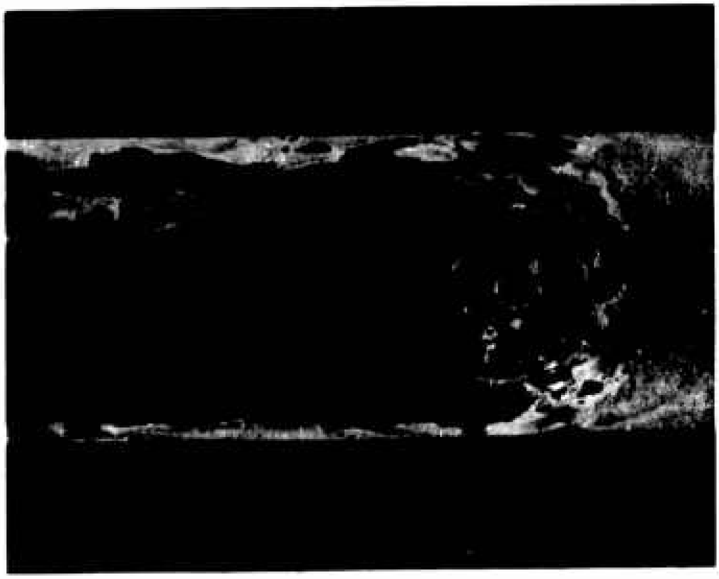

Figure 7. Enlargement of Major Leak Area in Iridium Crucible.

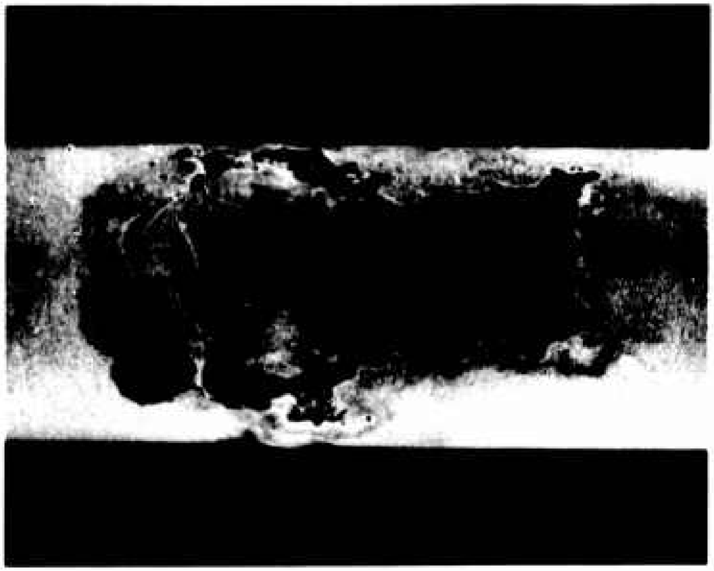

Figure 8. Leak Area in Iridium Crucible.

Figure 9. Damage in Iridium Crucible at Contact Point Area with Graphite Sink.

Figure 10. Iridium Cap Showing Bulge Due to Pressure Build-Up.

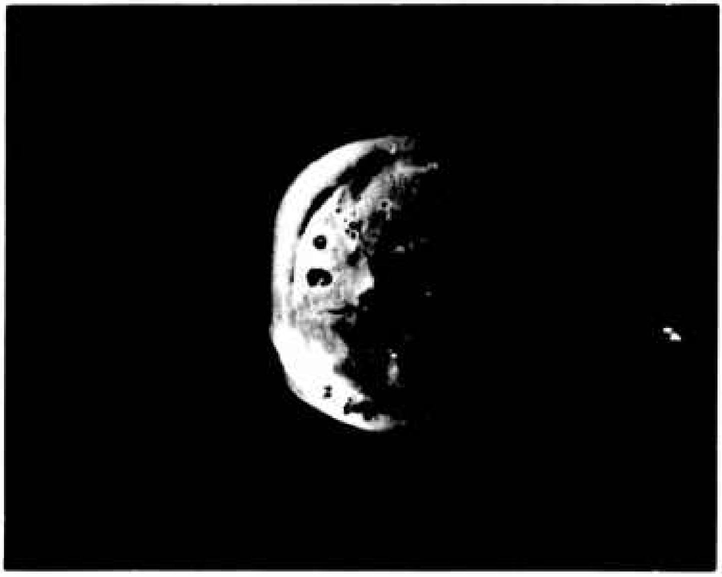

Figure 11. Pressure Stress Cracking in Iridium Cap Exhibiting No Leakage.

Figure 12 shows the core-drilled cylinder from Run #3 removed and displayed alongside the crucible at its same altitude position when intact in the crucible. The cone portion remained in the crucible and was recovered by further dissection of the crucible. It was a black crystalline mass showing cleavage perpendicular to the crucible axis, large voids in the crystalline cone and the remains of the c-axis oriented seed top near the cone apex. It appears that a regrowth start was made on the c-axis seed but did not progress beyond a large void above it, where oriented polycrystalline growth developed. Some edge melting was observed on a fracture perpendicular to the axis just below this area and leads to the impression that the seed had fractured and remained intact above this break without melting. Polycrystalline growth surrounds the seed and below the fracture.

Of interest is that at about the 11 cm mark on the photo scale the oriented crystals stop, for the next 2.5 centimeters the solid is finely polycrystalline, and then, at the 9.5 cm mark, a random polycrystalline growth starts with much larger crystallites. At about the 19.75 cm bench mark on the recorder trace for this run, a current trace anomoly occurred indicating a serious drop in the upper lance gas temperature while the Coloratio optical pyrometer sighting on the upper end of the crucible recorded a temperature drop of approximately 81°C over a ten minute period and a regain of 37°C over the following fifteen minutes. It is theorized that the crystalline material in the cone was gas-lance-controlled growth and that the 81°C temperature drop froze the balance into a fine polycrystalline mass. The recovery of 37° was apparently enough to remelt the upper 2-1/2 cm which again grew into large crystallites of random orientation. This run, although first appearing to be a failure, has provided substantial information about the furnace thermal pattern which could not have been deduced from a run without the current anomoly present.

As a result of the leakage of the crucible during Run #3, another crucible was ordered at once; and preparation for further experiments was made using iridium capsules to further study the reactions before further runs in the design crucible.

The first iridium capsule experiment designated as Run #4 was made on March 20, 1972. The capsule was constructed of iridium tubing .375" OD by .032" wall by 1-1/4" long. The capsule was charged with pellets of sintered YVO_4, and the assembly was then closed by TIG-welding a previously prepared cap in place. The capsule was then placed in a close-fitting graphite crucible which rested on the heat sink lance.

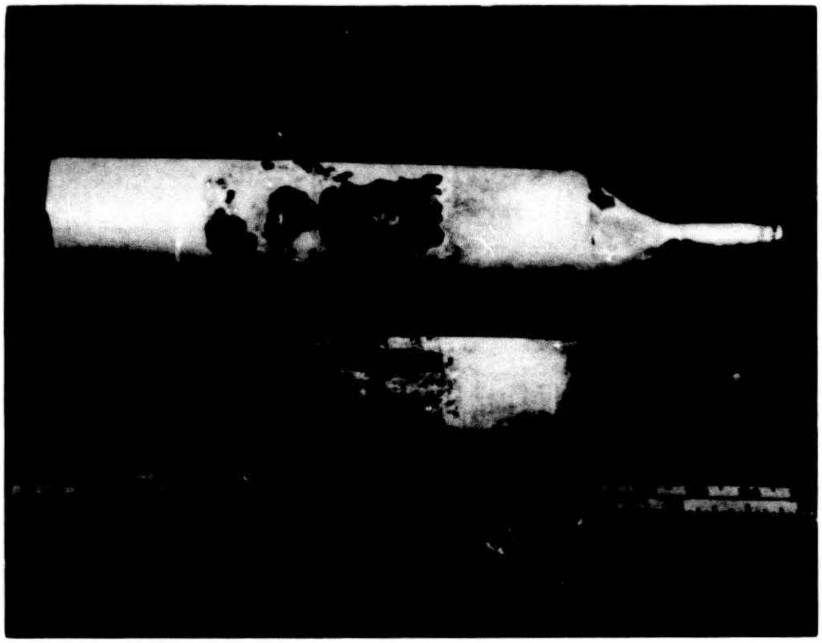

Figure 12. Iridium Crucible from Run #3 with Core-Drilled YVO_4 Growth. Displayed relative to position in growth.

Figure 13. Yttrium Vanadate Crystallites (25x), Capsule Growth.

The capsule did not leak and was opened by cutting off both ends. In the upper end was a clean, minute single crystal surrounded by black oxygen deficient YVO_4. See Figure 13.

The charge was removed and the capsule boiled in HCl to remove residual charge material. The first cap end was then TIG-welded in position, a new charge was added, and the second cap was TIG-welded in position using a heavy copper heat sink for the body of the capsule.

Some alloying at the TIG weld during closing was noted but not correctable. This capsule was used in Run #5; it leaked all of the charge into the graphite crucible and the Run and crucible were lost.

Run #6 was made in another capsule at .375'' diameter iridium tubing which was constructed and charged in the same manner as before except that the charge was not sintered material but was a piece of single crystal YVO_4 which had been hand-ground to fit the inside diameter. Because of previous alloying problems, the final closure was made by electron beam welding at the Solar Division of International Harvester Company. The weld had three spots in which alloying was suspected because of different structural appearance. It was used as-welded because it was not salvageable if the weld was at fault.

Heating in this case was done in an R.F. induction furnace surrounded by zirconia felt to avoid the complication of a reducing atmosphere surrounding the capsule. The time at melt temperature was limited to a 10-minute cycle, and the cool-down was not slow enough for proper crystallization. Once again, leakage occurred with the electron-beam weld area suspected; the probable point of leakage was a crack initiated due to bulging of the diameter of the capsule from internal pressure.

7.0 SUMMARY AND PLANS FOR SECOND HALF OF CONTRACT PERIOD

The iridium crucible has been designed and fabricated, and the growth furnace has been constructed and tested. The major problem encountered during the first half of the contract was the sealing of the iridium crucible. This sealing was not achieved for the large-growth crucible due to problems associated with the alloying of the iridium with vanadium from the charge; as a result, this restricted further welding attempts in the contaminated areas.

The main source of the leakage problem in use is the highly-reducing atmosphere encountered within the furnace particularly in the vicinity of the graphite heater and other support and insulation members. This can be shown to be on the order of two atmospheres at 2000°C; this condition is able to reduce the V_2O_5 which escapes from the crucible down to the metallic state. In order to preserve iridium in a reusable condition and to permit further experiments to be performed even with a leak, the more recent experiments used R. F. heating while the crucible resided in a slightly-oxidizing atmosphere.

Further experiments to be carried out will use smaller capsules to determine reproducible sealing conditions capable of retaining the melt. The melts will be studied to determine stoichiometry of single crystallites produced and determinations made with respect to alterations in starting composition. Experiments using the large crucibles will be resumed with the benefit of the small capsule data, and conditions necessary for growing large crystals employed. Modifications to the furnace to protect the crucible from the graphite environment will be made.

Single crystals produced during the second half of the contract will be characterized and optical quality evaluated. Fabrication effort will commence to develop the technique to produce a polarizing prism for delivery under the contract. Effect of crystallographic orientation on growth, both parallel to and normal to the growth axis, will be studied.

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