ERRATA SHEET

Technical report No. COO-4029-1
Contract No. EY-76-C-02-4029*.000

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4.0 KEY PERSONNEL

During the first quarter of this program, June 25, 1976 to September 25, 1976, approximately 25 percent of the Principal Investigator's time was expended in the performance of this contract. It is anticipated that during the remainder of the program, approximately 25 percent of the Principal Investigator's efforts will be allocated to this program.

REA

DISCLAIMER

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ABSTRACT

This program is an assessment of fusion cast polycrystalline calcium fluoride for optical components of 1.064 micrometer pulsed laser fusion systems. Task areas include casting of essentially stress-free 33 centimeter diameter, 5 centimeter thick ingots, developing surface finishing techniques for optically figured plane and spherical surfaces, and evaluate state-of-the-art antireflection coatings deposited onto the specimens of the cast material.

During the first quarter, a new casting furnace was installed in the laboratory, and put into operation. Two complete casting runs were made. Temperature profiles taken during the first run demonstrated the existence of unacceptably large radial gradients in the furnace and led to the design and installation of new heating elements prior to the second casting effort. Redesigned heating elements and other furnace modifications decreased the radial gradients by more than a factor of three during the second run, but the ingot was still badly strained. Furnace modifications made before a third run, which is now in progress, appear to have further reduced the gradients. Although the upper portion of the ingot from the second run contained growth defects, there is enough sound material to supply substrates for the antireflection coating task. Casting and post-casting annealing treatment studies are continuing.

Experimental work on the remaining task will begin during the second quarter. Equipment, supplies, and quotations for the casting work were assembled during the first quarter.

This report has been assigned Raytheon internal number S-2115.

1.0 INTRODUCTION

This program is an assessment of fusion cast polycrystalline calcium fluoride for optical components of high-power, short-pulse laser systems operating at 1.064 micrometers. In such systems, the maximum energy in the focused pulses is commonly limited by variations of refractive index in the optical elements which are produced by the enormous electric fields associated with the laser pulse. This self-focusing may in the limit cause the beam to collapse upon itself and exceed the intrinsic breakdown limit of the optical component, but the usefulness of the component in a diffraction-limited optical system is destroyed by pulses too small to cause permanent physical damage. The magnitude of the self-focusing effect is determined by a term in the expression for the index of refraction which is proportional to the square of the electric field in the light pulse. It has been shown[1] that this term increases in magnitude with the field-independent index, so that materials having the lowest indices of refraction should be capable of handling the highest energy laser pulses.

Calcium fluoride is an attractive material for pulsed high power laser applications because its index of refraction (1.428) and non-linear index (0.57×10^{-13} esu) are lower than those of most optical glasses. Figures of merit presented in Ref. 1 indicate that calcium fluoride components should have approximately twice the power handling capacity of those fabrication from the presently-employed BK-7 glass. Further, as a highly-purified cubic crystalline material, fusion-cast calcium fluoride should have none of the composition or density fluctuations which contribute to index of refraction inhomogeneity in glasses. Our fusion cast calcium and strontium fluorides, which have been under development at Raytheon for several years largely in response to requirements for optical components of long-pulse, high-power lasers operating in the 3-5 micrometer spectral band, are extremely pure and have the lowest reported optical absorptivities at these wavelengths. Although optical absorption is not an important contribution to the performance of these fusion laser components, we believe the high purity of fusion cast alkaline earth fluorides will assure maximum laser damage thresholds.

This program is broken into several more or less independent tasks which will eventually proceed in parallel to provide the fullest possible assessment of the material in the sizes and form required for the updated Shiva fusion laser system. The primary task is of course the fusion casting itself. During this program our fusion casting capability will expand from 15 centimeter diameter, one centimeter thick ingots to 33 centimeter diameter, 5 centimeter thick ingots. For this purpose, a new casting furnace has been purchased by the Research Division. Two aspects of the casting procedure will require particular attention. First, the furnace heating elements, insulation design, and cooling schedule must be chosen to minimize radial thermal gradients during solidification, and all gradients during the subsequent cooling to room temperature. To be useful, the cast material must be essentially free of residual stress birefringence (the program goal is < 4 nm/ cm). Residual stresses are produced by thermal gradients present during the cooling because the mechanisms for plastic flow which permit relaxation of the stresses cease to operate above room temperature. Stress-free material in a temperature gradient at some elevated average temperature becomes stressed as it cools because the differential thermal contraction cannot relax. Second, the fluoride purification procedures which have been developed for our smaller casting furnace must be adapted for the larger one. In our process, a dynamic atmosphere of carbon tetrafluoride is used to fluorinate metallic impurities, producing volatile compounds which are removed and to replace oxide and hydroxide anion impurities in the reagent grade starting material with fluorine ions. The presence of the atmosphere also permits some additional control over thermal gradients in the furnace which was not available during the initial stages of our process development which employed vacuum casting. Production of full-size, stress-free castings will constitute the major effort of the program.

The remaining program tasks evaluate operations which are required to fabricate finished optical components from the cast ingots. Optical polishing procedures which have been developed to produce highly perfect surfaces on smaller specimens of these polycrystalline materials will be extended to a 15 centimeter plane piece, a spherical surface on a 15 centimeter piece, and to a plane surface on a full 33 centimeter ingot. Standard procedures produce grain-to-grain relief on the surfaces during the final polishing stages.

Two commercial optical coating vendors will deposit their state-of-the-art high power laser antireflection coatings onto specimens of fusion cast calcium fluoride. These will be subjected to the standard environmental and adhesion tests and to laser damage thresholds measurements at Raytheon using 100 nanosecond 1.06 μm pulses and at Lawrence Livermore Laboratories using sub nanosecond pulses. Surface and bulk damage measurements will be made on uncoated material.

At the conclusion of the program, the assembled results of the tasks should provide an intelligent assessment of the usefulness of large fusion cast fluoride optical components and of their prospective availability.

2.0 FIRST QUARTER PROGRESS

2.1 Fusion Casting Experiments

During the first quarter, fusion casting efforts represented the bulk of the experimental work. Some preliminary work was done on the remaining tasks to prepare for the eventual insertion of fusion cast material into them. In this section we discuss the fusion casting work. To provide a perspective for the discussion we begin with a brief presentation on the fusion casting technique.

Fusion castings are produced by the unidirectional solidification of fluoride melts contained in graphite crucibles. The earliest stages of our casting research determined that castings made, as metal castings are, by the extraction of heat from all mold walls contained pores which were trapped as the solidification proceeded from all surfaces to the center. Figure 1 shows schematically a casting run in progress. The upper and lower heating elements have independent power supplies, but their heating and cooling rates may be controlled together through a common control unit. The charge is first completely melted in a carbon tetrafluoride atmosphere at a pressure of approximately ten torr. This treatment removes both metallic (cation) and oxide and hydroxide (anion) impurities from the fluoride and permits state-of-the-art castings to be produced from relatively inexpensive reagent grade stock. The reagent grade material, which is supplied as a fine powder, is held just below its melting point in the reactive atmosphere to permit its high specific surface area to increase the purification kinetics. Casting is also carried out under CF_4. The reactive atmosphere and fluoride melts of our process will attack all refractory materials except graphite and platinum. When melting and purification are completed, a vertical temperature gradient is established through the melt. The top of the mold is typically 15 degrees centigrade hotter than the bottom. This temperature gradient is maintained as the furnace is cooled through the melting temperature (~1400° C for CaF_2).

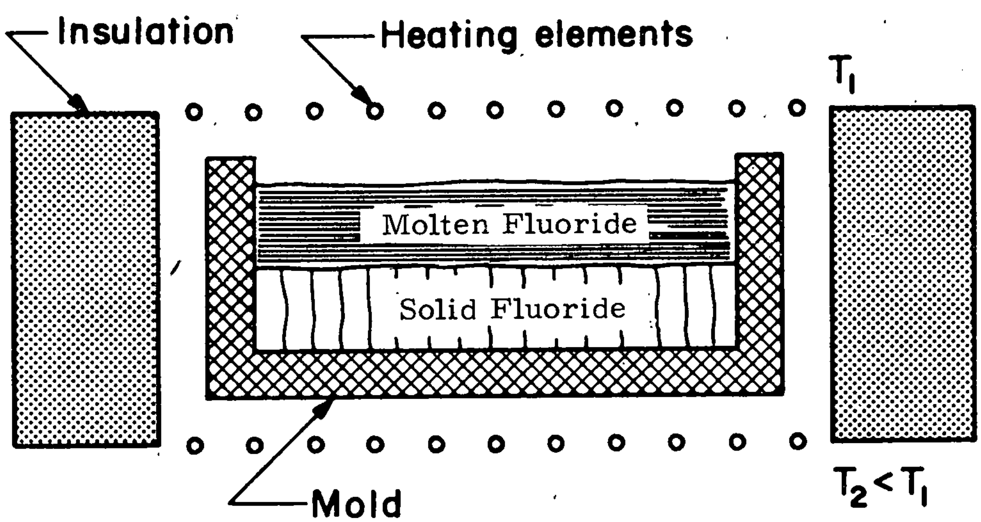

Figure 1. Fusion Casting Run - Schematic

As the furnace cools, the solid fluoride nucleates on the relatively cool mold bottom and, if a uniform vertical temperature gradient is maintained a planar, horizontal growth interface proceeds upward through the melt to the top surface. The flat growth interface prevents entrapment of impurities and exolved gases in the crystallizing ingot. In the small casting furnace we have used heretofore, cooling rates in the range of 1-5° C per hour have been used to produce inclusion-free castings.

After solidification is complete, the top and bottom elements are adjusted to the same temperature to eliminate the gradient and the furnace is slowly cooled to room temperature. It is this portion of the casting process which must be perfected during the program to eliminate residual stress birefringence. Two approaches to the problem may be considered. In the most straightforward approach, we simply avoid temperature gradients within the cooling ingots which are large enough to cause thermal stresses. The maximum stress birefringence goal for our cast ingots is 4 nanometers per centimeter, from which we may calculate maximum residual stress of 235 psi (0.17 kg/ mm^2) per centimeter of optical path length. For a 33-centimeter diameter, 5-centimeter thick ingots cooling uniformly, by losing heat primarily through its large circular faces, our present estimates limits the maximum cooling rate to approximately 15° C per hour.

Since residual stresses may be also produced by unavoidable temperature variations within the casting furnace, we must also consider the removal of stresses by annealing treatments. We have demonstrated substantial stress removal by annealing treatments at 1000° C[2] but have not yet studied the process quantitatively or determined its ability to produce very low residual stress birefringences throughout large ingots.

The furnace which is being used for the program is shown in Figure 2. It is a diffusion-pumped vacuum furnace with independent top and bottom graphite heating elements. In Figure 3, the furnace is opened and the "pie-slice" heating element sectors may be seen. The heated volume of the furnace is 56 centimeters diameter and 22 centimeters high. It is separated from the

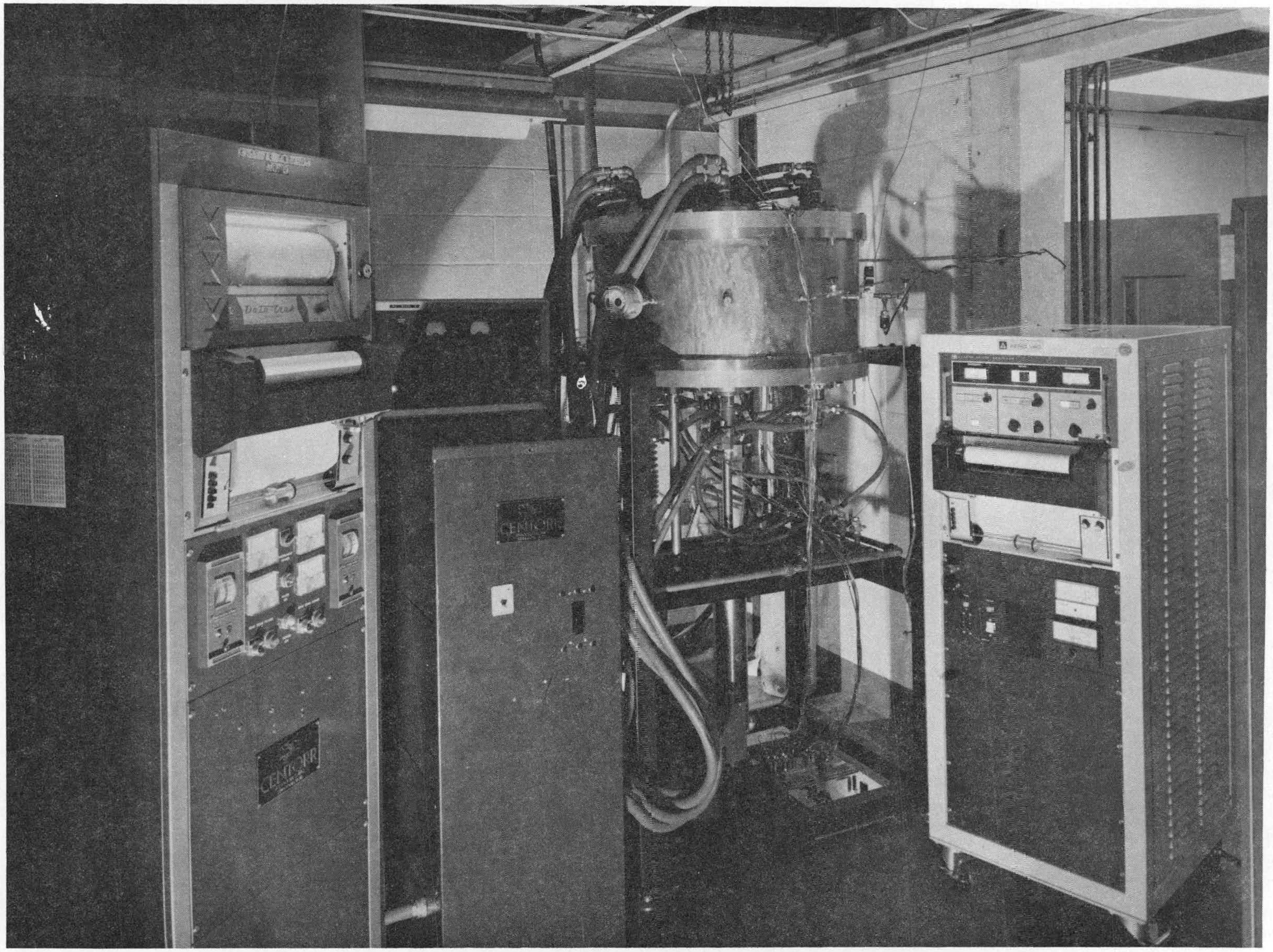

Figure 2. Photograph of Large Fusion Casting Furnace

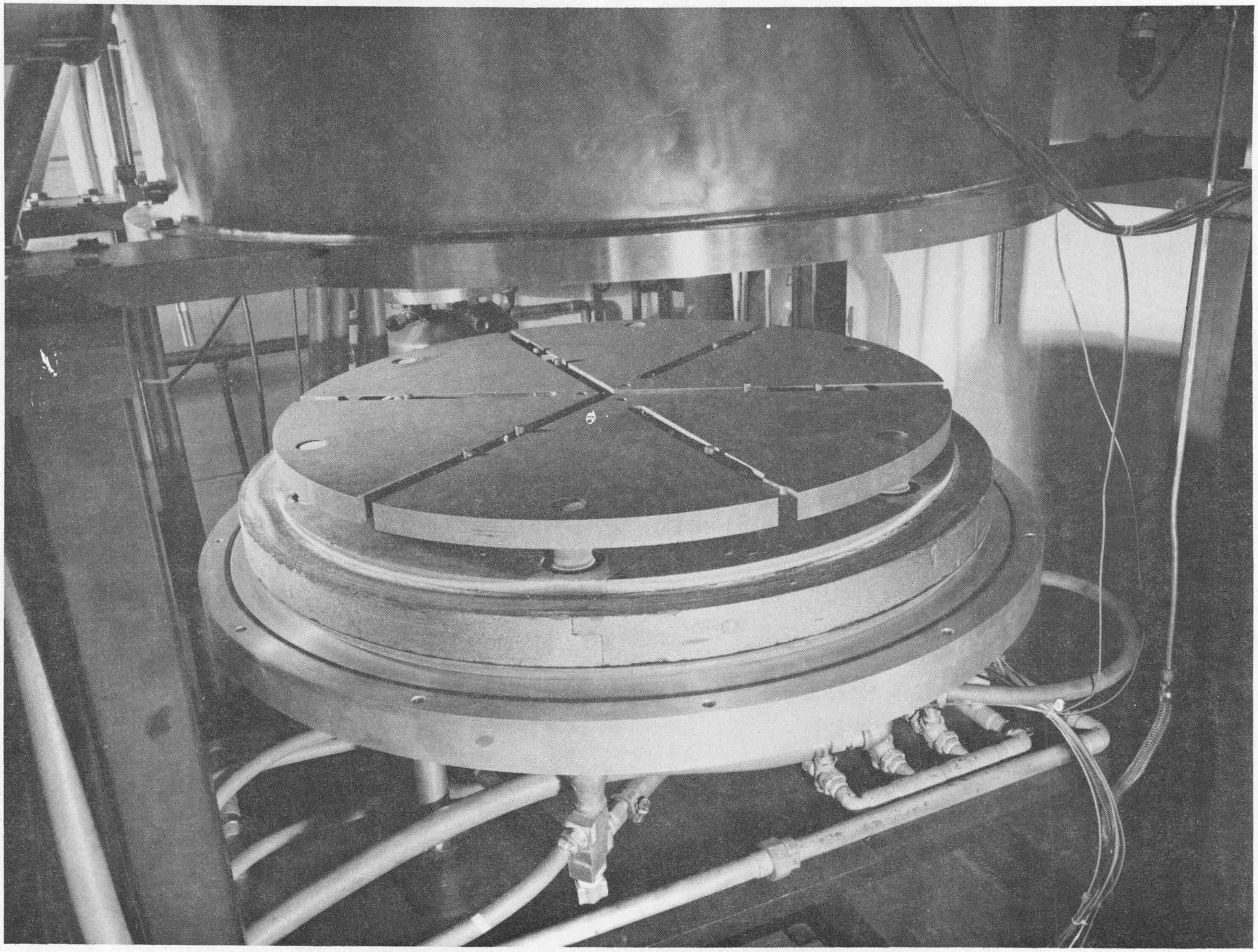

Figure 3. Lower Casting Furnace Flange and Heating Element Assembly

water-cooled furnace walls by porous graphite block insulation. There are 13 ports in the top and bottom flanges and another 12 around the circumference which may be used for thermocouples or other process sensors. The one on the front of the furnace is being used as the reactive gas inlet. The instrument panel to the right of the furnace is a residual gas analyzer, which is used to monitor the gases in the furnace during the process.

Figure 4 is a scaled cross-sectional view of the furnace which shows the radial thickness variation of the heating elements. The thickness is varied to control the radiation pattern of the elements. The thickness of the elements delivered with the furnace (during July) varied inversely with the radius. This profile makes the I^2R heating by the elements independent of their radius.

After installation and acceptance testing of the furnace were completed, two calcium fluoride casting runs were made. For these runs, the top and bottom of the furnace were each fitted with seven thermocouples; a central one, three at 120° to each other on three-inch radii, and another three on seven-inch radii. The six radial thermocouple beads were located in the slots between the heating element sectors approximately at the height of the elements.

The fluoride melts were contained in a covered thirty-five centimeter (13.75 in.) inside diameter graphite crucible. The crucible top had a one centimeter hole in the middle to admit the reactive atmosphere.

During the first casting run, radial temperature differences of more than 140° C were measured over the seven-inch radius of the crucible. The outer edge was cooler than the center. Temperatures measured close to the elements may not represent accurately the situation within the crucible. The furnace did not perform acceptably, and as a result the casting produced was badly cracked and stressed. However, it appeared to have solidified with a more or less horizontal growth interface. The upper portion of the ingot contained some defects (probably pores) and the plane of demarcation between good and defective material appeared to be horizontal. The demarcation line probably represents the position of the growth interface when the defects first appeared.

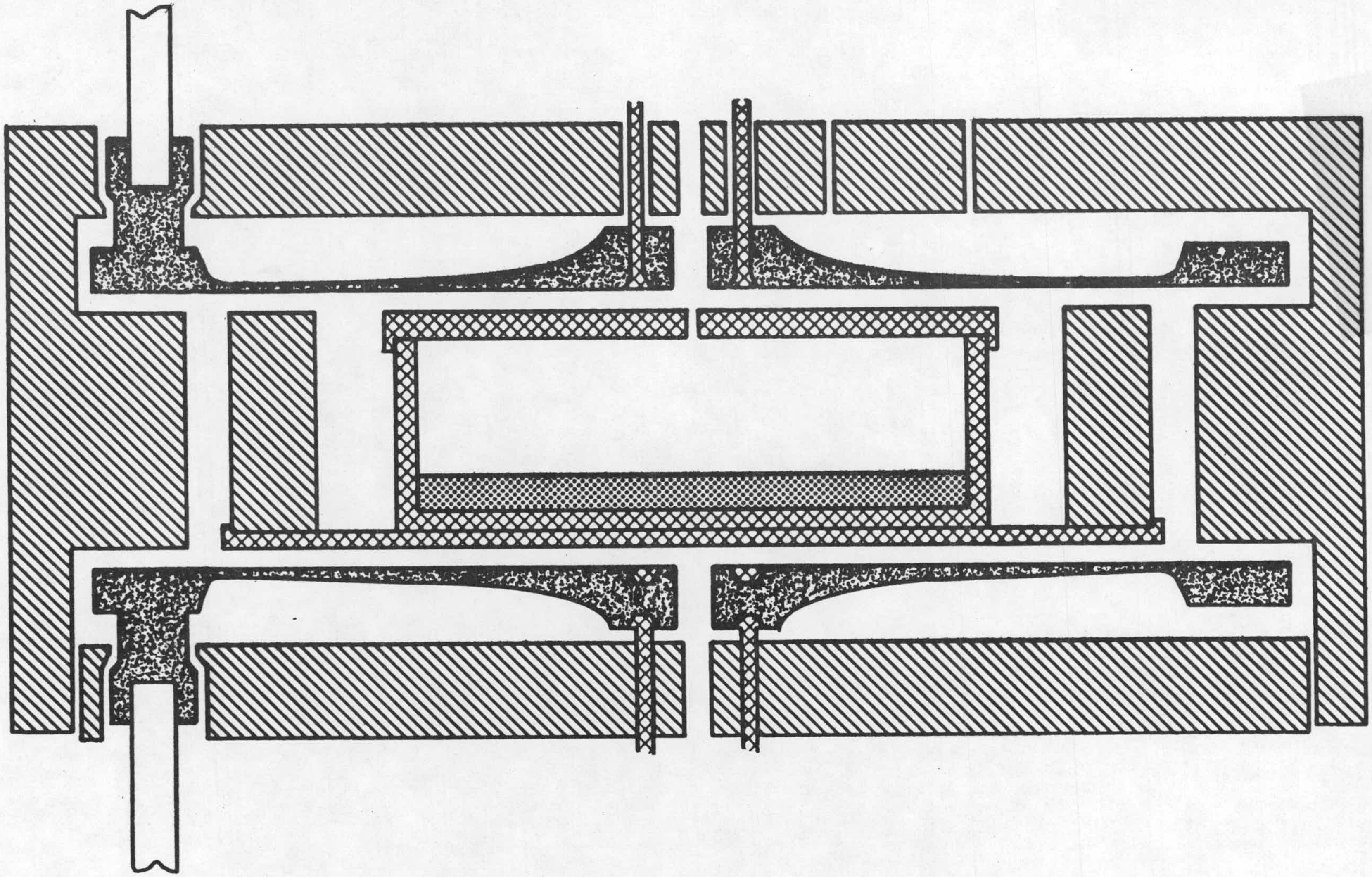

Figure 4. Cross-Sectional View of Large Casting Furnace

Two aspects of the furnace design which contributed to the large radial gradient were identified. First and most important, the design of the original furnace elements was incorrect. Although the element thickness variation required the total radiation to be independent of the radius, each successively larger radius segment radiated its energy over a larger arc length. As a result, the radiation flux density decreased in proportion to the element radius. To preserve a constant radiation flux density, the element thickness should vary inversely as the square of the radius. The second contribution to the gradient is heat lost through the outer furnace walls and through the water-cooled electrical leads to the graphite heating elements. Since the elements have very low electrical resistance, the leads must be made of copper and be quite massive to maximize energy dissipation by the heating elements. They are therefore good heat sinks. We had recognized these as heat leaks during the original design but had decided that the portion of the furnace cavity actually used for the ingot would be uniformly heated.

Using our suggested inverse square variation of element thickness with radius, the furnace manufacturer designed and fabricated a second set of graphite elements. This new set, which should radiate with a uniform flux density was used for the second casting attempt and is being used for a third, now in progress. We did not attempt to compensate for radial heat losses in this design. Graphite heaters of the size we require place conflicting restraints upon the design. They must simultaneously be massive enough to be structurally sound and electrically resistive enough to match the power supply. To increase the flux density at the outer radius by further modification of the original basic design would have weakened the elements. If (as it now appears) we must further "tune" the furnace, we will modify both the insulation and the elements.

Figure 4 shows the furnace as it appeared for the second casting experiment. The new elements were installed, and additional graphite insulation was placed in the heated volume of the furnace, adjacent to the casting mold. The insulation was to provide a hotter radiating surface with which the crucible could equilibrate. For this run a temperature difference of approximately 75° C was maintained across the furnace cavity, and the melt was cooled by approximately three degrees per hour to approximately 1000° C at which point the vertical gradient was eliminated insofar as possible. Between 1000° C and approximately 700° C, the furnace was cooled at approximately 10 degrees per hour. The ingot was annealed for two days at 700° C and then cooled at five degrees per hour.

The deformation behavior of calcium fluoride at elevated temperatures[3] has been shown to change dramatically in the temperature range 300° -500° C. In this range, the material becomes completely plastic, and the stress required to produce dislocation motion for both active slip type falls to approximately 200 psi. There are five independent slip systems, so any stress direction may be accommodated by plastic flow even in polycrystalline material. Below 300° C, only one slip system operates, so stressed polycrystalline materials generally cannot relax by plastic flow. Further, the stress required to produce plastic flow on the remaining slip system rises exponentially as the temperature falls. Our final slow cooling rate was chosen to minimize transient gradients in the ingot as it cooled through this final, critical region. Unfortunately the controller for the upper heating element failed when the furnace temperature was approximately 300° C and the power began to oscillate as it attempted to regain automatic control. The furnace power and cooling water were shut down and the furnace cooled to room temperature over 15 rather than the intended 60 hours. The ingot, while whole, was badly strained. It cracked spontaneously in the polarimeter while it was being examined.

The results of the thermocouple mointoring during the run may be summarized as follows: The lower thermocouples indicated a radial temperature difference between the center and 7-inch radius position of 21° -47° C. The gradient increased from the lower to the higher value as the furnace was cooled. The center was hotter than the outside circumference. At the top element, the outer thermocouples averaged approximately ten degrees warmer than the center at the onset of solidification, and cooled to average twenty degrees cooler than the center at 340° C. Had a measurement been taken at 700° C, the radial gradient at the upper element should have been zero. The lower thermocouples are positioned much closer to the graphite hearth and the molten charge than are the upper ones. The difference in behavior of the two sets is probably determined by their placement, but we do not presently understand the details of it. The measurements demonstrate that while the new element design substantially improved the radial gradients (from 140° C to 20-40° C) further improvements must be made. They also show that we must improve the thermocouple placement to make measurements which are more representative of the ingot itself.

A third casting run has begun. For this one the entire volume between the crucible and the furnace well has been filled with insulating graphite felt, the crucible height has been decreased, and plates of dense graphite (which has a relatively high thermal conductivity) have been installed above and below the crucible. We hope to reduce the radial losses further by the additional insulation and to "short out" remaining radial gradients between the elements and the melt with the high conductivity material.

The microstructure of the ingot produced in the second casting run is shown in Figure 5. Grain boundary locations are solid lines and the positions of the cracks which eventually appeared, as dashed lines. Grain boundary positions may be determined on ground because the surfaces are made up of small cleavage steps, the orientations of which vary from grain to grain. The boundary locations are traced onto a large piece of clear acetate and the drawing is reduced. This technique permits us to locate specimens which are cut from the ingots.

The grains in this ingot range in size from one to more than ten centimeters in length. There is an indication that at least some of the growth proceeded radially from the crucible edge - the longest crystal dimensions run roughly radially. There was no obvious correlation between the positions of the long crystals and any geometric feature of the furnace. They did not lie, for example, under the centers of the element sectors. Polarimetry of the ingot revealed stress birefringence on the order of 30 nm/ cm at various positions close to the outer circumference and close to the fracture lines. No analysis of stress in the fractured piece was attempted. Since the other

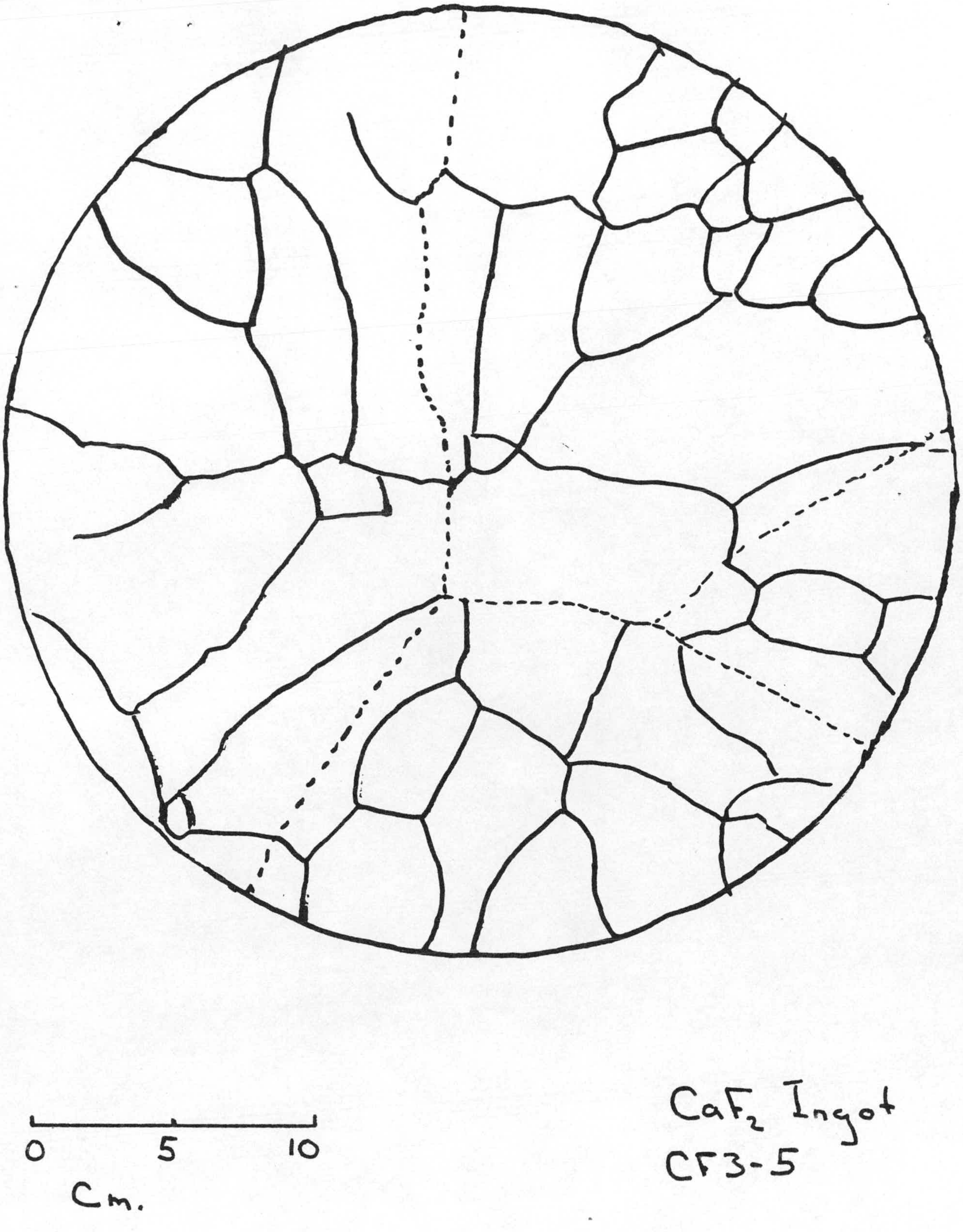

Figure 5. Microstructure of CaF_2 Ingot CF3-5

tasks of the program require fluoride specimens, the ingot was placed in a second furnace to be annealed. This furnace has a cylindrical heating element which should minimize the radial temperature variation.

The calcium fluoride in the lower one centimeter of this ingot appeared to be free of light-scattering defects in the preliminary examination. The upper two centimeters contained growth defects in the form of isolated pores. An example is shown in Figure 6. The pore is large, approximately 8-10 μm long. We believe the defects were produced either by too rapid solidification or by incomplete removal of impurities from the large crucible through the single opening in the lid. Accordingly, the run in progress is being cooled at one degree per hour through the solidification range. These steps should eliminate the defects; they are not seen in our small furnace castings. To better exchange the atmosphere in the crucible, additional openings have been made in the crucible top, and the CF_4 pressure was raised and lowered several times over the molten fluoride before the cooling began. Inspite of the disappointing defects and stress failure of this ingot, we will be able to obtain the substrate specimens we require for the antireflection coating evaluation task.

Summarizing, we believe that although our casting effort has proceeded more slowly than we had anticipated, the delays have been the unavoidable result of our scaling up the process on new equipment. We believe that substantial improvements have been made in the process and that castings made during the second quarter of the program will reflect the improvements.

2.2 Surface Finishing Experiments

Surface finishing will begin when more nearly stress-free material becomes available. During the first quarter, the necessary tooling for working the spherical surface and measuring its figure was purchased.

2.3 Antireflection Coating Evaluation and Laser Testing

Quotations for the coating task were obtained from vendors agreed

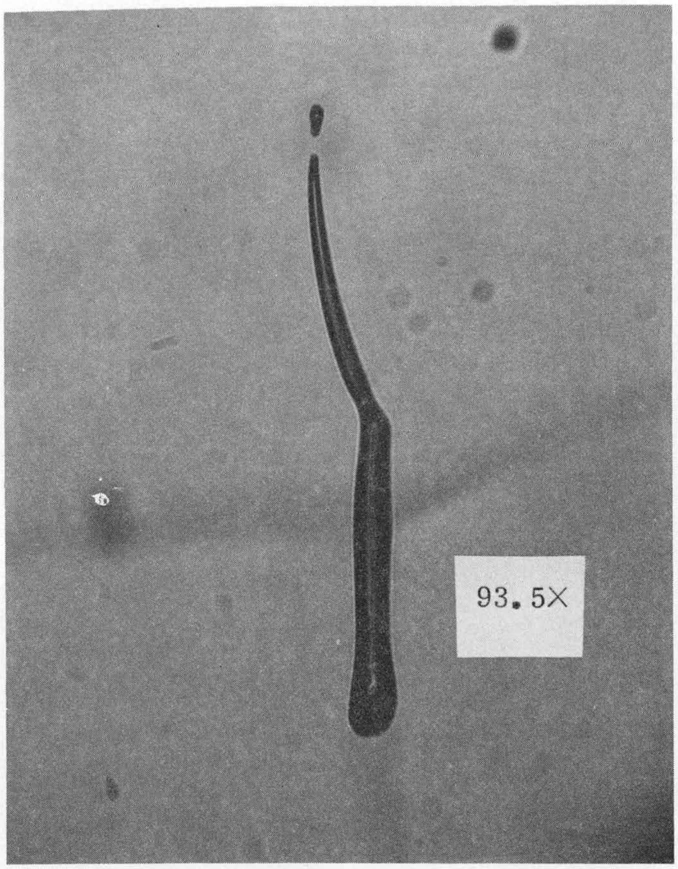

Figure 6. Defect (Pore) in CaF_2 Ingot

upon by the contract monitor and Raytheon. During the early part of the second quarter, substrates for the task will be available.

The Raytheon 1.06 micrometer laser damage apparatus was assembled and realigned.

3.0 PLANS FOR SECOND QUARTER

During the second quarter, experimental work in the remaining areas will begin. Substrates for the coating comparisons should become available early in the quarter and coated specimens by the end of the quarter. A six-inch diameter specimen will be produced for surface finishing work.

The major effort will continue to be the production of stress-free castings. Both the casting process and post-casting annealing treatments will be studied. An attempt to model the thermal distribution in the casting furnace which began this quarter will continue and be expanded to include an analysis of permissible temperature variations through the full-size ingots during the final cooling stages. Modification of the casting furnace will continue to be guided also by analysis of cast ingots. In this regard, the run presently in progress should be particularly instructive. Full five centimeter thick ingots will be attempted during the quarter.

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Distribution List

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