EXPLORATORY DEVELOPMENT OF FUSION CAST CALCIUM FLUORIDE
FOR 1.06 MICROMETER PULSED LASER OPTICS

Progress Report
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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 evaluating state-of-the-art antireflection coatings deposited onto specimens of the cast material.

During the second quarter, specimens for the optical coating evaluation were fabricated from material cast during the first quarter. The coated specimens should be delivered early in the third quarter.

One full-size casting was completed. Furnace modifications made after the previous casting lowered the residual stresses and produced a crack-free, although strained, ingot. The upper portion of the ingot contained trapped bubbles and pores from too rapid solidification. Further modifications of the furnace and crucible were made on the basis of this run and substantially improved 15-centimeter ingots apparently free of included defects were cast (for another program). These ingots were strained, but a furnace power supply failure produced contributory temperature gradients. A repeat of this casting to provide 15-centimeter specimens for surface finishing and annealing studies for this program is in progress.

A second furnace has been committed to the casting program and construction of the necessary flanges and crucible has begun.

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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. 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 indicate that calcium fluoride components should have approximately twice the power handling capacity of those fabricated 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. 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.

The 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 $< 4 \text{ nm/cm}$). 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 $1.06 \mu\text{m}$ 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 SECOND QUARTER PROGRESS

2.1 Fusion Casting

Development of the large casting furnace continued in the second quarter, during which further modifications of both the heating elements and the casting crucible were made, and the flexibility of the power control was improved. Unfortunately, several power supply failures during the period extended the casting runs unduly and limited our assessment of the value of our process modifications.

One full-size casting was completed during the period. Figure 1 is a photograph of the ingot and Figure 2 is a tracing of its microstructure. This casting was carried out, as discussed in our previous report, with additional insulation placed around the outer circumference of the crucible and additional graphite placed above the "short out" radial thermal gradients. The effect of these changes upon the crystallization behavior of the ingot may be seen by comparing its equiaxed microstructure with the radially-elongated grains of the previous casting shown in Figure 3 (reprinted from our first report). The measured radial temperature differences were still large (20-30° C over 7 inches), but the crystallization front appears to have passed vertically through the melt. Some of the temperature variation is produced by our placement of the thermocouples close to the heating elements rather than in contact with the crucible. In subsequent runs the thermocouple beads were extended into recesses drilled in the crucible top and bottom.

The upper half of this ingot contained the same large pore defects found in the previous casting. We believe the defects are caused by too rapid solidification. The actual growth front velocity is directly proportional to the cooling rate and inversely proportional to the temperature gradient in the growth direction. If the gradient is small, a small temperature decrease will crystallize a comparatively large volume of melt. For this casting, the temperature difference between the control thermocouple positions on the top and bottom of the crucible was 43° C at the beginning of the solidification and 77° C at the end. Cooling was at 0.76° C/hour.

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Figure 1. Photograph of Full-Size Calcium Fluoride Ingot

CF3-6

Figure 2. Microstructure of CaF₂ Ingot CF3-6

0 5 10
cm.

CaF_2 Ingot
CF3-5

Figure 3. Microstructure of CaF_2 Ingot CF3-5

As the solid ingot was cooled to room temperature, two characteristics of the furnace control system produced temperature gradients in the crucible which caused the cooled ingot to be stressed. First, the controllers sensed the power delivered to the elements directly rather than the crucible temperature. This arrangement was used because in earlier runs, the attack of the platinum thermocouple wires by the reactive carbon tetrafluoride atmosphere made direct temperature control unreliable. The vertical temperature difference for a pair of symmetrically placed thermocouples was set to zero at the beginning of the cooling step. It remained less than five degrees to approximately 900° C, but as cooling proceeded under power control, the vertical temperature difference increased, reaching a maximum of approximately 25° C. This, and the remaining radial differences were present as the ingot was cooled through the temperature range in which the stress relaxation mechanisms become inoperative.

At approximately 300° , the furnace power began to oscillate because the proportional band of the controller which was appropriate at higher temperatures produced overcompensation and "hunting" at the lower temperature.

This run demonstrated the necessity of far slower growth interface motion, and better thermocouple positioning. It also made a reasonable case for direct temperature sensing for the furnace control. These modifications were made for the second casting run completed during the quarter. In this run (for another program), three 6-inch diameter ingots were cast in a single multi-cavity crucible. To decrease the growth interface velocity, a steeper vertical gradient was imposed on the crucible. Since at the higher top heating element temperatures required by the steeper gradient, the reactive carbon tetrafluoride atmosphere attacks not only the platinum thermocouples but also the graphite elements themselves, it was necessary to isolate the reactive gases from the elements. This was done by eliminating the openings in the crucible top and feeding the CF_4 into the crucible by a separate piping system through the furnace bottom. Carbon tetrafluoride was passed over the fluoride at a pressure of approximately 7 torr inside the crucible while an argon pressure of 10 torr was maintained in the furnace chamber proper. Using

this arrangement, and direct temperature control, it was possible to maintain a 100° C vertical temperature difference across the solidifying melt without any measurable heating element degradation. Improved temperature measurement reliability was obtained by extending the thermocouple beads into recesses drilled into the crucible top and bottom. Direct temperature control maintained the temperatures of the control points above and below the crucible to within five degrees of each other from the end of solidification to approximately 200° C, where again the temperatures began to fluctuate. A second revision top heating element was installed before this run, which was to have been a real test of our furnace improvements. Unfortunately, the power supply to one of the top heating elements failed when the furnace was at approximately 900° C (after solidification). The two top elements were connected in parallel to the remaining power supply/ controller, but temperature control was not regained until the temperature had dropped to approximately 670° C. All three of the cast ingots were strained, and one was cracked. Nevertheless, the run demonstrated that the modifications had substantially improved the furnace operation. The corrosion of the elements has been eliminated. The defects found in the upper halves of previous castings have been avoided by the larger vertical temperature gradients made possible by the closed crucible. The revised heating element and thermocouple placement arrangement reduced radial differences to 5-9° C and circumferential differences to 3-6° C during solidification. Temperature differences remained generally less than 20° C during the cooling to approximately 200° C. Finally, a method of "fine tuning" the individual power supplies by means of variable bucking potentials in the thermocouple sensing circuits was successfully demonstrated.

The failed power supply has been repaired, a revised lower heating element has been installed in the furnace, and the conditions of the previous run are being repeated. The 6-inch diameter ingots being cast will be used for the surface finishing and annealing tasks of this program, and the results of the casting will be used to set the furnace conditions for the next full-size casting attempt. This run will be carried out with a crucible arrangement similar to that sketched in Figure 4. The crucible lid and grafoil gasket are bolted onto the crucible to produce a positive seal, and thermocouple beads are placed in wells in the crucible top and bottom.

Figure 4. Casting Furnace With Closed Crucible Installed.

It now appears likely that some heat should be applied radially to the cooling ingot to permit its temperature to be held more nearly uniform during the cooling after solidification. (We should point out here that stresses produced by the temperature gradient present during solidification should be relaxed as the ingot is brought to a uniform temperature above 1000° C.) The next two casting runs should demonstrate clearly whether this will be required. We have obtained a first proposed design for radial heating from the furnace manufacturer and have begun our own design. We will continue both design efforts as the next two castings proceed.

To expand the casting effort of this program, we are placing a second large furnace into operation. This is also a graphite element vacuum furnace, but in this case, the heating element is a hollow cylinder 17 inches in diameter and four feet high. The existing element will provide radial heating and we will control vertical gradients by means of additional flat elements above and below or by forced cooling. The first run will melt a full-size ingot and examine horizontal and vertical temperature gradients produced by cooling the bottom of the crucible with a forced helium stream. We will attempt to produce unidirectional solidification by cooling the furnace while a helium-induced gradient is imposed upon the melt. The top and bottom flange modifications which are required to admit our thermocouples and gas handling plumbing are being made. Thermocouple wire and protective tubing for the experiments have been delivered. A crucible similar to the one sketched in Figure 5 is being fabricated. This crucible, like the one to be used in the other furnace, is bolted closed. The reactive CF_4 atmosphere is introduced only to the fluoride-containing volume. The bottom of the crucible contains a closed baffled volume through which helium will be forced to establish a solidification-directing thermal gradient. We expect to be able to test this furnace by approximately the middle of February.

2.2 Antireflection Coating and Laser Testing

Forty (40) 25-millimeter diameter cast CaF_2 test specimens were fabricated for optical film coating. These were split into two sets of twenty

Figure 5. Closed Crucible for Helium-Induced Thermal Gradient.

each and one set was sent to each of two optical coating vendors, Optical Coating Laboratory, Inc., Santa Rosa, Calif., and Spectra Physics, Inc., Mountain View, Calif. Each vendor will coat his specimens in two separate depositions of ten (10) substrates. We have determined the microstructures of the substrates and laid out the specimens to be coated together so that both single crystal and polycrystal (2-3 grains) substrates will be included in each deposition.

Coatings are to be antireflective ($< 0.1\%$ is the goal) at 1.06 micrometers and normal incidence. They are to be durable coatings capable of passing the standard MIL spec hardness and durability tests. We expect delivery of the coated specimens in early February. We will determine the reflectivity spectra of the coated specimens, paying particular attention to the results obtained on the polycrystalline substrates. Specimens from each deposition will be forwarded to Lawrence Livermore Laboratory for laser damage testing using subnanosecond pulses. Durability testing and damage measurements using 100 nanosecond pulsed 1.06 micrometer radiation will be carried out at Raytheon.

2.3 Surface Finishing

Fabrication of plane and spherical surfaces on a 15-centimeter (6-inch) specimen will be carried out this month. A full-size casing should also be available during the period. A 25-millimeter specimen is being superpolished on both sides for laser surface breakdown measurements. One side will be polished by our diamond polishing procedure, the other by a bowl-feed procedure which uses alumina abrasives.

3.0 PLANS FOR THIRD QUARTER

During the third quarter, the existing casting furnace will be used to produce both 15-centimeter and full-size castings, and a second furnace will be used to cast full-size ingots. These castings will be used to determine whether further furnace modifications are required, and any indicated modifications will begin promptly.

Evaluation of the coated specimens and fabrication of plane and spherical surfaces on a 15-centimeter cast CaF_2 specimen should be completed during the quarter.

4.0 KEY PERSONNEL

During the second quarter of this program, September 25, 1976 to December 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.