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MANUFACTURING PROCESS FOR LARGE SHEETS OF TRANSPARENT SINGLE CRYSTAL ALUMINUM OXIDE FOR THE CZOCHRALSKI METHOD

AUGUST 31, 1969

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THIRD INTERIM REPORT - CONTRACT NO. DAAG46-69-C-0002

Prepared for

ARMY MATERIALS AND MECHANICS RESEARCH CENTER
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A. INTRODUCTION AND SUMMARY

The scheduled aims of the third quarter of the contract were set out in general terms at the end of the report for the second quarter and shown graphically on the milestone chart (Figure 1). Our main effort was scheduled to be spent on the "Initial Growth" stage using the large (9-1/2" x 2-1/2" x 6") crucible with a back-up effort on the intermediate size crucible to further improve our growth techniques and overall reproducibility; this included a raw material survey and an improved afterheater designed to reduce fracture during growth.

The schedule has not been strictly adhered to due to difficulties encountered with methods of furnace construction and much of our development effort during the past quarter has been spent in overcoming these difficulties. We have been forced to reassess the processes and materials used for furnace construction and this has affected the growth effort on both crucibles.

The development work, however, has been successful and most of the problems have now been overcome. Crystals of a larger size than was previously possible have been successfully grown, and work has proceeded with an afterheater designed to reduce the tendency to fracture during growth.

This report is divided into four sections as follows:

1. Fundamentals of Furnace Design

2. Crystal Growth

3. Quality Improvement

4. Fabrication

B. EXPERIMENTAL WORK

1. Fundamentals of Furnace Design

The furnace design has been described previously[1] and apart from the obvious size difference, the scaled up models are basically similar. The outer ceramic jacket which has been the source of the arcing problems is used mainly to keep the refractory insulation in place and serves very little to reduce the heat loss. A well-proven material for this purpose is fused silica, and sleeves of usable size for cylindrical and small rectangular crucibles are available commercially. No such material, however, is available for the larger size rectangular furnaces, and as described in earlier reports,[1) 2)]

1) First Quarterly Technical Report. Contract No. DAAG46-69-C-0002
2) Second Quarterly Technical Report. Contract No. DAAG46-69-C-0002

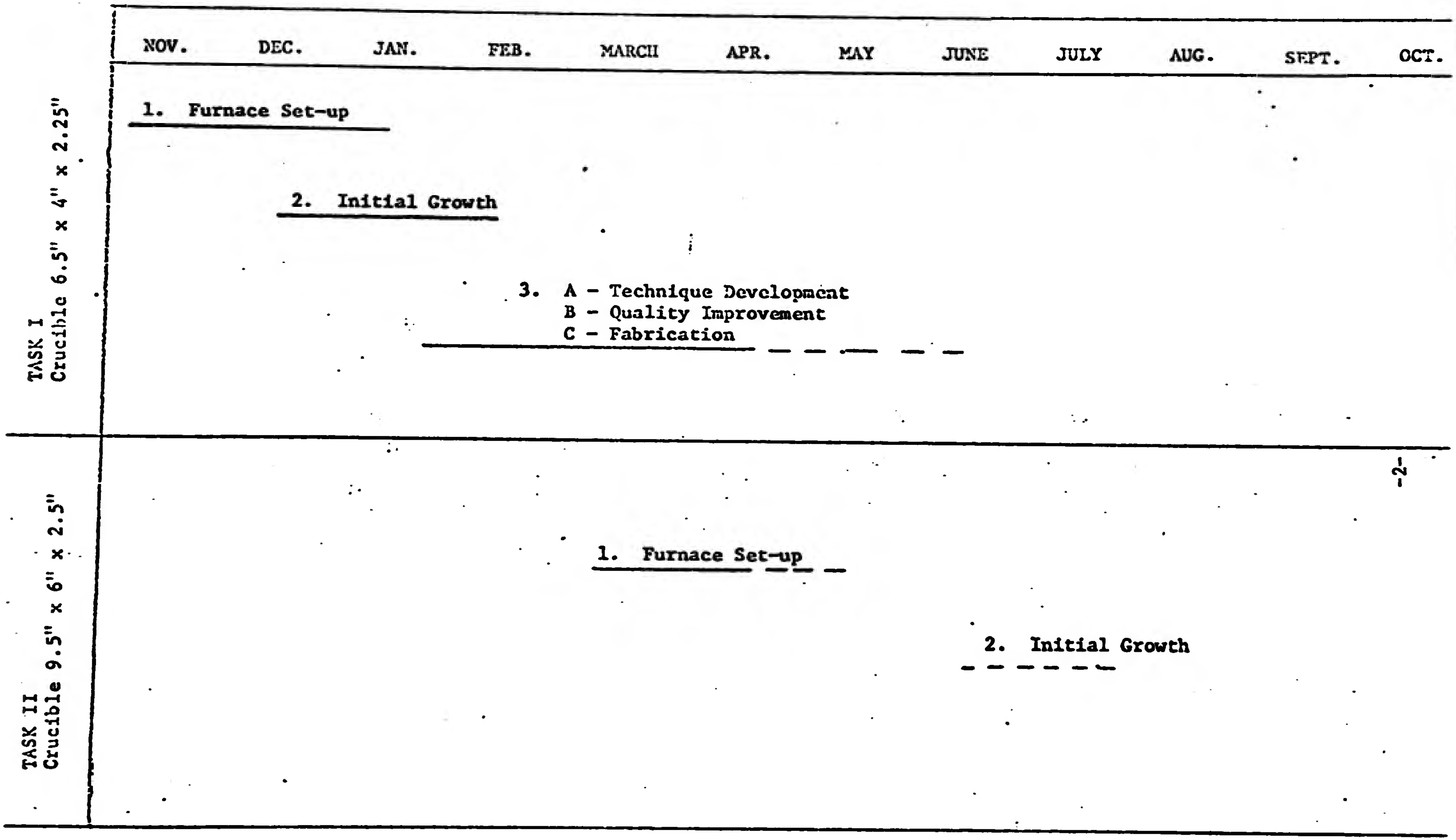

Figure 1 - MILESTONE CHART SHOWING PROGRESS TO DATE WITH ANTICIPATED FUTURE DEVELOPMENT TAKEN FROM THE SECOND QUARTERLY REPORT.

we have had to fabricate our own outer jackets from castable alumina cement.

For optimum efficiency it is important to keep the thickness of this outer jacket as small as possible to accommodate the maximum thickness of thermal insulating material between the inner and outer sections, and casting techniques were developed to allow casts to be made with nominal 1/4" wall thickness; the cement used for this purpose was Norton R-A-1034 containing Al_2O_3: 95%, SiO_2: .06%, Fe_2O_3: .13%, CaO; 3.9%, and heat treatment figures are given by the manufacturers for normal use. Our casting process is not standard as it involves the use of paraffin wax to prevent sticking between the mold and the ceramic and this results in some organic contamination of the alumina. This wax can be removed by baking the casts in air but this necessitates a deviation from the manufacturer's treatment specification resulting in problems with fabrication.

As of the end of June and well into July, results from the intermediate size crucible have been disappointing, and we had been unable to repeat the growth of the nominal 8" x 4" crystal because of a spate of arcing problems within the furnace. Five successive growth attempts ended in severe arcing between the coil and the outer alumina jacket, with the shut-down occurring in each case after a melt had been established and the furnace had been brought to its scheduled operating temperature. Initial attempts to correct the situation by re-adjusting various furnace parameters and improving the overall stability of the system, met with little success. Eventually it was noticed that the "handling" consistency of the wet cement used to make the outer cast was not the same as previously experienced, and when the cement suppliers were questioned, it was found that our material came from a batch which may have been damaged during last winter's flooding in the Los Angeles area. This may or may not have been the trouble, but it was requested that we be supplied with material of known history and origin; in addition it was decided to introduce an extra step into the fabrication of the alumina jackets by annealing them to remove the last trace of moisture and possibly convert any ionic impurities to metal oxides or higher oxides. A very large (7KW) annealing furnace capable of reaching temperatures of 1200°C was built, and casts for both size crucibles were removed from the usual 400°C furnace and annealed overnight at 1000° in the new furnace. The relative time spent at the lower temperature is important as this step is essential for the removal of the paraffin wax used in the casting procedure, and influences the performance and consistency of the alumina after the high temperature anneal. The procedure has been most successful and five growth attempts have been made since its inception without showing any tendency to arc.

Attempts have been made to explain the phenomenon of arcing from coil to furnace and within the cast. The normal spark breakdown in air is about 30,000 volts per inch and since the R.F. coil is ostensibly operating at a maximum of 12KV (6KV with push-pull output as

Figure 2: Typical arcing damage in the outer alumina furnace jacket.

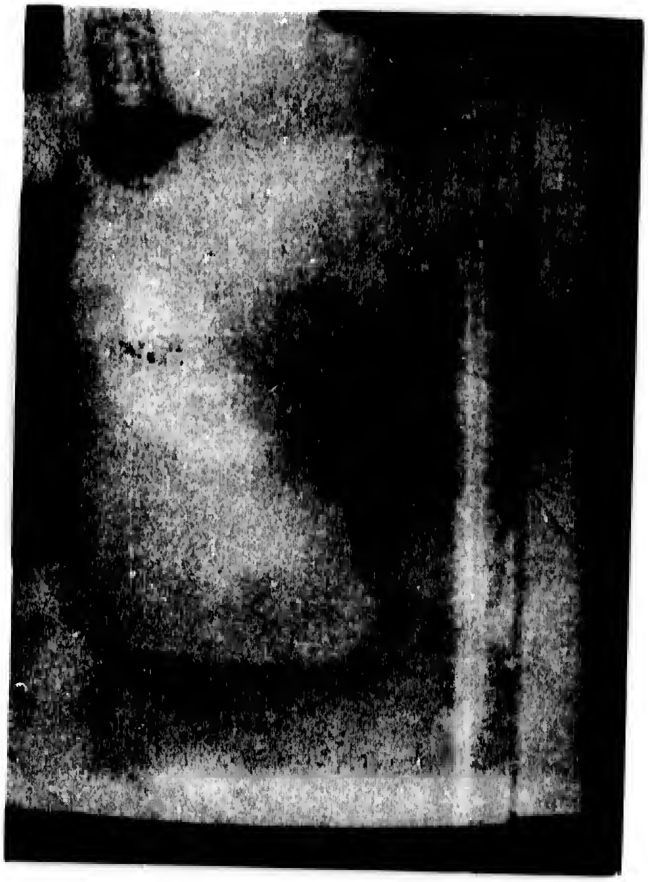

Figure 3: Typical arc damage on the inner ZrO_2 furnace jacket.

on the 75KW generator) and the coil to cast distance is a minimum 1/2", arcing should not occur. However, the wave-shape of the R.F. voltage from one of our generators was displayed on an oscilloscope and it was found that very short lived peaks occasionally occur up to 22KV and this sort of potential could cause an arc if there were any conductive material, possibly as an impurity, in the alumina cast. (For example FeO is conductive). Casting experiments were carried out using other types of cement, such as Norton RA 1145 with 98% alumina, but these did not give a satisfactory product and annealing appears to be the best approach.

Figures 2 and 3 show examples of the result of arcing. Figure 2 illustrates how the outer alumina jacket is fused by the intense heat of an arc, becoming locally conductive when molten and thus perpetuating the arc. Figure 3 shows heat erosion of the inner ZrO_2 jacket, a situation which often causes crucible failure.

2. <u>Crystal Growth</u>

The main growth effort in the period covered by this report has been concentrated on the large size crucible using the 75KW Westinghouse generator, with the first growth being made in June; this boule was of poor quality, having problems with shape control and internal quality. However, the 75KW Westinghouse generator operated continuously for more than four days, at a level well within its power limit. The furnace design was more than adequate and survived the growth cycle with no cracking of the ceramics and no arcing across the coil; the afterheater design also proved good enough to allow growth of the larger sizes without fracture due to thermal stresses. The bad quality was explainable, and due to the following:

a) Too rapid a pull rate as the utilized speed of 1/4"/hr. was not slow enough to compensate for the increased size and inadequately set control system.

b) A severe air leak into the bell jar had developed during growth. This would account for both poor quality and poor size control.

c) The sensitivity of the control system was set too high but this could not be changed once the run had started.

This first growth yielded a boule with a maximum width of 6"; it is shown in Figure 4. Second growth was made from the large crucible, from a small seed. As expected, the thickness to width ratio became too large in the initial growth stage and the crystal was in danger of fouling the sides of the crucible lid. The oversized crystal was withdrawn from the melt, the sides were ground to 1/2" thickness, and growth re-established on a prepared shoulder 2-1/2" - 3" wide. The resulting crystal, which is shown in Figure 5, represents our largest growth to date and would be capable of yielding a

Figure 4: First boule grown from the large crucible.

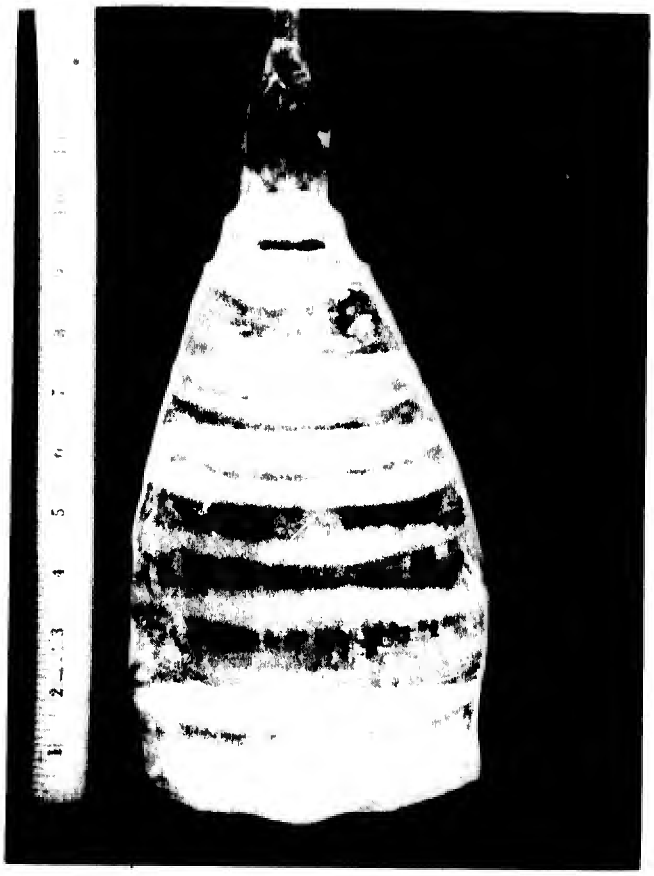

Figure 5: Second boule grown from the large crucible.

plate 5" x 6" exclusive of shoulder. As can be seen, the internal quality is still not good but is vastly improved compared with that shown in Figure 4.

3. Quality Improvement

Some consideration has been given to the problem of crystals cracking while being pulled from the melt, and during cool-down. The cracking is thought to be due to thermal stresses introduced through the large temperature difference along the length of the sheet; the gradient is from 2000°C in the melt to an estimated 400°C or less at the seed.

An afterheater set up with externally powered electric heating elements has been designed so that maximum heating is obtained within the homogeneous volume occupied by the coolest part of the grown crystal as it is being withdrawn from the melt. It is calculated that the combined heating from the crucible and from the heating elements should greatly reduce the temperature gradient along the crystal and, therefore, reduce the cracking. The afterheater set-up has not yet been tried with a hot furnace but a bench run gave a temperature distribution as shown in Figure 6, which agreed with calculated values.

As mentioned previously, trace impurities in the raw materials are one of the main sources of second phase formation and limit the rate at which a good quality crystal can be successfully pulled. A source of raw material has been located which combines low impurity content with a moderate price in the cracked single crystal form, and this has been ordered for further evaluation.

4. Fabrication

Figure 7 shows our largest plate which cracked during fabrication into a shoulder. The plate is mounted with adhesive resin onto a 10" steel disk and the lower transverse line is the first saw cut which would have given a 6-1/4" shoulder. This saw cut initiated a crack which can be seen running in an arc across the crystal. A second saw cut was then made above this crack at the position of the upper transverse line, this time without cracking, and giving a shoulder width of 5-1/8". The sides of this piece were ground down to 1/2" thickness in the usual manner to give the prepared shoulder shown in Figure 8.

The following surface grinding tests were completed for large surface area sheets of sapphire to determine the most suitable parameters for fabrication. The details of the grinding machine and wheel were as follows.

Machine - DoAll D-6. 6" x 18" Surface Grinder 3450 rpm spindle speed.

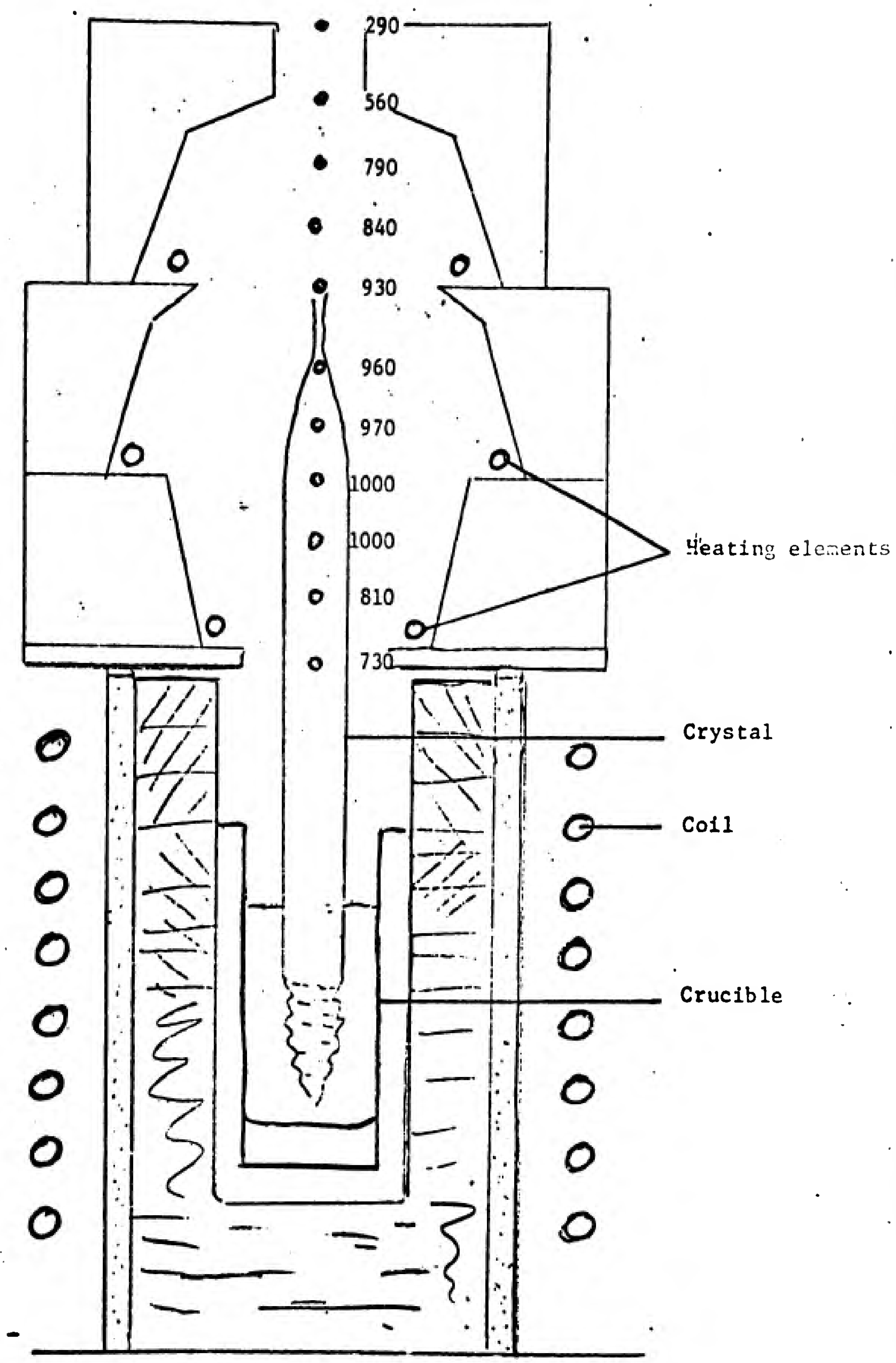

Figure 6 - Temperature distribution (normalized to 1000°) inside the externally-heated afterheater set-up. Note that temperature maximum occurs at the shoulder of crystal.

Figure 7: Large plate mounted for fabrication.

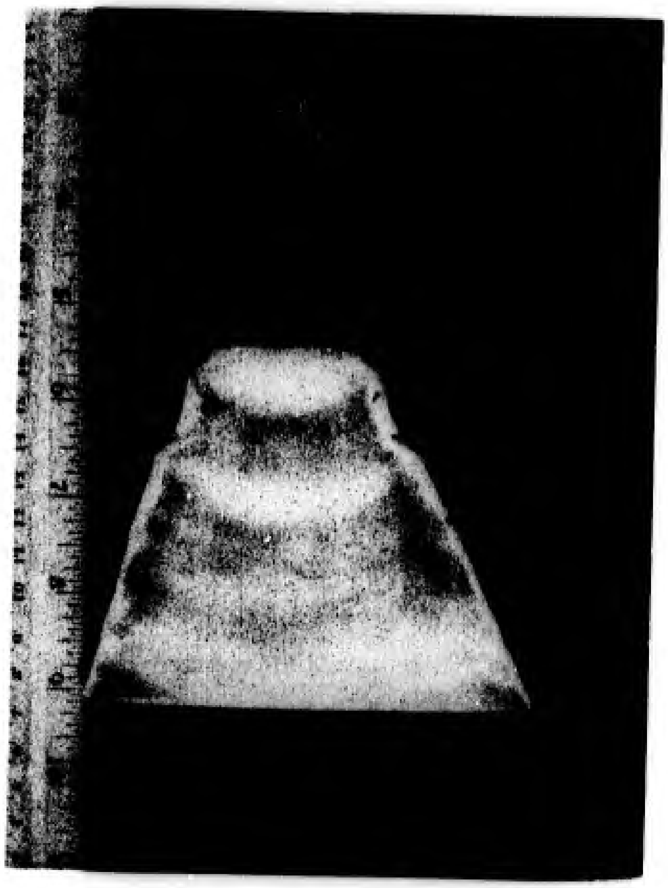

Figure 8: A prepared shoulder cut and fabricated from a large plate.

Table feed - hydraulic

Index feed - hydraulic - one side only

Downfeed - manual

Wheel - Resinoid Diamond - 8" x 3/4" x 1-1/4", 180 mesh, 100 conc.

Test No.	Down Feed	Cross Index	Table Speed	Surface Finish
1	0.001"	0.080"	4 ft./min.	300µ inch
2	0.0005"	0.060"	5 ft./min.	120µ inch
3	0.00025"	0.040"	6 ft./min.	96µ inch
4	0.0001"	0.040"	6 ft./min.	88µ inch

The maximum observed pit depth was less than 0.0005" as measured with a Tally surf 4 instrument. The finishes observed in test 2, 3, and 4 are considered acceptable for lapping and polishing.

Plans For Future Development Work

Our efforts during the fourth quarter will concentrate on growing good quality sapphire plates aiming at dimensions of 8" x 4" using the 6" x 2-1/4" x 4" crucible and the modified afterheater described above and shown in Figure 6 and on growing the largest size possible from the 9-1/2" x 2-1/2" x 6" crucible aiming at dimensions 8" x 8".

Development work will continue in order to find the most effective method for fabricating the large size plates into polished windows.

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13. ABSTRACT

Work has continued to develop the Czochralski process for the growth of high crystal alumina oxide in plate form. More emphasis has been placed during the third quarter in the development of the large size furnace.

This transaction to the larger size has introduced a number of problems with furnace construction. Inadequate control of furnace material quality has led to electrical breakdown and control problems.

Some large size material with approximate dimensions of 6" x 6" x ½" thick development work is required in order to improve the optical qualities. Some fabrication work was carried out to develop a suitable technique for grinding and polishing the large plates.

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Sapphire Fabrication						
Czochralski Growth						
Single Crystal Plate						
Aluminum Oxide						
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