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Southbridge, Massachusetts

PREPARATION OF PLATINUM-FREE LASER GLASS

Semi-Annual Technical Report
Number Four

1 January - 31 July 1966

ARPA Order No. 306-62
Project Code No. 4730
Contract Nonr 4656(00)

Prepared by

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This research is part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, Department of Defense, and the Office of Naval Research.

ABSTRACT

The purpose of this project is to produce high optical quality laser glass free of platinum particles. It was found that glass melted under an inert atmosphere in a platinum crucible contained no detectable platinum particles. Methods to prevent evaporation of various oxides that caused inhomogeneities in the glass were investigated. Data was accumulated to determine the effect of time, temperature, and atmosphere on the weight loss of platinum and alloying of platinum with ingredients in glass. A parallel approach to this problem is the melting of glass in a high purity all-ceramic system. Modifications of the system, based on results of the initial runs, have been completed. Failure of a high temperature sprinkler head during testing of the furnace has seriously delayed this phase of the project.

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1. INTRODUCTION

This Technical Summary Report covers work performed during the period 1 January-31 July 1966 on Contract Nonr 4656(00) entitled Preparation of Platinum-Free Laser Glass.

The object of this research is to develop a method of preparing optically homogeneous glass, with high transmission at 1.06 μ, free of platinum inclusions and of such a composition that it can be used for high energy laser applications. The program was divided into two phases to be performed concurrently. One phase was designed to investigate the possibilities of melting glass in platinum crucibles without introducing platinum particles into the glass; the other phase was to develop an all-ceramic system, entirely free of platinum, capable of producing iron-free glass of high optical quality.

2. PLATINUM IMPROVEMENT PROGRAM

The primary purpose of this program is to determine the source of platinum particles in laser glass and to develop a method of melting glass in platinum which will eliminate the formation of these particles.

2.1 SUMMARY OF PREVIOUS WORK

In the early work various mechanisms were considered as possible sources of platinum particles. These were mechanical abrasion, dissolution of platinum by the glass, intergranular attack, oxidation of platinum and subsequent reduction of platinum. The size, shape and morphology of the platinum particles appeared to eliminate mechanical abrasion and intergranular corrosion as major sources of contamination. A series of experiments were carried out that indicated the solubility of platinum was less than one part in 10^{10}.

A number of experiments were performed which demonstrated that an oxidizing atmosphere attacks platinum. This work further showed that platinum could be transported through the atmosphere, presumably in an oxide form, and subsequently be redeposited in another area. Melts made in argon or nitrogen atmospheres showed no measurable attack on the platinum or any indication of transport of platinum at 2450° F.

One of the steps in producing optical glass is the fining process in which the glass is held for several hours at a moderately high temperature to remove small bubbles in the glass. It was found that laser glass in platinum crucibles under a nitrogen atmosphere could be held at 2450° F for 100 hours without introducing platinum inclusions. These conditions exceed those required in the fining process. Several dozen bars 12" long by 2¼" diameter were processed in this manner with no indication of platinum contamination. As previously reported a two step process was used in which the glass was first reacted in a ceramic pot and then fined in the platinum crucible under a nitrogen atmosphere. The two step operation is necessary as it is well known that the carbonates used in the batch material will attack platinum at the temperatures used to complete the initial reaction of the glass batch (2600-2700° F).

Upon inspection of the bars, it was found that they contained a fine striae pattern. Attempts to homogenize the glass by bubbling inert gas through it or by thermally induced convection currents were unsuccessful. Two approaches to the problem of homogenization were suggested: first to prevent evaporation from the surface while fining in a nitrogen atmosphere and second, to use mechanical stirring.

2.2 STRIAE RESULTING FROM EVAPORATION

During the homogenizing experiments, careful examination of the glass bars revealed several interesting points: (1) the striae pattern in the finished bar was entirely different from the striae in the raw glass, (2) the striae appeared more concentrated at the top of the bar, and (3) the striae appeared to be very directional.

A series of experiments was conducted in which the surface of the melt was covered, or partially covered, with a platinum lid to prevent evaporation. This lid, which must allow for expansion and contraction of the glass as it is heated and subsequently cooled, was frequently used in the form of a cup floating on the surface of the glass. The results indicated that striae was formed at the glass to atmosphere interface by changes in composition as a result of preferential evaporation of some of the glass ingredients. This layer of altered composition at the top surface was then drawn into the body of the melt by gravity, or some other means, thus forming striae.

This was shown most dramatically in a crucible configuration designed to separate a small reservoir of glass at the top containing the striae from the rest of the melt. The cylindrical crucible contained a platinum diaphragm, with a 1/2" hole in its center, welded to the crucible wall at an inch or more below the surface of the glass. As can be seen in Fig. 1, the glass at the surface sank in a funnel shaped pattern to the hole in the diaphragm and then down into the body of the glass below.

When a floating cup is used as a cover, striae formation is confined to the ring between the cup and the crucible wall and stays near the outside surface as it sinks into the melt. This surface layer can later be removed by grinding. Bars formed in this manner show great improvement over the glass as it comes from the ceramic crucible (the first step in the process) but there still remains a rather diffuse mottled striae pattern in the bars when viewed lengthwise.

Glass made in this experimental atmosphere furnace has been fabricated into rods for testing of high energy durability. Damage thresholds as high as 1100 j/cm^2 were obtained with these rods. By comparison, the damage threshold of commercially available 3835 laser glass averages about 400 j/cm^2. Attempts to produce high optical quality glass with this furnace were not continued in view of the results obtained when a nitrogen atmosphere was added to the extruder furnace.

2.3 EXTRUDER FURNACE EXPERIMENTS WITH INERT ATMOSPHERE

Because of the difficulties involved in introducing mechanical stirring into the experimental atmosphere furnace it was decided to flood the platinum lined extruder furnace with nitrogen. This allows us to combine an inert atmosphere with a furnace already equipped with stirring facilities which is presently producing glass of high optical quality. Without going into costly redesign of the furnace it was possible to maintain an atmosphere over the glass containing only 1% oxygen.

Several bars of glass produced in this manner were given careful optical examination using a microscope and a xenon lamp as the light source. No platinum particles were detected. Laser rods fabricated from this glass had a damage threshold of 900 j/cm^2. The damage tends to occur at or near the surface and although small in size, has the characteristic appearance of damage caused by a platinum inclusion. Further work must be done to study the effect of small amounts of oxygen on the formation of platinum inclusions.

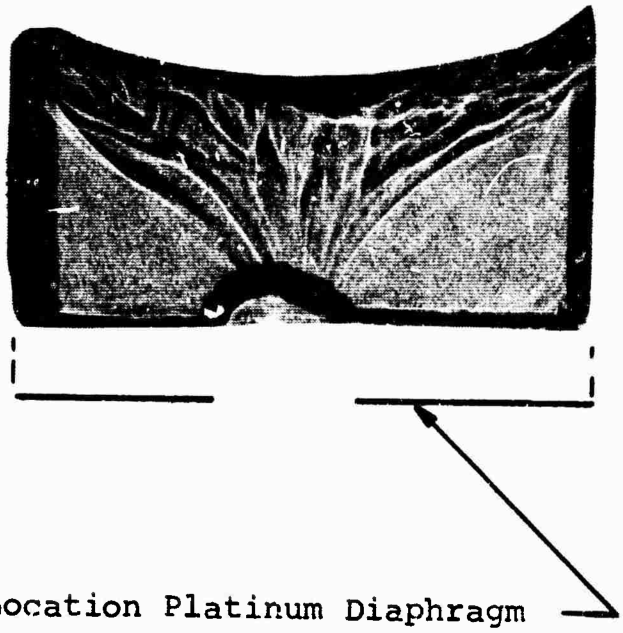


Figure 1. Shadowgraph Showing Striae Formed by Surface Evaporation.

2.4 PLATINUM ATTACK VS. TIME, TEMPERATURE AND ATMOSPHERE

In our experimentation we have found that laser glass can be held in platinum crucibles for as long as 100 hours at 2450° F under an inert atmosphere without introducing platinum particles into the melt. It was also noted, however, that when platinum crucibles were subjected to neutral atmospheres at high temperatures, (2700-2800° F), the platinum became contaminated with small percentages of metals such as antimony and zinc contained in the glass as oxides. Furthermore, when the atmosphere was made reducing by the addition of 3% hydrogen, the platinum was alloyed with these materials to the eutectic composition. The melting point of this eutectic is below the fining temperature of the glass thus causing a great deal of erosion of the platinum crucible.

These results indicate that the use of an inert atmosphere to solve the problem of particle formation by the transfer of platinum from the crucible to the glass in the form of an oxide could introduce another problem; namely, the formation of platinum particles by alloying of the platinum with some of the glass ingredients. This, plus the possibility that significant platinum may be getting into the glass even at oxygen concentrations as low as 1%, indicates that a more detailed study of the effect of melting conditions on particle formation should be made. Ideally, this study should reveal information on the relative importance of oxidation vs. alloying as an inclusion forming mechanism.

A program is underway using several laser glasses to investigate the effect of varying time, temperature, and atmosphere on the weight changes and compositional changes of platinum. The first series of experiments were carried out to determine the effects of oxygen and nitrogen atmospheres on platinum. Two laser glasses were used in this study. One was a standard laser glass composition, MG 3835, and the other, MG 1503, was the 3835 composition with antimony and zinc oxides removed. Weight changes are tabulated in Table I and are shown graphically in Figs. 2 through 5.

The experimental runs were made at three temperatures (2450° F, 2550° F, 2650° F) and three time durations (25, 50 and 100 hours). The nitrogen gas flow was kept at a constant rate (5 cu ft/hr) in all experiments. The platinum samples used were .030" diameter pure platinum wire cut to 4-inch lengths (about 1 gram) giving a surface area of 2.4 cm^2. Each sample was carefully weighed to .1 milligram before and after each run. The bulk glass used to immerse each sample was maintained at a constant volume, a cylinder 1" diam.

TABLE I

Weight Changes* of Platinum as a Function of Time, Temperature and Atmosphere

Sample in O_2 Atm.				Sample Submerged in 835 Glass. Atm. O_2		
Temp F°	25 Hrs	50 Hrs	100 Hrs	25 Hrs	50 Hrs	100 Hrs
2450	-7.0	-15.1	-27.0	+0.3	-0.6	-0.5
2550	-11.9	-22.7	-47.3	-0.2	-0.0	-0.1
2650	-19.1	-32.7	-57.7	-.1	-.5	+1.0
Sample in O_2 Atm.				Sample Submerged in 1503 Glass. Atm. O_2		
2450	-6.2	-11.9	-23.0	+.3	0.0	+0.5
2550	-10.0	-17.8	-40.4	0.0	0.0	0.0
2650	-17.6	-37.6	-58.1	+0.1	0.0	-0.5
Sample in N_2 Atm.				Sample Submerged in 835 Glass. Atm. N_2		
2450		-0.3	0.0	0.0	0.0	0.0
2550	+.5	+.6	0.0	0.0	0.0	+0.6
2650	0.0	-0.7	-0.1	0.0	-.3	+0.8
Sample in N_2 Atm.				Sample Submerged in 1503 Glass. Atm. N_2		
2450	0.0	0.0	0.0	0.0	0.0	0.0
2550	0.0	0.0	+0.6	0.0	0.0	0.0
2650		0.0	-0.1		0.0	-0.6

*Weight changes in the table are total weight changes, in milligrams, for pure platinum samples weighing 1 gram and having a surface area of 2.4 cm^2.

by 1" high. Two platinum samples were used in each experimental run; one sample was exposed directly to the gas atmosphere, the other was completely submerged in the glass sample.

As shown in Figs. 2a and 3a the platinum exposed directly to an oxygen atmosphere lost weight as a function of both time and temperature. No weight loss was observed for platinum exposed directly to a nitrogen atmosphere, Figs. 4a and 5a. These samples in addition to serving as a standard for the corresponding submerged samples serve as an indicator of the amount of platinum available in oxide form for possible particle formation.

The samples that were submerged in glass during exposure to oxygen and nitrogen atmospheres, Figs. 2b to 5b, showed no weight change within experimental limits of error. This does not exclude however the possibility of particle formation through the process of alloying of platinum with glass ingredients. These platinum samples are being analyzed by Battelle Memorial Institute to determine the extent of changes in composition as a result of alloying with glass ingredients. Results of this study will be needed before any valid conclusions can be made.

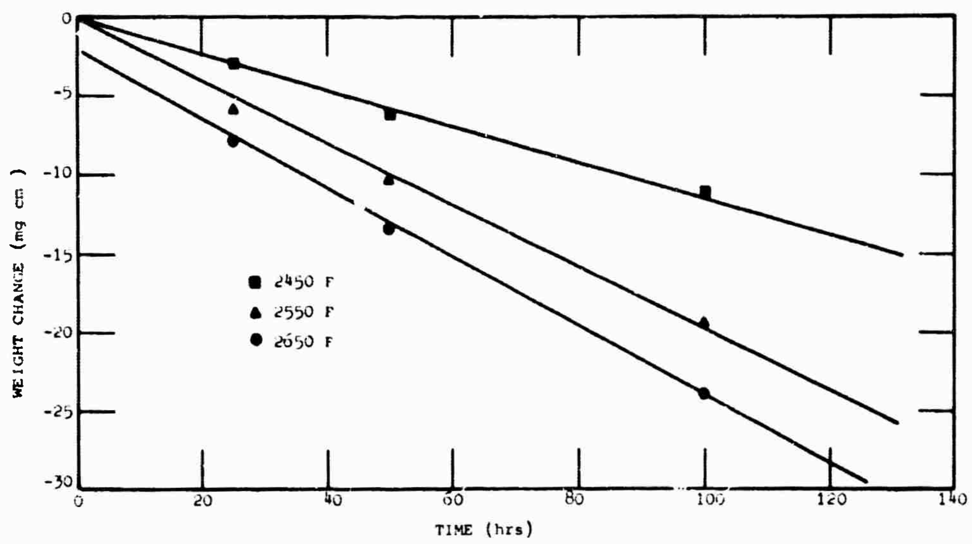
2.5 FUTURE WORK

The results of the chemical analysis of the platinum by Battell, will be correlated with the conditions of the test. Further experiments using small amounts of oxygen and hydrogen added separately to an otherwise inert atmosphere will be conducted to determine their effect on platinum. This will provide data on the degree of inertness required for a variety of melting conditions.

More work is being contemplated to improve the neutral atmosphere used in the extruder furnace if the results of the above experiments indicate that this is feasible.

3. ALL-CERAMIC PROGRAM

The purpose of this phase of the program is to develop an all-ceramic melting system capable of producing glass suitable for laser applications. This requires the glass to be of high optical homogeneity and free of iron contamination which in turn requires the ceramic materials to be of ultrahigh purity with high resistance to attack by the glass.



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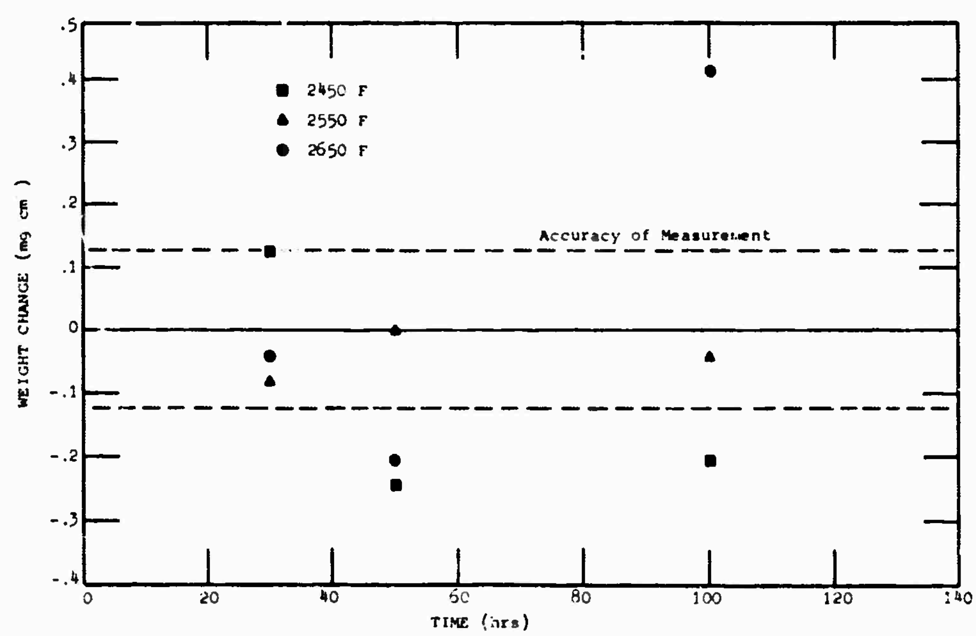

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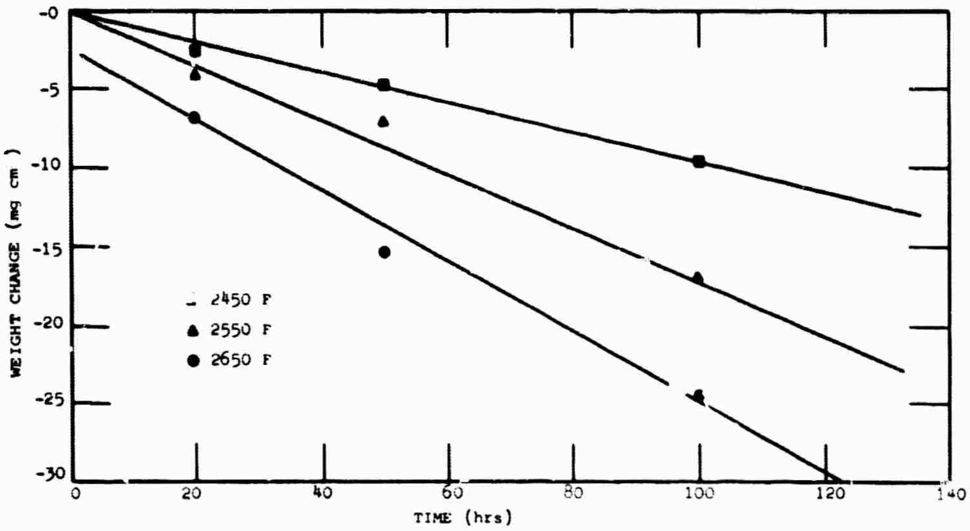
Figure 2. Graph of Weight Change of Platinum (a) in an oxygen atmosphere (b) completely submerged in 835 laser glass in an oxygen atmosphere.



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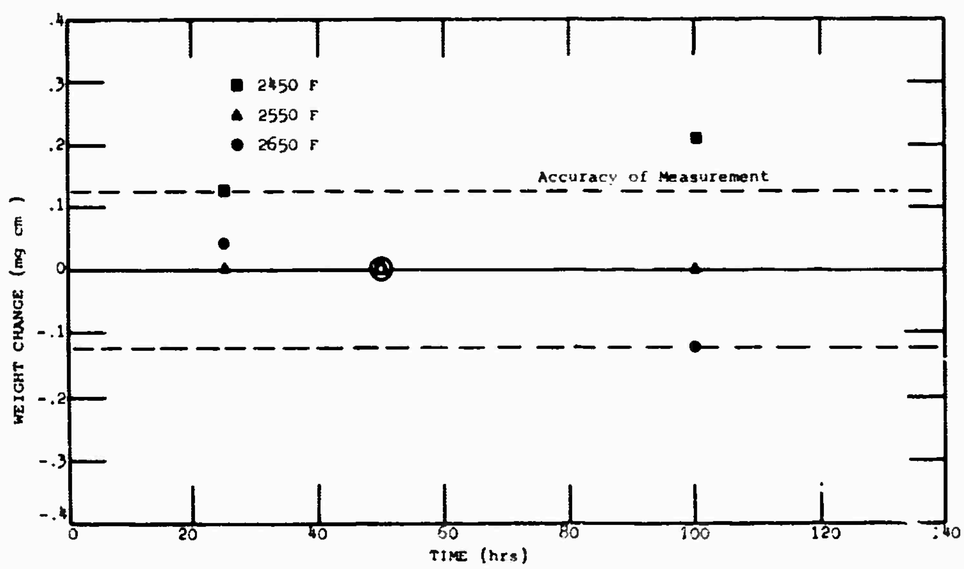

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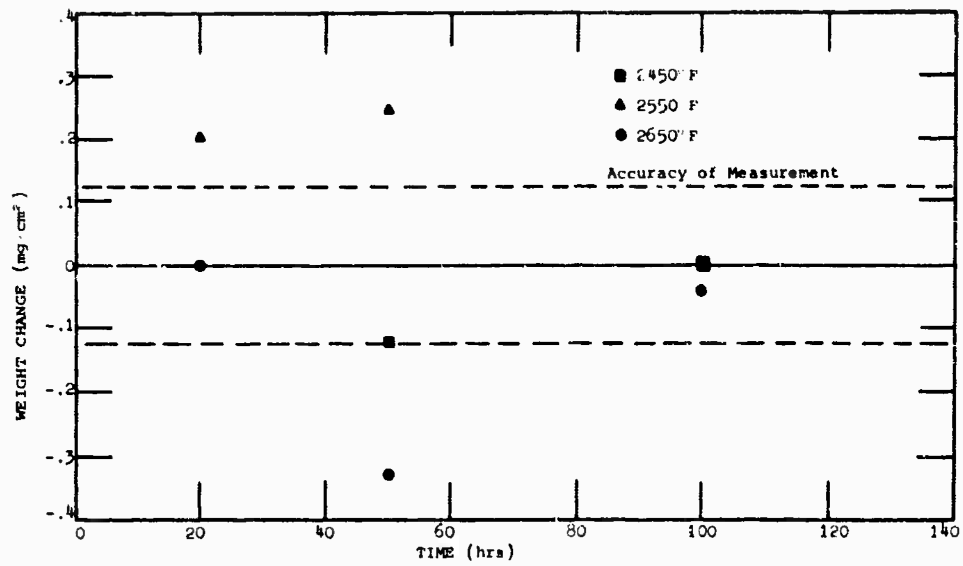
Figure 3. Graph of Weight Change of Platinum (a) in an oxygen atmosphere (b) completely submerged in 1503 laser glass in an oxygen atmosphere.



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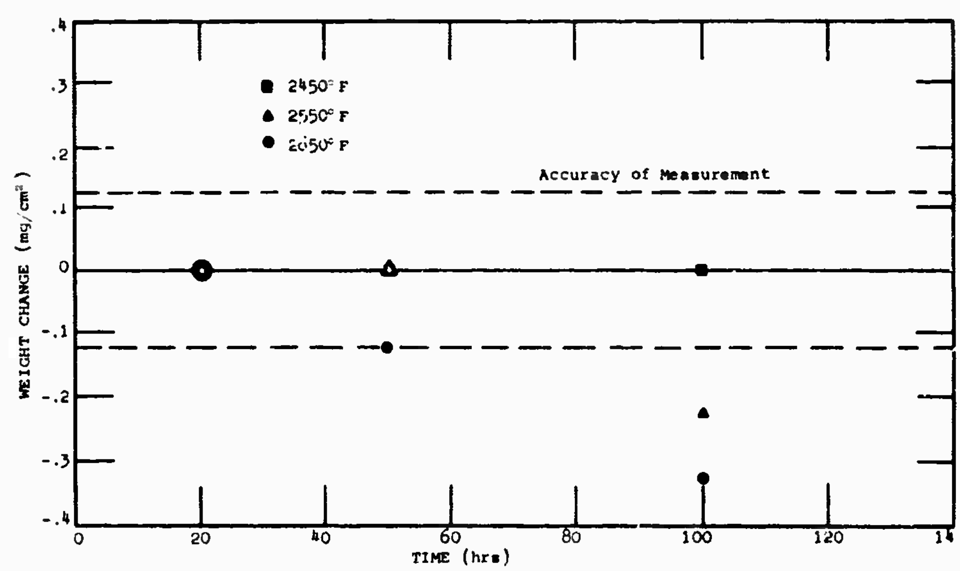
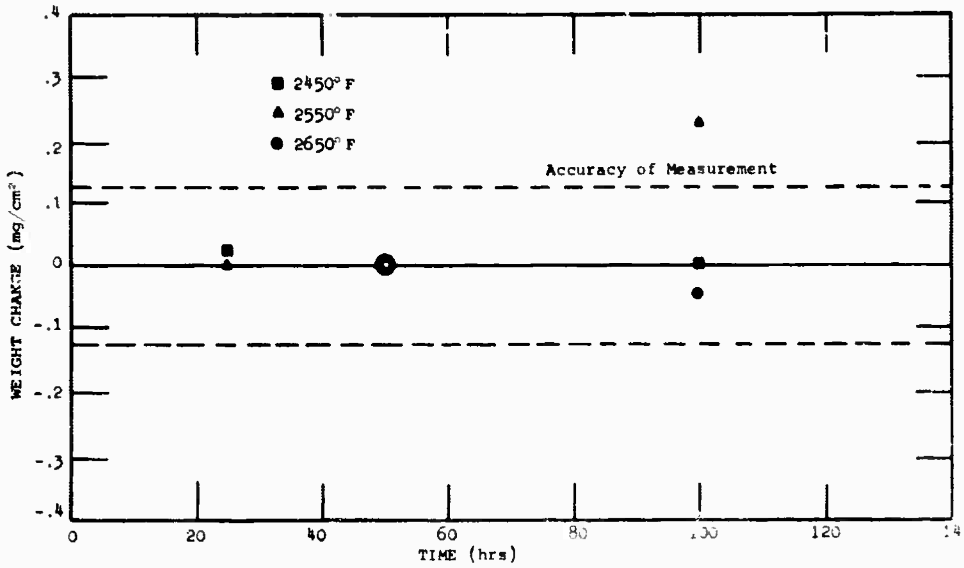


(b)

Figure 4. Graph of Weight Change of Platinum (a) in a nitrogen atmosphere (b) completely submerged in 835 laser glass in a nitrogen atmosphere.



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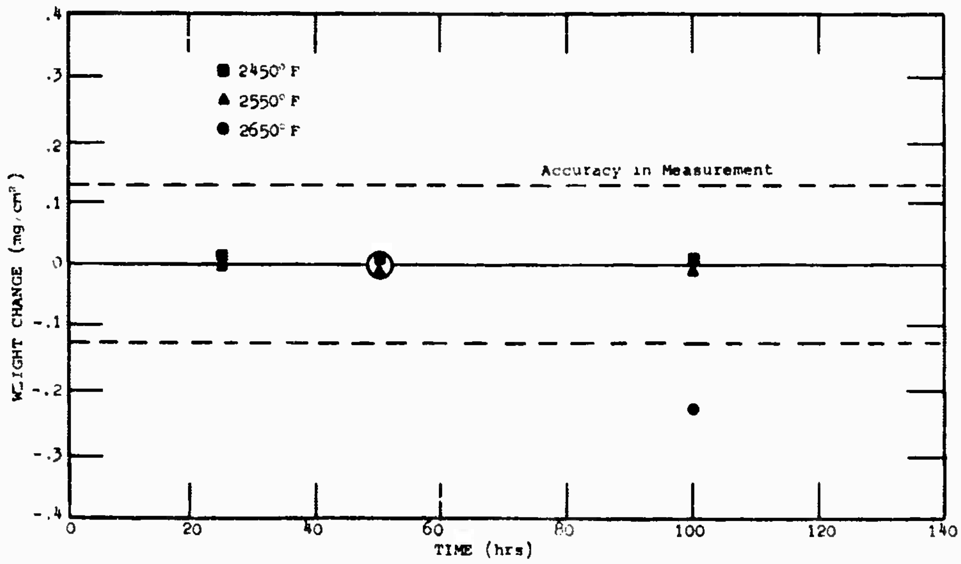

(b)

Figure 5. Graph of Weight Change of Plati. um (a) in a nitrogen atmosphere (b) completely submerged in 1503 laser glass in a nitrogen atmosphere.

3.1 SUMMARY OF PREVIOUS WORK

A high purity mullite was selected as the best material to be used for fabrication of both the crucible and stirrer. A furnace has been constructed using this material and a design based on the 50 lb. platinum extrusion furnace. Glass from the initial runs with this system showed some striae but in general the results were quite encouraging for an initial melt. The initial runs also showed several areas where modifications were required.

The main problem areas in the system were thermal control of the ceramic extrusion orifice and warpage of the rotating hearth. This was due in part to the heat required to overcome the thermal lag and low conductivity of the ceramic extrusion tube. This part of the system was redesigned where necessary.

The initial run also indicated that the use of finely ground batch ingredients, used to shorten reaction times, cause excessive dusting resulting in "crown drip" and changes in composition. To circumvent this problem the batch will be added in pellet form. An all ceramic pelletizer was made to produce contamination-free pellets.

3.2 TESTING OF SYSTEM

Design modifications of the unit were completed and testing of the modified system was carried out. Repeated "dry run" cycles, up to a temperature of 2640°F have been made which indicate that the problems of thermal warpage of the hearth have been solved.

Techniques for pelletizing the batch have been worked out and a load was pelletized for the initial run of the modified furnace. Before this run got started a high temperature sprinkler head above the furnace failed causing almost complete destruction of the unit which was at operating temperature at the time of the accident. Items not initially destroyed by the water were so saturated with iron rust that they had to be replaced. Problems in securing replacement items have delayed rebuilding.

Because of anticipated delays in reconstruction of the system a six-month extension of time was requested on this project. The cost of rebuilding the furnace is covered by insurance.

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Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) American Optical Company Research Division Southbridge, Massachusetts 01551	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP N/A

3. REPORT TITLE

PREPARATION OF PLATINUM-FREE LASER GLASS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Semi-Annual Technical Report Number Four, January-July 1966

5. AUTHOR(S) (Last name, first name, initial)

Woodcock, Richard F.
Granitsas, George A.
Silverberg, Carl G.

6. REPORT DATE December 1966	7a. TOTAL NO. OF PAGES 15	7b. NO. OF REFS

8a. CONTRACT OR GRANT NO. Nonr 4656(00) b. PROJECT NO. 4730 c. ARPA Order No. 306-62 d.	9a. ORIGINATOR'S REPORT NUMBER(S) N/A 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) N/A

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11. SUPPLEMENTARY NOTES N/A	12. SPONSORING MILITARY ACTIVITY Physical Sciences Division Office of Naval Research Department of the Navy Washington, D. C. 20360

13. ABSTRACT

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DD FORM 1 JAN 64 1473

Unclassified
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14. KEY WORDS	LINK A		LINK B		LINK C	
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