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JTA GRAPHITE COMPOSITE MANUFACTURING METHODS

ROBERT A. REUTER

UNION CARBIDE CORPORATION
CARBON PRODUCTS DIVISION

TECHNICAL REPORT AFML-TR-69-57

MARCH 1969

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JTA GRAPHITE COMPOSITE MANUFACTURING METHODS

ROBERT A. REUTER

**Union Carbide Corporation
Carbon Products Division**

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FOREWORD

This technical report covers work performed under Contract F3361567C-1498 from April, 1967, to December, 1968. The manuscript was released by the authors February, 1968, for publication.

This contract was initiated under Air Force Materials Laboratory, Manufacturing Technology Division, Project 450-7 with Leo J. Conlon as Project Engineer for the Materials Processing Branch.

The Contractor was Union Carbide Corporation, Carbon Products Division, Cleveland, Ohio. The Principal Investigator was Mr. Robert A. Reuter. Mr. Robert G. Fenish was responsible for the Phase II technical effort. Mr. Lincoln D. Stoughton was the Contract Administrator.

This project has been accomplished as part of the Air Force Manufacturing Methods Program; the primary objective of which is to implement, on a timely basis, manufacturing processes and techniques for use in economical production of USAF materials and components. The program encompasses the following technical areas:

- Metallurgy - Rolling, Forging, Extruding, Drawing, Casting, Powder Metallurgy, Composites
- Chemical - Propellants, Plastics, Textile Fibers, Graphite Fluids and Lubricants, Elastomers, Ceramics
- Electronic - Solid State, Materials and Special Techniques, Thermionics
- Fabrication - Forming, Material Removal, Joining, Components

Suggestions concerning additional Manufacturing Methods projects required on this or other subjects will be appreciated.

This technical report has been reviewed and is approved.



H. A. Johnson
Chief, Materials Processing Branch
Manufacturing Technology Division

ABSTRACT

Manufacturing techniques were developed for handling, firing, and hot-pressing graphite composite materials in 57-in. o. d. by 40-in. high graphite molds. Consumable wooden supports were used to achieve almost perfect float-molding conditions. Forming parameters were established for manufacture of Grade JTA plates 30 in. by 15 in. by 3 in. thick, and solid billets 29-in. o. d. by 15 in. high. The solid billet weighed 1090 pounds and is believed to be the largest ceramic billet ever hot-pressed. Hollow cylinders up to 14-in. o. d. were also hot-pressed. Cracking was eliminated in large Grade JTA composites by removing the pitch binder from the formulation. Limited progress was achieved in pressing Grade JTA composites into small leading edge shapes.

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TABLE OF CONTENTS

	<u>Page</u>
I INTRODUCTION	1
II SUMMARY	3
A. Phase I - Manufacturing Technology Development	3
B. Phase II - Press-to-Shape	4
III PHASE I - MANUFACTURING TECHNOLOGY DEVELOPMENT	5
A. Scale-up for Hot-Pressing	5
1. Prior Art	5
2. Float Mold Technique.	5
3. Mold Design	8
4. Subscale Solid 14-in. Billets	8
B. Large Flat Plates	11
1. Rectangular Graphite Mold.	11
2. Base.	12
3. Ram Train	12
4. Retainer.	12
5. Firing.	12
C. Hollow Cylinders	15
1. Powder Mandrels	15
2. No Mandrels	15
3. Hollow Mandrels	16
D. Solid 29-in. o. d. Billets	19
1. Hot-Pressing Assembly	19
2. Firing.	22
IV PHASE II - PRESS-TO-SHAPE	22
A. Grade JTA Process Variable Study	22
1. Mold-Fill Ratio by Cold-Pressing	22
2. Mold-Fill Ratio by Warm-Pressing	25
B. Press-to-Shape Grade JTA	25
1. Warm-Pressed Shapes	25
2. Hot-Pressing Grade JTA Preforms	25
3. Hot-Pressing Grade JTA Blend to Shape.	25
C. Grade JTA Bending	28

TABLE OF CONTENTS (CONT'D)

	<u>Page</u>
D. Leading Edge Fabrication	30
1. Design	30
2. Warm-Pressing	30
3. Hot-Pressing in a Confined Mold Assembly	30
4. Isostatic Hot-Pressing - 600-Ton Press	32
V PHYSICAL PROPERTIES.	35
A. Large Flat Plate	36
B. Solid 29-in. o. d. Billet	38
C. Solid 14-in. o. d. Grade JTA Billet	39
D. Nondestructive Testing.	39
1. Physical Properties Versus Density	39
2. Ultrasonic Testing of Grade JTA	39
3. X-ray Examination	45
4. High Temperature Properties	45

APPENDIX A

Working Stress in Graphite Molds	46
Simple Graphite Cylinder.	46
Mold Deformation	47

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Closed End JTA Mold. Single Acting Ram Design Was Used for Hot-Pressing 3-in. Through 14-in. o.d. Billets.	6
2	Illustrating Movement of Rams and Mold During True "Float" Molding. Bottom Ram is Stationary, Pressure Is Applied by Downward Movement of Top Ram. Mold Downward Movement Should Be Exactly One-Half of the Top Ram Movement	7
3	Hot-Pressing Mold for 30-in. by 15-in. Rectangular JTA Plates	11
4	JTA 30-in. by 15-in. by 3-in. Component Assembly.	13
5	Firing Data, JTA 30-in. by 15-in. by 3-in	14
6	3-in. o.d. JTA Hollow Cylinders Made by Baking and Hot-Pressing Without a Supporting Mandrel	16
7	Collapsed 14-in. o.d. Hollow Cylinder, Baked and Hot-Pressed Without a Supporting Mandrel.	17
8	Hot-Pressing Assembly 14-in. Hollow JTA	18
9	Placement of Wooden 2 x 4's Around the Bottom Ram Train to Support RVA Mold.	19
10	Lowering Insulation Retaining Ring Over 57-in. o.d. Graphite Mold. JTA Blend is Placed in the Mold Cavity, the Top Ram Assembly Added, and Gas Black Insulation Added to the Top of the Retaining Ring	20
11	Position of Assembly Components at Beginning of Pressing 29-in. o.d. Solid Billet.	21
12	Firing Data for 29-in. o.d. Solid JTA Billet	23
13	Density Versus Forming Pressure Regular Grade JTA	24
14	Grade JTA Shapes Prepared by Warm-Pressing	26
15	Male and Female Rams for Hot-Pressing Grade JTA to Shape .	27
16	Hot-Pressed to Shape JTA	28
17	Fractured Bend Specimen Depicting Runout at a Maximum Temperature of $2255 \pm 10^\circ\text{C}$	29
18	Split Cylinder Leading Edge After Warm-Pressing	31
19	Hot-Pressing Assemblies for Press-to-Shape Leading Edge Trials	33
20	Sampling of 30-in. by 15-in. by 4-in. Thick Modified JTA Plates	36
21	Sampling of 29-in. o.d. Modified JTA Billet.	38
22	Dependence of Young's Modulus on Bulk Density.	42
23	Dependence of Flexural Strength on Bulk Density	42
24	Property Variations in JTA 14-4.	43
25	Property Variations in JTA 14-5.	44
A-1	Graph of Strength Multiplier (T_f) Versus Temperature	48

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Results of Special JTA Firing Run	9
II	Modified JTA 30-in. by 15-in. by 3-in. Plate Room Temperature Physical Properties	37
III	Modified JTA 29-in. o. d. by 15 in. High Billet Room Temperature Physical Properties	40
IV	Modified JTA Piece 14-15 Room Temperature Physical Properties	41

SECTION I

INTRODUCTION

The graphite-refractory composite designated Grade JTA is an excellent candidate to satisfy the needs of weapons and aerospace systems for a structural material exhibiting high temperature oxidation resistance, good thermal shock resistance, refractoriness, and good machinability. Refractory nonmetallic materials are the most logical contenders for structural applications above 3000°F, an area of urgent need. Oxidation protection in depth is available in the Grade JTA graphite-refractory composite, a distinct advantage not offered by coated materials systems. This composite exhibits higher strength than conventional graphite while retaining the desirable property of nearly isotropic thermal expansion.

Grade JTA has been used in the thrust chamber assemblies and nozzles in the storable liquid propellant motors manufactured by the Rocketdyne Division of North American Aviation and has been used for attitude control and guidance on the highly successful Gemini and Apollo flights. Motors containing uncooled parts made of the JTA composite are regularly pre-flight fired and qualified in the same way as the conventional liquid fueled rocket motors of the regeneratively cooled designs.

These rocket motors are in the 25-150 pound thrust class. A need has been expressed by the Thompson-Ramo-Wooldridge Systems Group and other for the JTA composite material in larger sizes so that motors in the 1,500-5,000 pound thrust class may be designed. Possible use in the LEM excursion motor was discouraged due, in part, to uncertainty that cylinders larger than seven inches in diameter would have reproducible properties. Availability in larger sizes and in hollow cylinder form should lead to applications of Grade JTA in restartable motors in many future space-travel programs. Uncooled motors which do not require the weight and space apparatus needed for regenerative cooling are appealing to the space-propulsion systems designer.

Grade JTA composite is also being considered as a candidate material for a leading-edge application at temperatures above 3000°F. Bell Aerosystems Company, under Contract No. AF 33(615)-2376, is conducting a component design and environmental test program on Grade JTA composite. Illinois Institute of Technology Research Institute, under Contract No. AF 33(615)-3028, is conducting a design data program to fully characterize the JTA composite in support of the Bell program.

Grade JTA refractory graphite composite has been developed, for the most part, under Contracts No. AF 33(615)-6915 and No. AF 33(657)-11171. This work is reported in WADD TR 61-72, Volume XXX, "Oxidation Resistant Graphite-base Composites," by K. J. Zeitsch and J. M. Criscione, and in ML-TDS-64-25, "Improved Graphite Materials for High Temperature Aerospace Use," Volume II - "Development of Graphite-refractory Composites." The development work was limited to making billets of sizes up to five inches in diameter.

Union Carbide Corporation has extended this technology to produce a substantial number of 7 1/2-in. diameter by 6-in. long billets with good reproducibility. A few pieces of 14-in. diameter by 7-in. long Grade JTA composite have been produced.

Further exploitation of Grade JTA composite material for aerospace and defense use requires that capability be developed to produce large-size cylinders, rectangular billets, and special shapes. The major objective of this Contract No. F3361567C-1498 was to develop manufacturing methods for the hot-pressing of JTA graphite-refractory composite material with reproducible properties in various shapes and sizes larger than 14 inches in diameter. The program was divided into two phases: Phase I included determination of the manufacturing technology necessary to produce large sizes of solid cylinders, hollow cylinders, and flat plates; Phase II included feasibility studies for hot-pressing the JTA composite in the shape of curved plates.

This report covers the work completed during the contract effort from April 1, 1967 to December 31, 1968.

SECTION II

SUMMARY

A. Phase I - Manufacturing Technology Development

One significant result of this program was the development of a technique which allowed true "float" molding conditions in large, 57-in. o. d. graphite molds. In any open-ended mold, with one stationary ram and one moving ram, the mold must be free to move (float) without restriction if uniform pressure transmission by both rams is to be achieved. Float molding with the 2 1/2-ton graphite hot-pressing molds was accomplished by suspending the mold over the bottom ram with wooden supports. The blend was placed in the mold cavity, top rams placed, and pressure applied. As the assembly was heated, the wooden supports burned away leaving the mold free to move. The wood was completely charred at 300°C and had essentially no residual strength.

A number of 15-in. by 30-in. by 30-in. thick plates and 29-in. o. d. by 15-in. to 22-in. long billets were hot-pressed before the effect of the pitch binder component was realized. All of these pieces contained numerous vertical cracks. Variations in heating rate, load train design, pressure application, and delayed cooling had no apparent influence on billet cracking.

Experimentation showed that cracks occurred during final densification as the billet was approaching 80 percent of theoretical density. The minimum acceptable density of regular Grade JTA is 3.0 g/cc or 92 percent of theoretical. To attain this value, the billet height must be reduced to one-half of its baked (1000°C) height during final hot-pressing at 2150°C. Thus, large changes in volume are encountered.

It is theorized that, as the billet densifies, the rigid pitch-carbon network deforms and is stressed. The stress increases as the volume decreases until, finally, at approximately 80 percent theoretical density the pitch bond is broken, causing massive fracture in the billet.

To test the theory, hot-pressings were made with no-pitch, regular-pitch (13.4 percent), and high-pitch (17.4 percent) levels. The regular-pitch level billet was cracked, the higher-pitch level billet was very badly cracked, and the no-pitch billet was not cracked.

So that the same ratio of constituents in the no-pitch Grade JTA formulation would be maintained, the graphite flour component was slightly increased to compensate for the carbon in the pitch coke. The new formulation is called "modified Grade JTA."

A large flat plate 30 in. by 15 in. by 3 in. was hot-pressed from this modified material to a density of 3.14 g/cc. No flaws could be detected in this piece.

A 14-in. o. d. by 8-in. i. d. by 6-in. high hollow modified Grade JTA cylinder was hot-pressed to a density of 3.07 g/cc. A novel, thin-walled hollow graphite mandrel technique was utilized. Use of wood supports for both the mandrel and the mold allowed freedom of movement for both of these critical items. The X-ray and ultrasonic inspections of the piece detected two thin 1/2-in. long areas of higher-than-normal graphite content.

A 29-in. o. d. by 15-in. high solid billet of modified Grade JTA was hot-pressed to a density of 3.02 g/cc. The billet weighed 1090 pounds. The X-ray inspections of a 5/8-in. thick section cut through the diameter revealed areas of 2-3 percent density variations.

The presence of component variations in the hot-pressed bodies indicates a need for improved mix handling techniques after blending.

Samples of the modified Grade JTA pieces were tested and room temperature physical properties were found to be equal to or better than previously reported values from 5-in. billets. No high temperature properties or oxidation tests were run on the modified Grade JTA. Curves have been developed which may be used to predict average physical properties from hot-pressed billet density.

B. Phase II - Press-to-Shape

Warm-pressing regular blends of Grade JTA above the melting point of the pitch additive (180°C) was shown to be an excellent method for preforming. Warm-pressing prior to hot-pressing has no detrimental effect on final Grade JTA physical properties.

Hot-pressing curved shapes directly from the powder blend was demonstrated on small-scale experiments. However, scaling-up to an 8-in. long leading edge section did not prove to be feasible. The female base section of the mold assembly continued to fail in tension above 3000 psi pressure.

Attempts to bend Grade JTA by reheating high density hot-pressed specimens near the eutectic temperature and applying bending forces were unsuccessful. Very little plasticity was observed at these temperatures and Grade JTA fracture occurred moments after the pressure was applied.

Minor modifications in temperature and releasing agents were required to warm-press the 8-in. long split cylinder leading edges. Hot-pressing warm-pressed preforms in a confined graphite mold was hampered by base failures. Applied pressures in excess of 3000 psi result in failure.

Attempts were made to isostatically hot-press a preform by surrounding the leading edge with a gas black. Pressure was applied to the gas black through a graphite ram. A number of promising, but low density, leading edges were hot-pressed in this manner at pressures up to 7000 psi. Gas black appears to be a poor pressure transmittal medium at high temperatures.

SECTION III
PHASE I - MANUFACTURING TECHNOLOGY DEVELOPMENT

A. Scale-up for Hot-Pressing

1. Prior Art

Grade JTA graphite is prepared from a blend of the following ingredients:

Graphite flour	36%
175° pitch	14%
Zirconium diboride	41%
Silicon metal	<u>9%</u>
	100%

The blend is hot-pressed in a graphite mold at 2150°C. The minimum acceptable density is 3.0 g/cc (92 percent of theoretical) in the hot-pressed JTA piece.

The original JTA development work was performed on 1-in. and 3-in. diameter right circular cylinders. Since temperatures during these early trials at times exceeded the melting point of the composites, the molds were designed for high retention of liquids. A close-fitting, screw-on base effectively sealed the bottom of the mold, as shown in Figure 1. The only available pitch for material loss was upwards, around the top ram. When larger JTA composites were desired, this mold design was directly scaled to the size of interest. Thus, 5-in., 7-in., and eventually 14-in. o. d. solid billets were made in the closed-end mold.

The obvious disadvantage of this design was that pressure could only be applied uni-axially. If the material being pressed acted as a fluid, uniform pressure transmittal was realized; however, JTA is now hot-pressed 100°C below its eutectic melting. At this temperature, it is far from being liquid, and uniformity of pressure transmittal cannot be ideal. More uniform physical properties from top to bottom of a billet would occur if the billet could be successfully "float" molded (i. e., press both ends of the billet simultaneously). This procedure would be particularly desirable in very large sizes because the greater mass offers greater internal friction. Poor uniformity would be expected if the original hot-pressing method were used. One of the major accomplishments of this program was the development of manufacturing technology that allowed us to "float" a 2 1/2-ton graphite mold.

2. Float Mold Technique

In a float molding operation, with the pressure applied by downward movement of the top ram, the mold must be free to move down around the stationary bottom ram. A mold which is not restricted will move exactly one-half the distance that the top ram moves. The downward movement of the mold produces the same effect as an upward movement of the bottom ram. When these conditions are met, the molding action is essentially equivalent to that achieved with two movable rams.

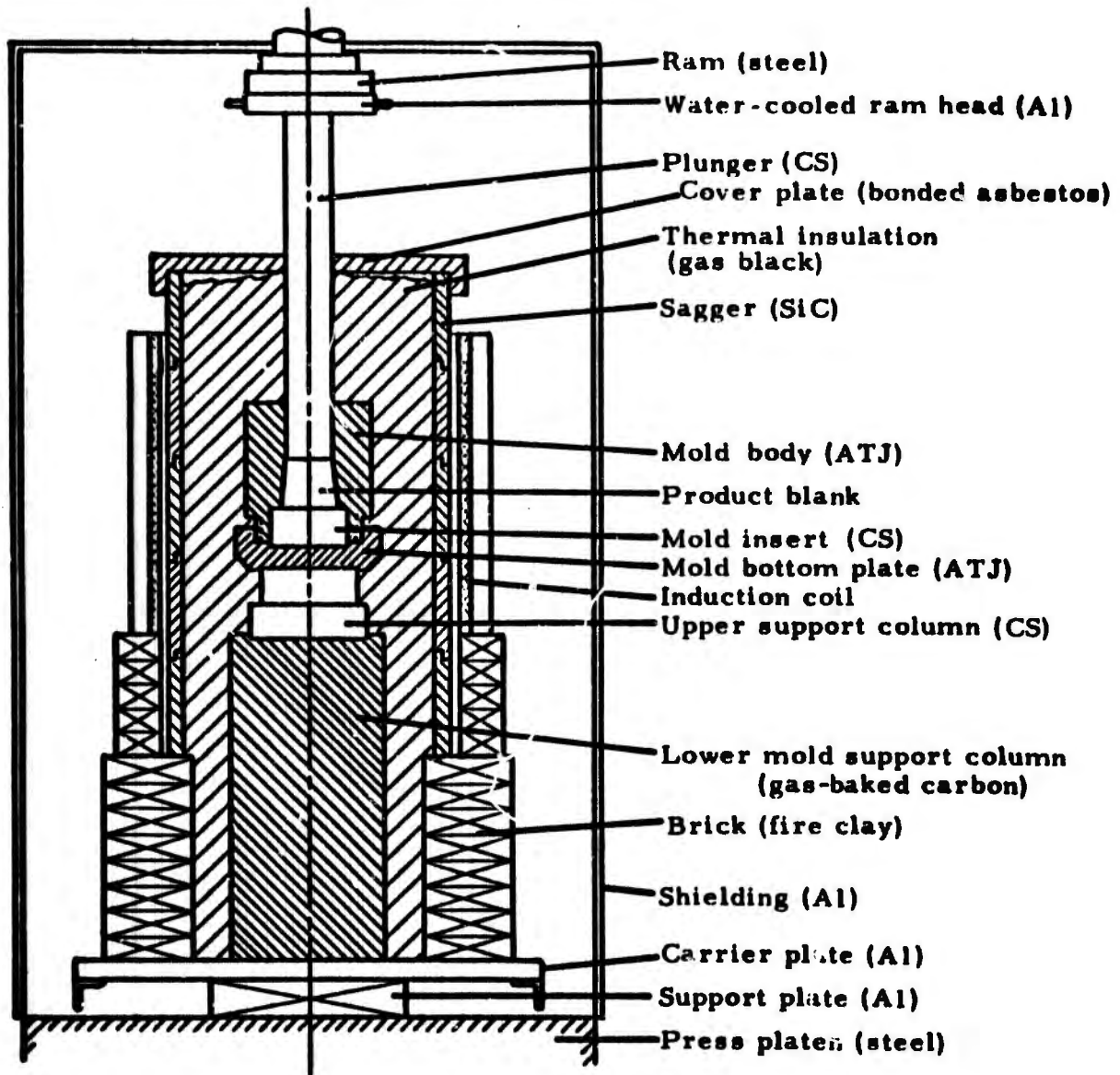


Figure 1. Closed End JTA Mold. Single Acting Ram Design Was Used for Hot-Pressing 3-in. Through 14-in. o. d. Billets.

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Figure 2 illustrates the movement of the mold in relation to the rams in a true float molding process. Both rams move an equal amount into the mold; thus, the billet is subjected to the same pressure from above and below.

In practice, float molding can be achieved easily with small assemblies. A spacer is placed under the mold to support it over the bottom ram. The mold cavity is filled with mix, the top ram placed in the mold, and pressure applied until the side wall friction of the mix against the inner wall of the mold is sufficient to support the weight of the mold. At that time, the spacer is withdrawn, and the mold is free to "float."

The use of extremely large, heavy molds and ram trains in this scale-up program did not allow use of a spacer which could be withdrawn. Even if the spacer could be withdrawn, the subsequent movement of the assembly into an insulation retaining ring preparatory to hot-press might break loose the tamped mix and allow the mold to drop. The mold could be supported on a bed of insulation. However, such a bed will only compress a few inches at best; at that point, pressure transmittal will continue with the top ram only.

Successful float molding was accomplished for the large RVA graphite molds by use of upright wooden 2 by 4's which supported the mold during loading and tamping and were then burned out at low temperatures. An air space, equal to the calculated downward mold movement was left between the mold and bottom insulation. Wood begins to char at 225°C; by 300°C, it is completely carbonized and has essentially no residual strength. Thus, at temperatures as low as 250°C-300°C, the mold is free to move, with the result that float molding is achieved.

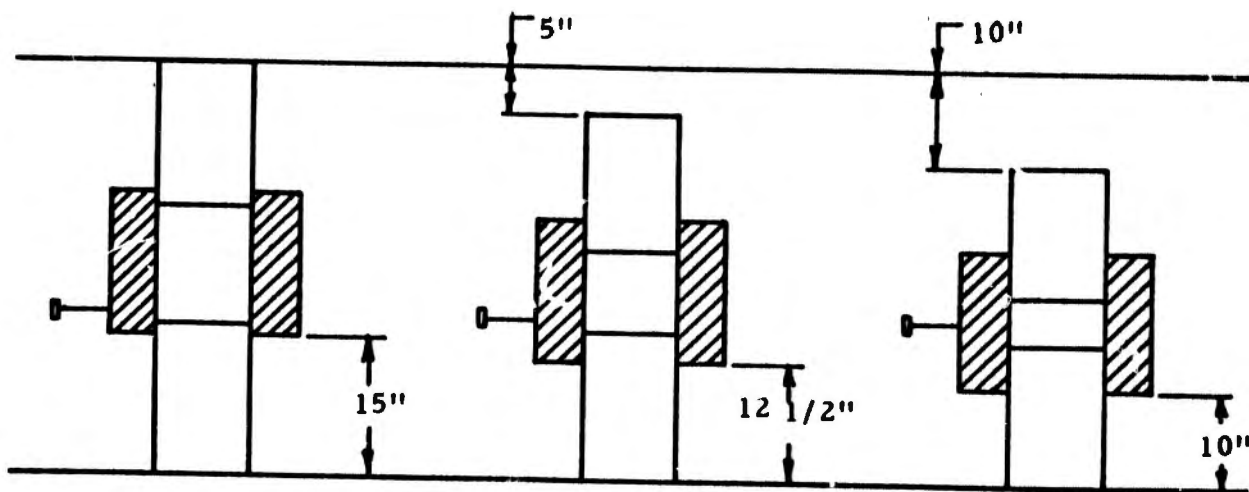


Figure 2. Illustrating Movement of Rams and Mold During True "Float" Molding. Bottom Ram is Stationary, Pressure Is Applied by Downward Movement of Top Ram. Mold Downward Movement Should Be Exactly One-Half of the Top Ram Movement.

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3. Mold Design

Billet molds with a slight taper are best for JTA manufacture. The mold inner diameter was machined so that, after a short straight section, the opening was increased with a 0.003 inch per inch taper running through to the opposite end. Molds can be used twice before re-machining. During hot-pressing, the graphite "hot-works" to form a bulge which will lock successive billets in place if the bulge is not eliminated.

Grade RVA graphite was used exclusively for all graphite mold requirements because of its high tensile strength. An empirical formula was developed (Appendix A) which accurately predicted the maximum permissible applied pressure. It must be cautioned that this formula would not be appropriate for more fluid bodies.

Graphite load train parts also distort during use, depending on time held at temperature and the pressure history of particular parts. Refacing of rams after each run was often necessary and aided in preventing excessive breakage.

Three grades of graphite and one carbon grade were used in the load-bearing rams. For the subscale 14-in. JTA investigations, Grade ATJ graphite proved to be an excellent material. Both Grade RVA and ATL graphites were used in the larger full-size assemblies. Grade RVA is the preferable material because of its greater compressive strength and lower tendency to hot-work with temperature and pressure.

Insulation is needed in the ram train to reduce heat flow from the JTA mix during hot-pressing. An all graphite ram train would act as a very large heat sink. Several methods for minimizing this heat loss were investigated. Combinations of "Grafoil," carbon felt, gas blacks, and gas-baked carbon were used.

The greatest reduction in heat loss resulted from the use of gas-baked carbon (Grade GA) usually baked to temperatures of 850°C-1000°C. This grade has approximately one-tenth of the thermal conductivity of graphite. Large sizes are available, and they may readily be machined into convenient shapes. Some cracking problems with carbon insulators have occurred when they are placed in areas of highest temperature; for this reason, the blocks are normally set at the ends of the ram train. Cracking was further reduced when the insulators were cut such that the load is applied across-the-grain direction.

The only other successful insulator was a carbon felt gas black "sandwich." Felt is placed on the ram and a 1/2-in. thick layer of gas black is sprinkled on the felt by screening through a sifter. The sifter aids in depositing a lump-free uniform layer. The gas black is leveled with a straight edge and the next ram placed on the gas black. When this method was used, the "sandwiches" had to be placed in every joint to insure effective thermal insulation.

4. Subscale Solid 14-in. Billets

The float-mold technique was evaluated by hot-pressing 14-in. o. d. by 7-in. long Grade JTA billets in 30-in. o. d. Grade RVA graphite

molds. Wood mold supports were used, and in each case the downward mold movement was within 1/2 inch of being exactly one-half of the total downward ram movement. During the course of the program, 3-in. o. d., 14-in. o. d., 29-in. o. d., and 30-in. by 15-in. hot-pressings were made. All of the larger pieces that were hot-pressed to densities greater than 2.85 g/cc contained numerous vertical fractures. None of the 3-in. billets, made to investigate various processing conditions, were cracked. All 21 of these small hot-pressings were free from fractures, irrespective of their forming parameters.

So that the exact moment at which the fractures in the larger sizes were occurring might be determined, a single 14-in. diameter JTA billet was hot-pressed to 1000°C, 1800°C, and 2150°C. The billet was cooled to room temperature after reaching each of these temperatures and examined for cracks. The 2150°C firing was run at lower-than-normal pressure so that complete densification would not occur.

Fracture did not occur until a temperature of 2150°C was reached and the density of the block was 2.79 g/cc (85 percent of theoretical density). See Table I.

TABLE I
Results of Special JTA Firing Run

Temperature	O. D.	Length	Weight	A. D.	Remarks
1050°C	35.30 cm	95. cm	21,100 g	2.27 g/cc	OK
1800	35.25	9.8	21,050	2.20	OK
2150	35.65	7.5	20,870	2.79	Fractured

This experiment confirmed observations from metallographic mounts of fracture areas prepared from cracked Grade JTA billets. These metallographs showed SiC crystal growth into the open fracture, inferring that the crack must be present while the billet was at hot-pressing temperature; otherwise, there would be no void into which the crystals could grow. Until that time, it had been surmised that cracking occurred as a result of thermal stresses during cooldown.

One theory that explains fracturing when a certain volume is attained, is as follows. It may be assumed that when 1000°C is reached, the pitch in the Grade JTA blend is completely coked into a random lacework of brittle carbon. During final densification, the volume of the billet must be reduced to one-half of its baked volume. As the volume shrinks, the carbon bonds must be stressed. At some critical point during densification, the accumulated stress on the carbon network reaches the tensile strength of the billet and is released by fracture. The tensile strength could be quite low at this point because sintering of the ZrB₂ and the SiC reaction are probably not complete. So that this theory of mechanical damage

to the pitch-carbon bond might be tested, an 18-in. by 15-in. by 3-in. plate with a higher-than-normal pitch level was hot-pressed. At the same time, but in another press, a 14-in. o. d. by 5-in. high billet containing no pitch was hot-pressed. Time did not permit hot-pressing of both a high-pitch and a no-pitch piece of the same geometry in the same hot-pressing assembly. While the large hot-pressing assemblies were cooling, two 3-in. o. d. billets, one with the higher pitch level and one with no pitch, were formed and sampled.

Regular JTA graphite has a pitch binder level of 13.4 percent. An experimental blend, containing 17.4 percent pitch, was formed into the 18-in. by 15-in. by 3-in. plate by using the standard JTA forming techniques. When the plate was unpacked, it was badly cracked and was removed from the mold in many pieces. There was a greater-than-normal amount of Grade JTA sticking to the mold and much Grade JTA flash round the rams. These conditions indicated that the mix was very fluid during baking. The density of this billet was 3.05 g/cc. The increased pitch level was obviously harmful.

To keep the same carbon-zirconium-silicon-boron content in a no-pitch formula as regular Grade JTA, the minus 200 mesh graphite flour component of the blend was increased slightly to compensate for the lack of carbon from the pitch. The modified formula is:

Graphite flour	48.06 w/o
Zirconium diboride	42.42 w/o
Silicon	9.52 w/o
	<hr/>
	100.00 w/o

The theoretical density of this mixture is 3.27 g/cc the same as that of regular Grade JTA and is based on the following component densities: Carbon = 2.267 g/cc; ZrB_2 = 6.10 g/cc; SiC = 3.216 g/cc.

A blend of the new formula was hot-pressed into a 14-in. diameter billet. No sticking occurred when the Grade JTA was removed from the mold. The billet had a density of 3.07 g/cc and contained no apparent flaws. The internal structure proved to be good when the piece was cut in half to sample for physical properties.

Processing time of large JTA blocks is of the order of 3-4 weeks. Most of this time is used in cooling from 2150°C to 250°C-350°C, the point at which unpacking can begin. In order to provide a rapid evaluation of the effect of pitch content, 3-in. o. d. by 3-in. long billets containing 17.4 percent pitch and containing no pitch were hot-pressed. Both billets were flaw free. These billets were cut into 1/2-in. by 1/2-in. by 3-in. samples, and density, sonic modulus, and flexural strength values were determined. These values were compared with those obtained on similar samples of a regular pitch bonded 3-in. Grade JTA plug. There was no significant difference in any of the physical properties measured.

B. Large Flat Plates

Three attempts were made to produce a 30-in. by 15-in. by 3-in. thick flat plate; all three plates were cracked. All were made with regular pitch-bonded JTA. Further attempts with 18-in. by 15-in. by 3-in. plates also resulted in cracked pieces.

Because of the success achieved with the modified JTA 14-in. billet, it was decided to make once again a full size 30-in. by 15-in. by 3-in. plate, this time employing the new mix formula. This plate had an excellent density of 3.14 g/cc, weighed 165 pounds, and was flaw-free. The manufacturing conditions for full-size rectangular plates follow.

1. Rectangular Graphite Mold

A 36-in. o. d. hole was trepanned through the axis of an RVA graphite cylinder 57-in. o. d. by 40 in. high. The ATL inserts were machined on a horizontal milling machine such that, when they were inserted into the RVA cylinder, a 30-in. by 15-in. rectangular mold was formed (see Figure 3). The assembled graphite mold weighed slightly more than 2 1/2 tons.

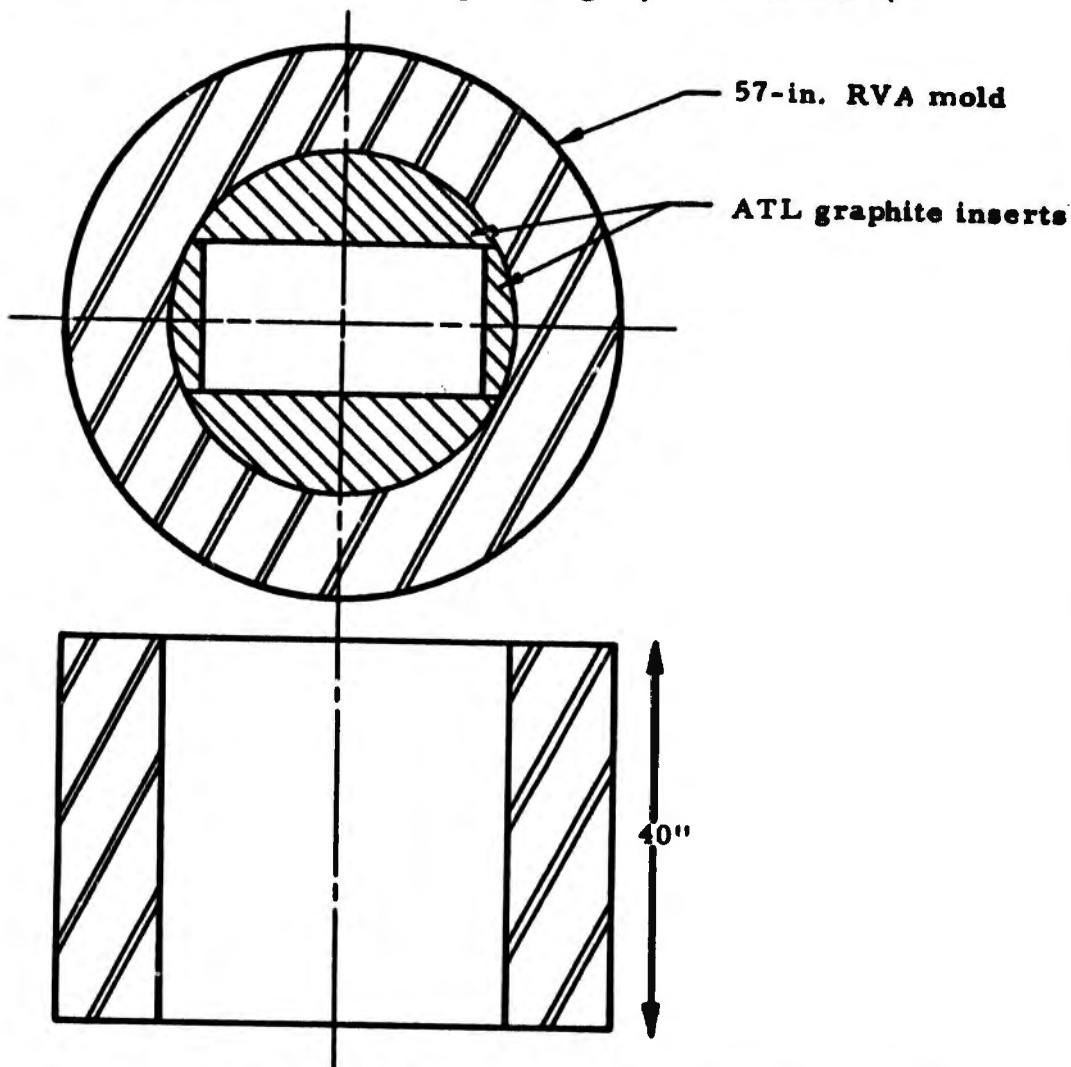


Figure 3. Hot-Pressing Mold for 30-in. by 15-in. Rectangular JTA Plates.

2. Base

The hot-pressing assembly was built upon a water-cooled aluminum block 3 ft. by 3 ft. by 4 in. thick. Water cooling is necessary to prevent metal distortion from heat loss through the bottom ram train. An 8 ft. square, 2-in. thick aluminum "skid" is placed over this block. The insulation retaining structure is built up from, and supported upon, this "skid."

3. Ram Train

The load transmitting parts of the assembly were machined from carbon, graphite, and 1-in. thick asbestos panels.

Carbon rams 30 in. by 15 in. by 23 in. thick were machined from a 24-in. by 30-in. by 72-in. Grade GA block, such that pressure transmission was across-the-grain direction. Two grades of graphite were used in this ram train. Three rams, 15 in. by 30 in. by various thicknesses, were machined from a broken RVA mold. Two additional rams were machined from a 30-in. o.d. by 72-in. long ATL cylinder. Both grades worked well.

A 1-in. thick panel of "Marinite" ⁽¹⁾ was placed at the base and at the top of the ram train to correct for warpage and irregularities in the metal surfaces. The carbon and graphite rams are rather inflexible, and breakage from slightly heat-warped metal surfaces has been prevented by use of such panels. The asbestos board is soft and quickly conforms to the mating surfaces. It must be replaced each time the joint it serves is disassembled.

4. Retainer

A circular wall is built up around the mold and ram train to hold the carbon black insulation. A nine-course refractory brick base was built upon the 2-in. thick aluminum skid. A large cast refractory cylinder, cooled with imbedded 1/2-in. copper tubing was placed upon the skid.

The various components were arranged as illustrated in Figure 4. The graphite mold was supported by eight yellow pine 2 x 4's. When the assembly was heated, the wood charred losing strength and permitting the mold to "float." Approximately 2400 pounds of gas black was poured into the retainer and lightly tamped. The completed assembly weighed in excess of 9 tons when it was placed under the 1250-ton press ram.

5. Firing

The firing plan called for raising the temperature to 2150°C as fast as the power supply would allow and holding at temperature for 24 hours. As the holding temperature was approached, a small water leak developed in the retainer between the cast refractory and brick base. After 22 hours at temperature, the water leak suddenly increased and a large fire resulted which aborted the run. The actual firing conditions are illustrated in Figure 5. The modified JTA plate had a very high (3.14 g/cc) density and excellent structure. Lower pressure or shorter hold time at temperature could, undoubtedly, be used in future runs because of the ease with which density was reached.

⁽¹⁾ Johns-Manville, 22 East 40th Street, New York, New York.

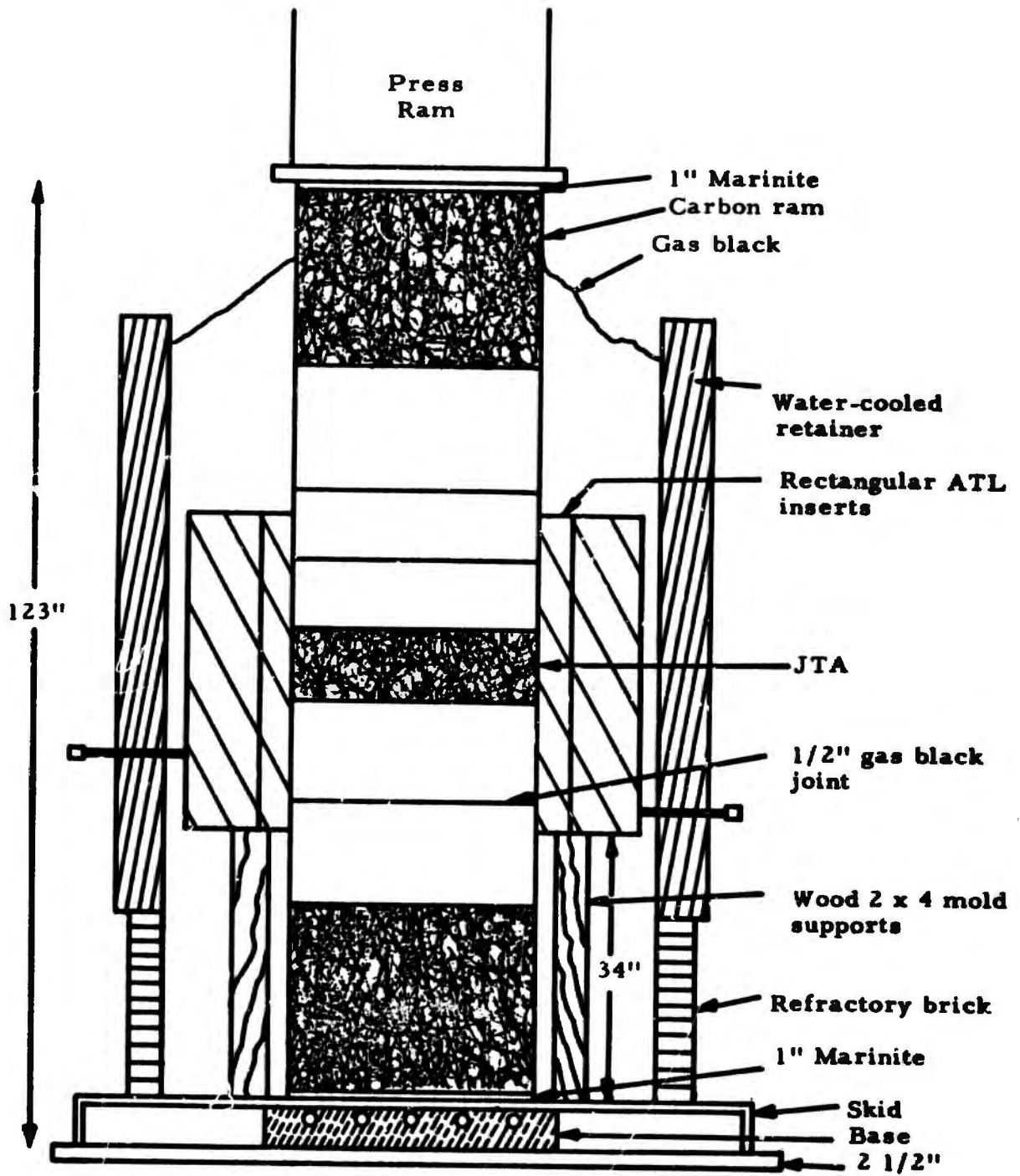


Figure 4. JTA 30-in. by 15-in. by 3-in. Component Assembly.

N-20930

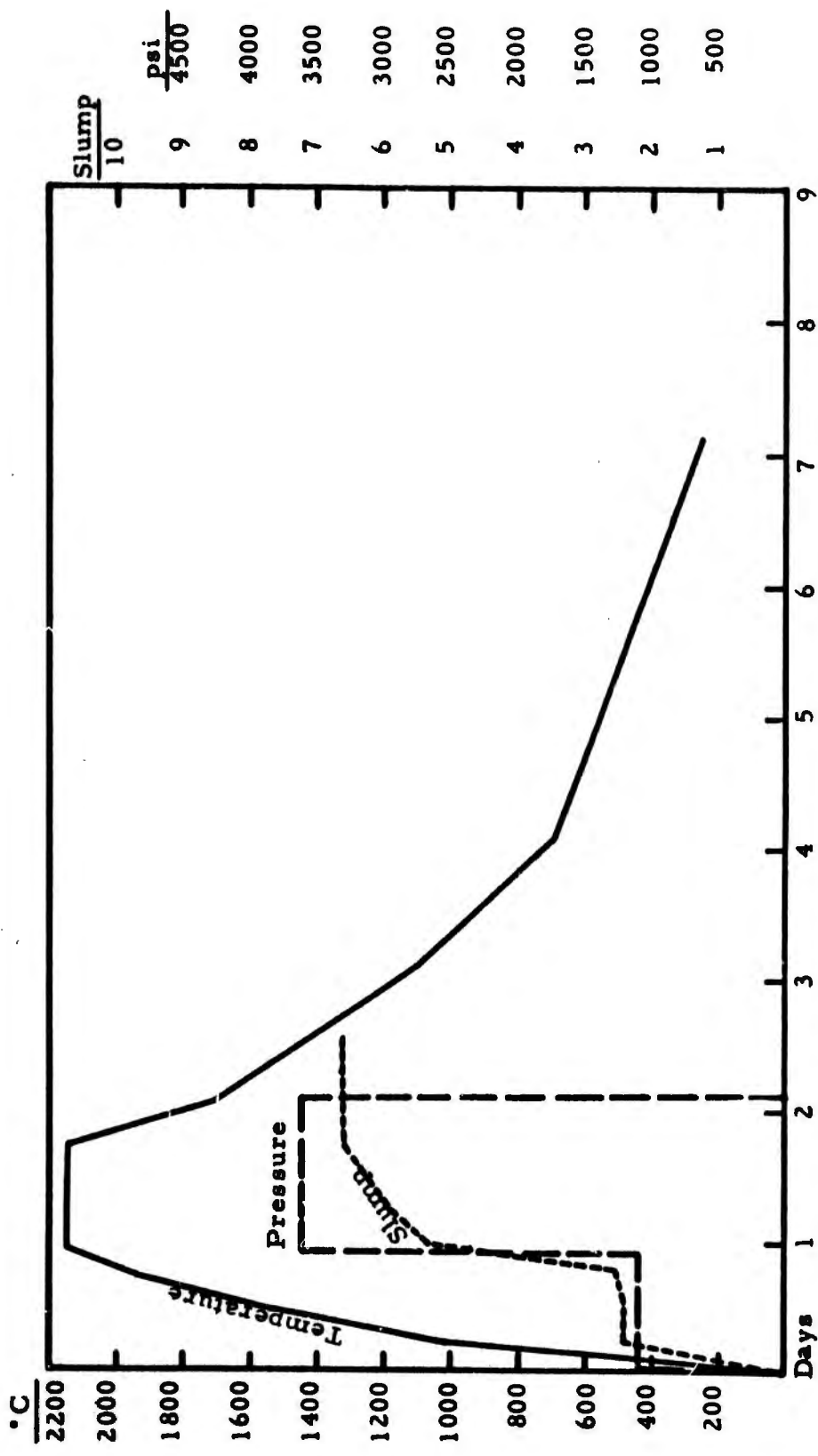


Figure 5. Firing Data, JTA 30-in. by 15-in. by 3-in. N-20931

C. Hollow Cylinders

Since JTA raw materials are expensive, a significant cost reduction would result if the material could be formed in shapes such that little JTA would be lost by machining a billet to a finished shape. Grade JTA is already used for applications in a number of small attitude control rockets; thus, hollow cylinders would be of interest.

The classical method of forming hollow bodies is to form them around a solid mandrel. Graphite is one of the few mandrel materials which can withstand the hot-pressing temperature without reacting with the Grade JTA components. Grade JTA has a coefficient of thermal expansion twice that of conventional graphites. Thus, Grade JTA will shrink more than the graphite mandrel. This differential shrinkage stresses the cylinder and results in fracture. The manufacturing development for hollow bodies was started with 3-in. o. d. cylinders since this subscale size required little JTA blend and could be rapidly processed.

1. Powder Mandrels

One method of eliminating the differential shrinkage problem of solid mandrels would be to place Grade JTA blend around a collapsible carbon powder and compress the composite with solid graphite rams. It was expected that the powder would act as a fluid, transmitting pressure to the inner wall of the Grade JTA and aiding in rapid densification. Then, when the pressure was released, the cooling JTA would be free to shrink because the binderless powder would offer no resistance to deformation.

Gas black was used as a powder mandrel in a number of runs without success. Each time the gas black compacted and densified in such a manner that it acted as a solid body. It did not deform when the Grade JTA cooled and the cylinders broke each time. The gas black was packed so densely at the completion of a run that it had to be removed with a hammer and chisel. The densities of the Grade JTA bodies were usually under 3.0 g/cc, indicating that the gas black did not act as a fluid.

Other powders such as fluid coke, natural graphite, and combinations of these materials also densified into rigid bodies with no indication of acceptable fluid action at temperature.

2. No Mandrels

A 3-in. o. d. by 2-in. i. d. Grade JTA cylinder with a density of 2.6 g/cc was placed between two solid graphite rams with no mandrel and re-hot-pressed. The cylinder had a final density of 3.10 g/cc, was 3-in. o. d., 1 3/4-in. i. d., 2 1/2 in. high, and was flaw free. This experiment indicated that low density cylinders could be repressed to acceptable densities with no supporting mandrel. Additional work showed that we could duplicate this procedure with any 3-in. cylinder which had been performed and baked to 1000°C. One technique that showed particular promise was to warm mold (200°C) a Grade JTA preform around a solid mandrel, remove the Grade JTA cylinder, and place it in a graphite mold between solid rams. With no applied ram pressure, the "green" preform was baked to 1000°C. At this point, pressure (4000 psi) was applied and the temperature increased to 2150°C. A number of good, flaw free 3-in. o. d. by 2-in. i. d. hollow cylinders were formed in this manner (see Figure 6).

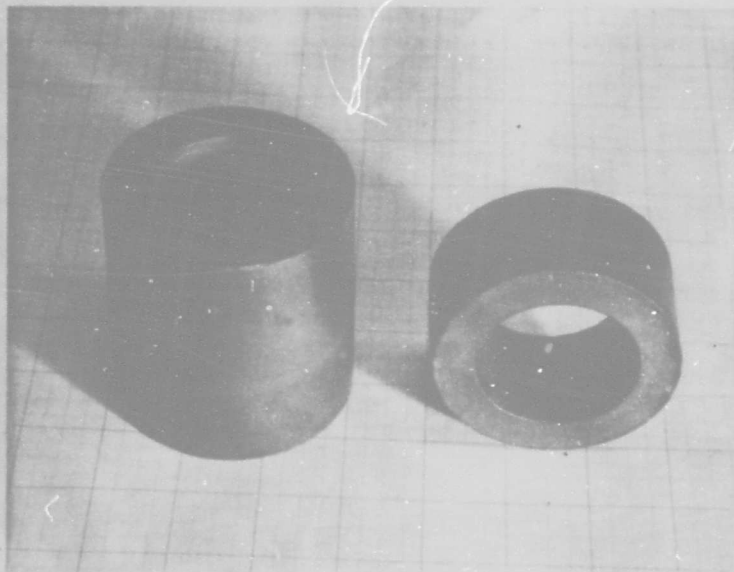


Figure 6. 3-in. o. d. JTA Hollow Cylinders Made by Baking and Hot-Pressing Without a Supporting Mandrel.

N-18786

Attempts to duplicate this process in 14-in. o. d. by 8-in. i. d. cylinders failed. In every case, the side walls collapsed as shown in Figure 7. It is believed that the method would be successful in cases in which the final wall height was not more than 3 inches. Unfortunately, in the larger sizes, wall heights in the order of 7 inches or greater are of interest. These higher walls tend to shear and buckle as they densify when no supporting mandrel is used.

3. Hollow Mandrels

It was evident that some support was necessary to resist wall collapse during high temperature densification. However, a solid mandrel which prevented Grade JTA shrinkage during cooling would cause the cylinder to crack. An attempt was made to design a compromise. It was reasoned that a hollow graphite mandrel could be machined with a wall thickness that would just withstand the applied forming pressure. The additional forces from the shrinking Grade JTA would, at some point, cause the mandrel to fracture and completely free the cylinder.

An experiment was run using modified JTA blend in the 14-in. mold assembly. An 8-in. o. d. graphite mandrel, with a 1/4-in. wall thickness, was supported by 1-in. wood strips in hollow ATJ rams. The mandrel supports burned out at the same temperature as the mold supports and allowed the mandrel to move freely (see Figure 8).

The hot-pressed cylinder was 14-in. o. d., 8-in. i. d., and 6 in. high. Its density was 3.07 g/cc. The thin-walled mandrel did not break but was hot-worked by the inward pressure of Grade JTA and bulged (approximately 5/8 inch) toward the center. No flaws were visible externally. Both X-ray and ultrasonic examinations detected two small areas of low density. Subsequent metallographic sampling revealed two, 1/2-in. long by .009-in. wide lines with slightly greater-than-normal graphite flour concentration. This apparently resulted from segregation during mix handling after blending. Development of improved blend handling techniques is indicated.

Time did not permit an attempt to make a 29-in. hollow cylinder. However, it is believed that this thin-walled mandrel technique certainly appears promising and should be a fruitful avenue for further investigation.

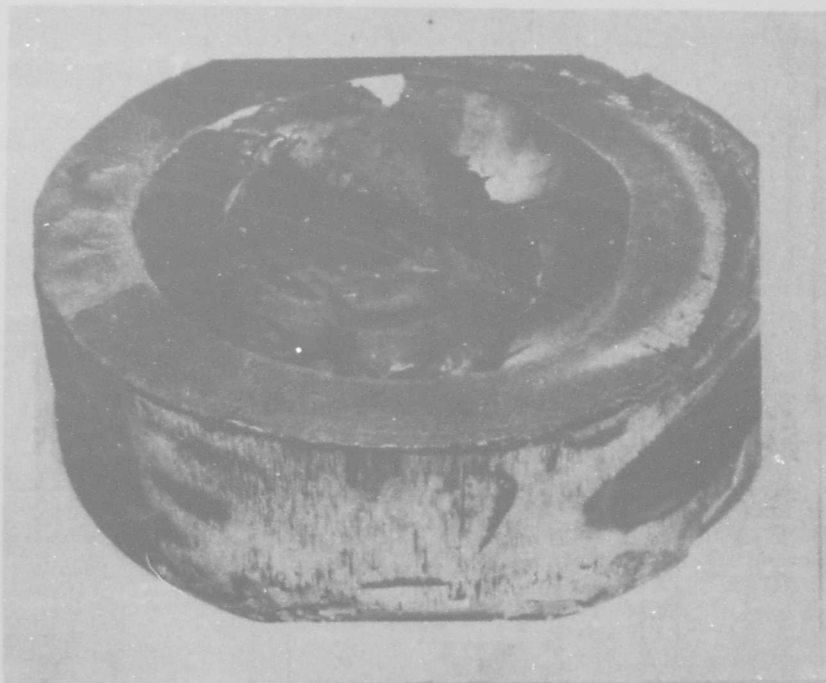


Figure 7. Collapsed 14-in. o. d. Hollow Cylinder, Baked and Hot-Pressed Without a Supporting Mandrel.

N-21127

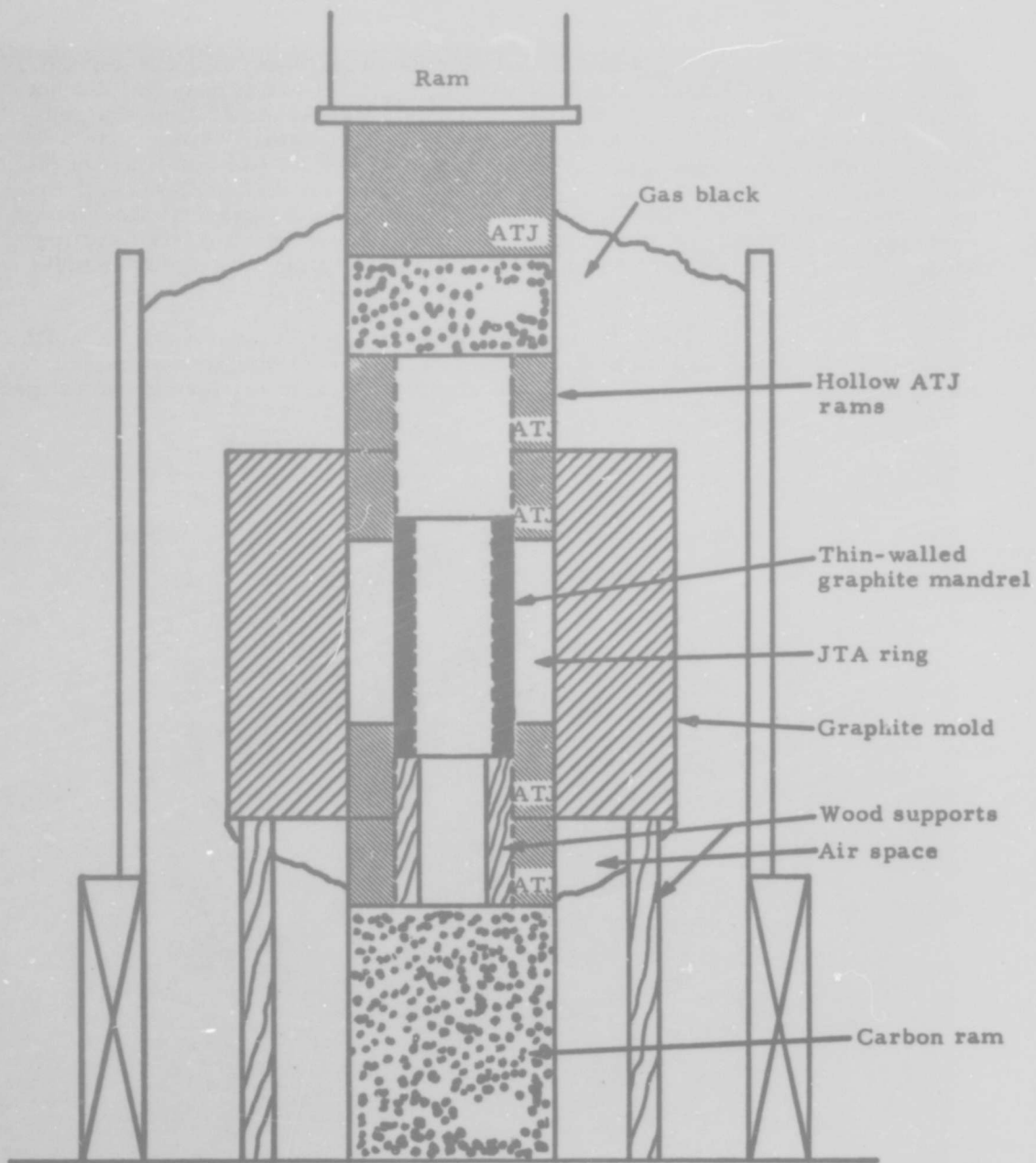


Figure 8. Hot-Pressing Assembly 14-in. Hollow JTA.

N-19962

D. Solid 29-in. o. d. Billets

Three full-scale 29-in. o. d. solid billets (15 in., 22 in., and 24 in. lengths) were processed with regular pitch bonded Grade JTA blend before the pitch effect on cracking was discovered. Changes in heating and cooling rates, greater insulation in the ram train, and variations in pressure application did not succeed in preventing numerous vertical cracks in these large pieces.

A fourth full-size billet (29-in. o. d. by 15 in. high) was hot-pressed with the modified Grade JTA blend. The manufacturing conditions for this billet follow.

1. Hot-Pressing Assembly

A 57-in. o. d. by 40-in. long RVA cylinder was machined so that the 29-in. i. d. had a straight section of 12 inches and a taper of 0.003 inch per inch for the remaining 28 inches. The mold was supported over the bottom ram train with six 2 x 4's as shown in Figure 9. The ram train was machined from 24-in. by 30-in. Grade GA carbon and 30-in. o. d. by 72-in. long Grade ATL graphite. The base, skid, placement of insulation, and retaining ring were the same as those described for the flat plate assembly. Figure 10 shows the lowering of the retaining ring over the 57-in. o. d. mold. Note the space for downward mold movement between the mold bottom and insulation. A schematic of the final assembly ready for firing is illustrated in Figure 11.

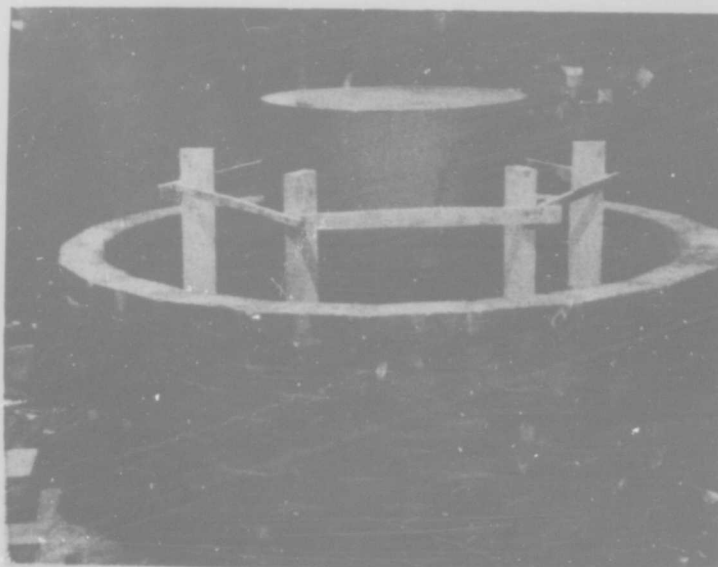


Figure 9. Placement of Wooden 2 x 4's Around the Bottom Ram Train to Support RVA Mold.

N-21128



Figure 10. Lowering Insulation Retaining Ring Over 57-in. o.d. Graphite Mold. JTA Blend is Placed in the Mold Cavity, the Top Ram Assembly Added, and Gas Black Insulation Added to the Top of the Retaining Ring.

N-21129

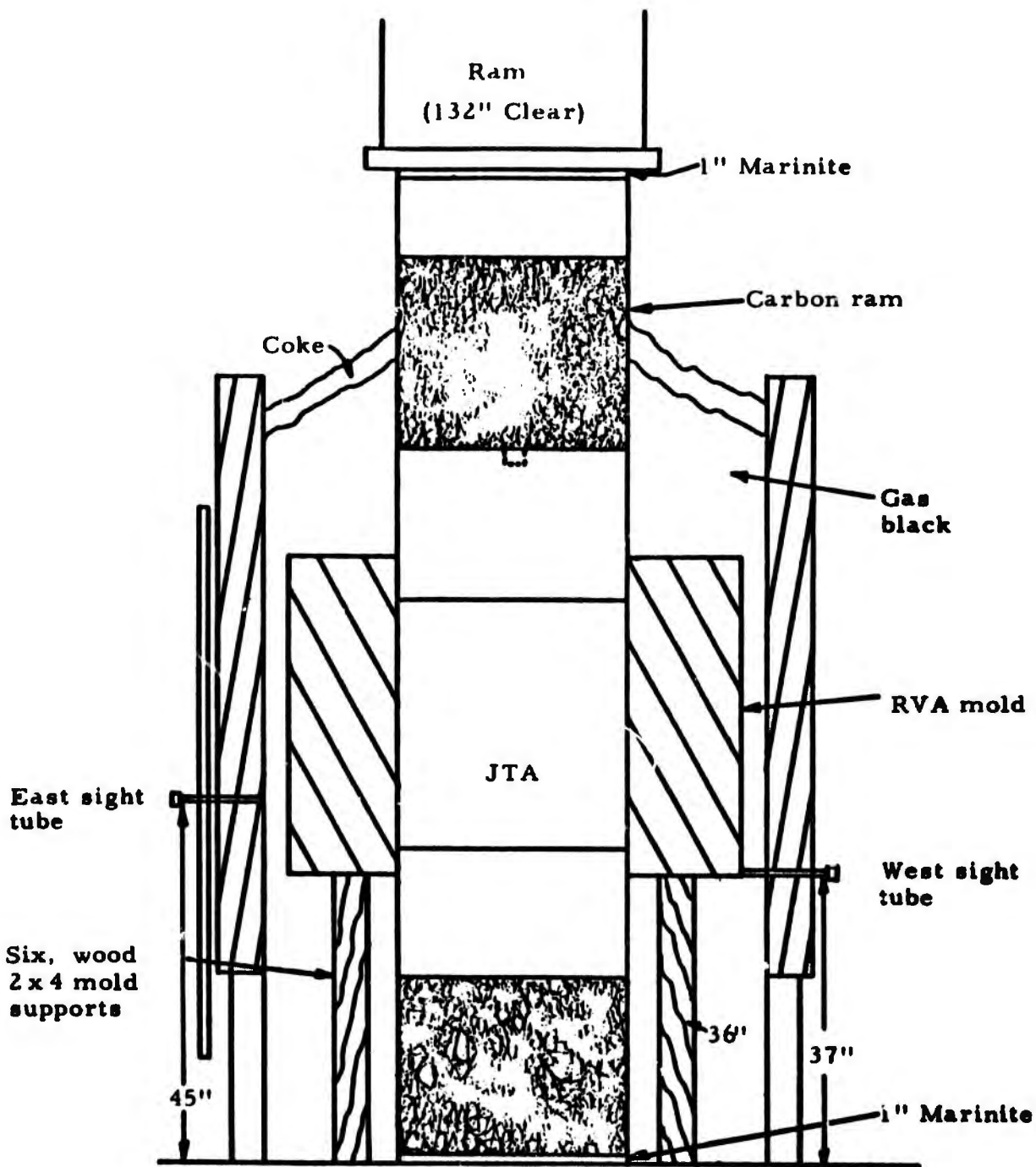


Figure 11. Position of Assembly Components at Beginning of Pressing 29-in. o. d. Solid Billet. N-20932

2. Firing

The firing plan called for raising the temperature to 2150°C and holding at pressure for 48 hours. The maximum allowable pressure on the mold (using the formula in Appendix A) was 2600 psi. Pressures of 3500-6000 psi are normally used in Grade JTA production. These higher pressures could not be attained because of the relatively thin mold walls. Although the hydraulic press could deliver 4000 psi to a 29-in. ram, no larger Grade RVA graphite is manufactured. Assuming that densification is a time-temperature function, we hoped to reach density by long hold times.

The actual firing conditions for this run are summarized in Figure 12. The total downward movement (slump) of the top ram was 20 15/16 inches. The large Grade RVA mold moved down 10 3/16 inches during this time, indicating almost perfect float molding conditions.

During removal of the billet from the mold, the Grade JTA moved freely about 6 inches and then stuck, splitting the mold. The long hold time at temperature apparently hot-worked the mold inner diameter into a slight barrel shape that restricted the billet. Tapers greater than 0.003 inch per inch may have prevented this difficulty.

The billet was 15 in. high, weighed 1090 pounds, and had a density of 3.02 g/cc. There were no visible flaws or cracks on the billet surface nor on any of the internal faces when a 5/8-in. thick slab was removed from the center of the billet for physical property samples (see Figure 21, Section V, Physical Properties).

X-ray examination of the 5/8-in. thick slab revealed broad areas of small density variations. Two small hair line areas of higher graphite flour concentration similar to those found in the 14-in. hollow cylinder were also found. The density variations are of the order of 2-3% based on estimates made from the X-ray negative. Again, these variations are believed due to mix handling after blending.

SECTION IV

PHASE II - PRESS-TO-SHAPE

A. Grade JTA Process Variable Study

1. Mold-Fill Ratio by Cold-Pressing

The process variable studies were undertaken to provide useful information to aid in the Phase I part of the program being carried out at Lawrenceburg. A series of cold-pressing experiments with regular Grade JTA material was made to determine the mold-fill ratio. Three-inch diameter billets were room temperature molded at six pressures ranging from 600-2000 psi. Results of the cold-pressing experiments are illustrated in Figure 13. A maximum density of 1.7 g/cc was measured at the highest pressure of 2000 psi representing 52 percent of theoretical density.

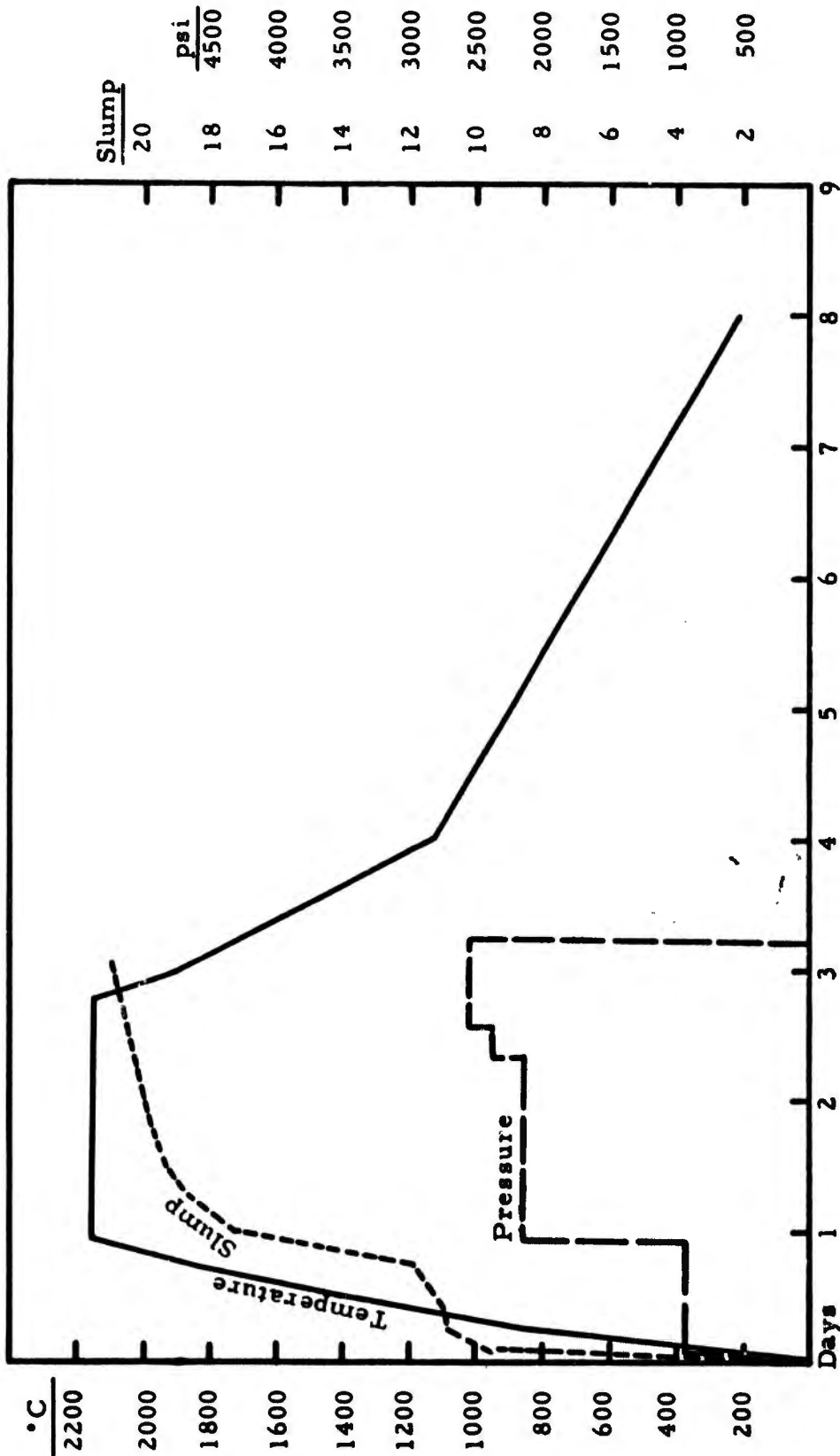


Figure 12. Firing Data for 29-in. o.d. Solid JTA Billet.
N-20933

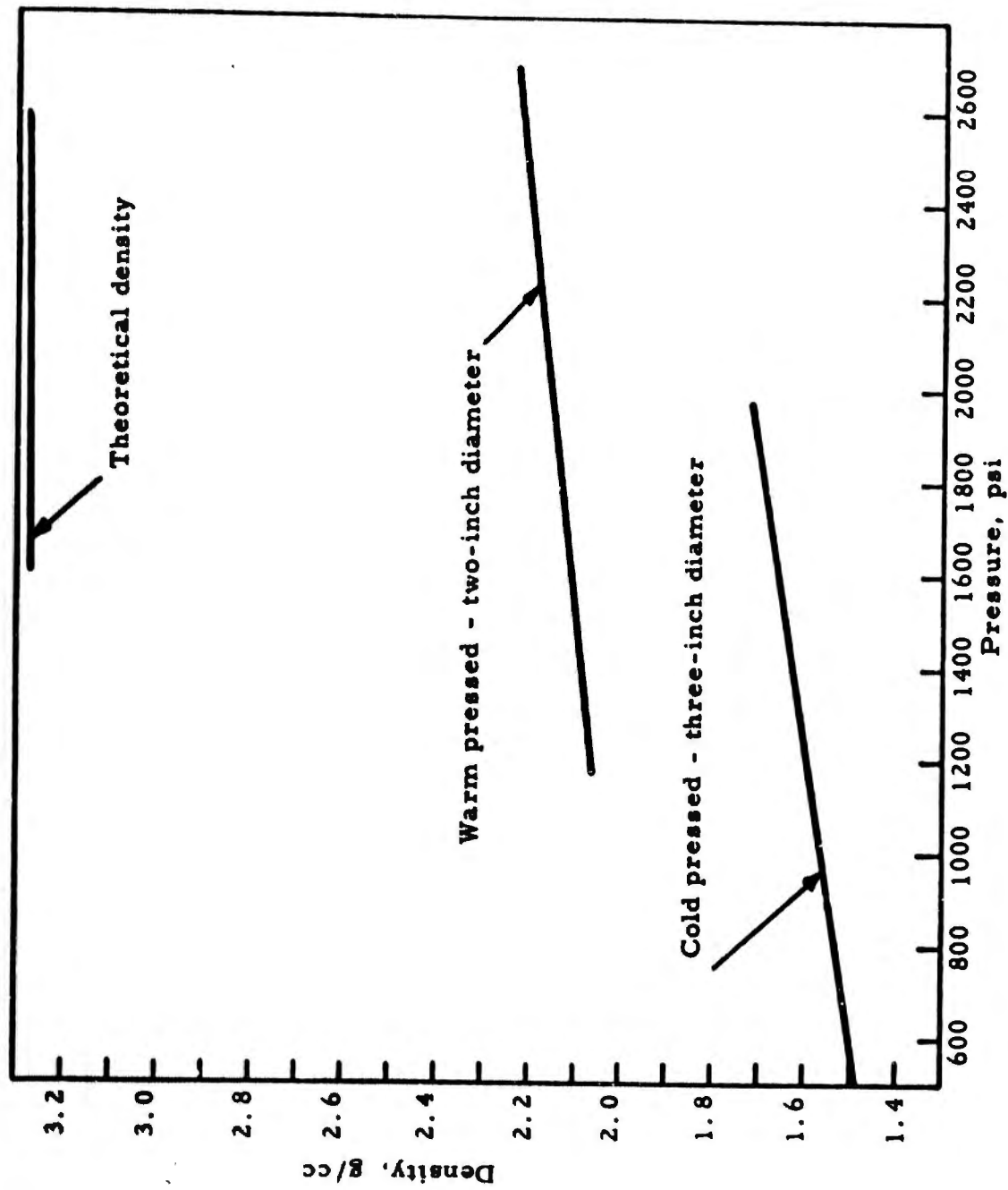


Figure 13. Density Versus Forming Pressure Regular Grade JTA.
N-16886

2. Mold-Fill Ratio by Warm-Pressing

Warm-pressing regular Grade JTA material above the melting point of the pitch additive proved to be an excellent method of preparing preforms. A series of warm-pressing experiments with 2-in. diameter billets was made to determine the mold-fill ratio, and the results have been compared with the mold-fill ratio obtained by cold-pressing.

Warm-pressing temperatures were measured with a thermocouple placed near the center of the mold cavity. The blended regular Grade JTA mix was charged in the mold cavity, hand tamped, and the entire mold assembly placed in a large oven. When the thermocouple reached 250°C, the assembly was transferred from the oven to the press and pressure applied. Pressure was maintained until the mold temperature was below 170°C, and all the pressure was removed when the mold temperature cooled to 100°C. Results are summarized in Figure 13.

B. Press-to-Shape Grade JTA

1. Warm-Pressed Shapes

Simple and complicated Grade JTA shapes were warm-pressed at 245°C in Grade ATJ graphite dies with regular pitch-bonded blend. Figure 14 illustrates some of the shapes prepared by warm-pressing. The strength of the preforms after pressing is more than adequate for normal handling and also sufficient for machining if necessary. Using the procedures outlined in Section 2 (above), densities ranging from 65-71 percent of theoretical were achieved. Attempts were then made to hot-press these preforms into acceptable density Grade JTA.

2. Hot-Pressing Grade JTA Preforms

A 3-in. diameter warm-pressed preform with a density of 2.11 g/cc was hot-pressed to a bulk density of 3.08 g/cc. Test bars were prepared from the hot-pressed billet both with- and against-the-grain. Results indicated that physical properties of hot-pressed preforms are equal to or better than Grade JTA prepared by standard hot-pressing techniques.

3. Hot-Pressing Grade JTA Blend-to-Shape

Male and female rams, shown in Figure 15, were machined from Grade ATJ graphite. Grade JTA blend was placed in the trough-shaped die and hot-pressed. An initial pressure of 2300 psi was applied and maintained until the mold temperature reached 1800°C; at this time, the maximum pressure of 3000 psi was applied. The specimen was held for 30 minutes at a temperature of $2240 \pm 10^\circ\text{C}$. Maximum pressure was maintained during cooling to a temperature of 1700°C, at which time the pressure was released.

The hot-pressed shape had a bulk density of 2.9 g/cc and is shown in Figure 16.

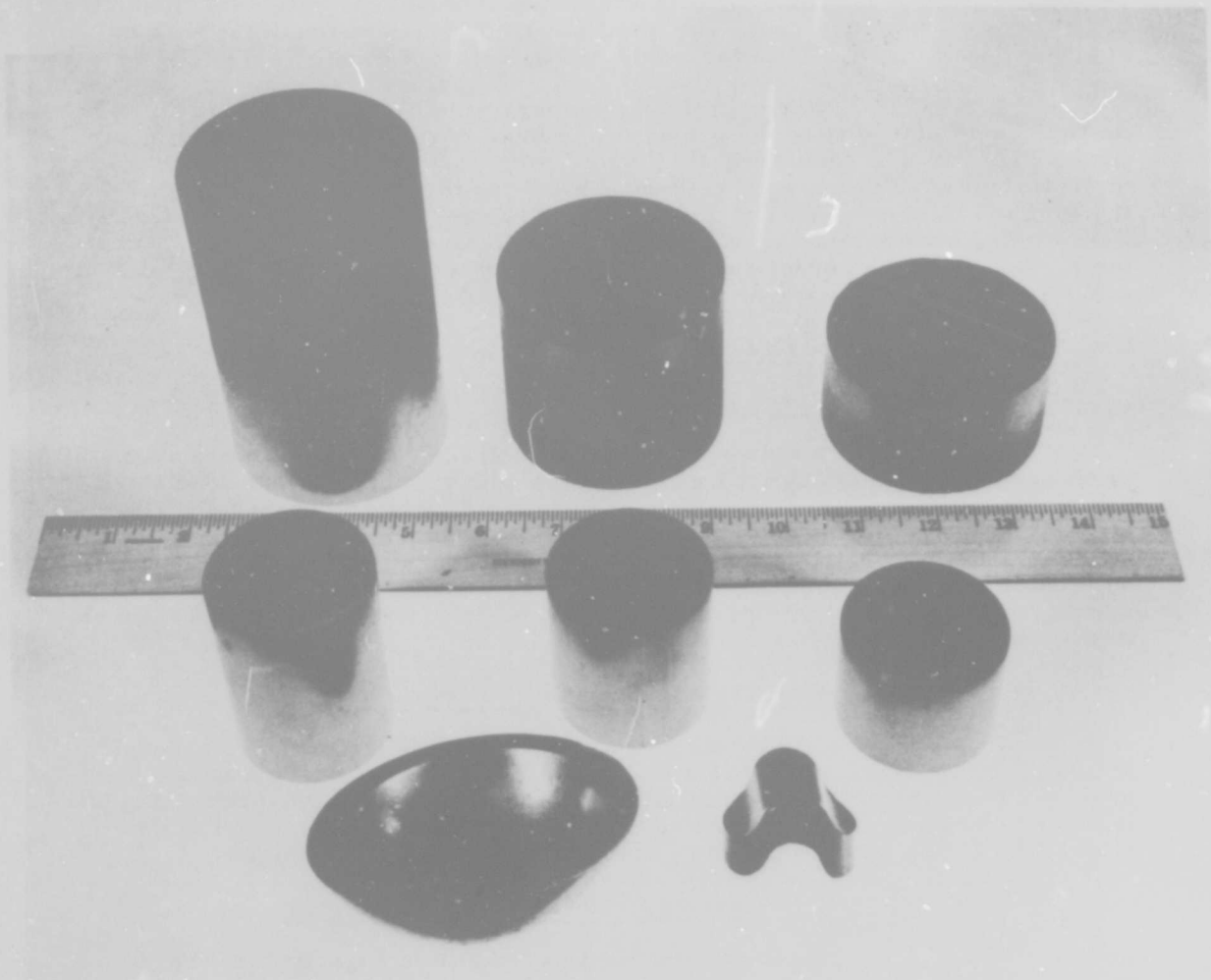


Figure 14. Grade JTA Shapes Prepared by Warm-Pressing.

N-11512

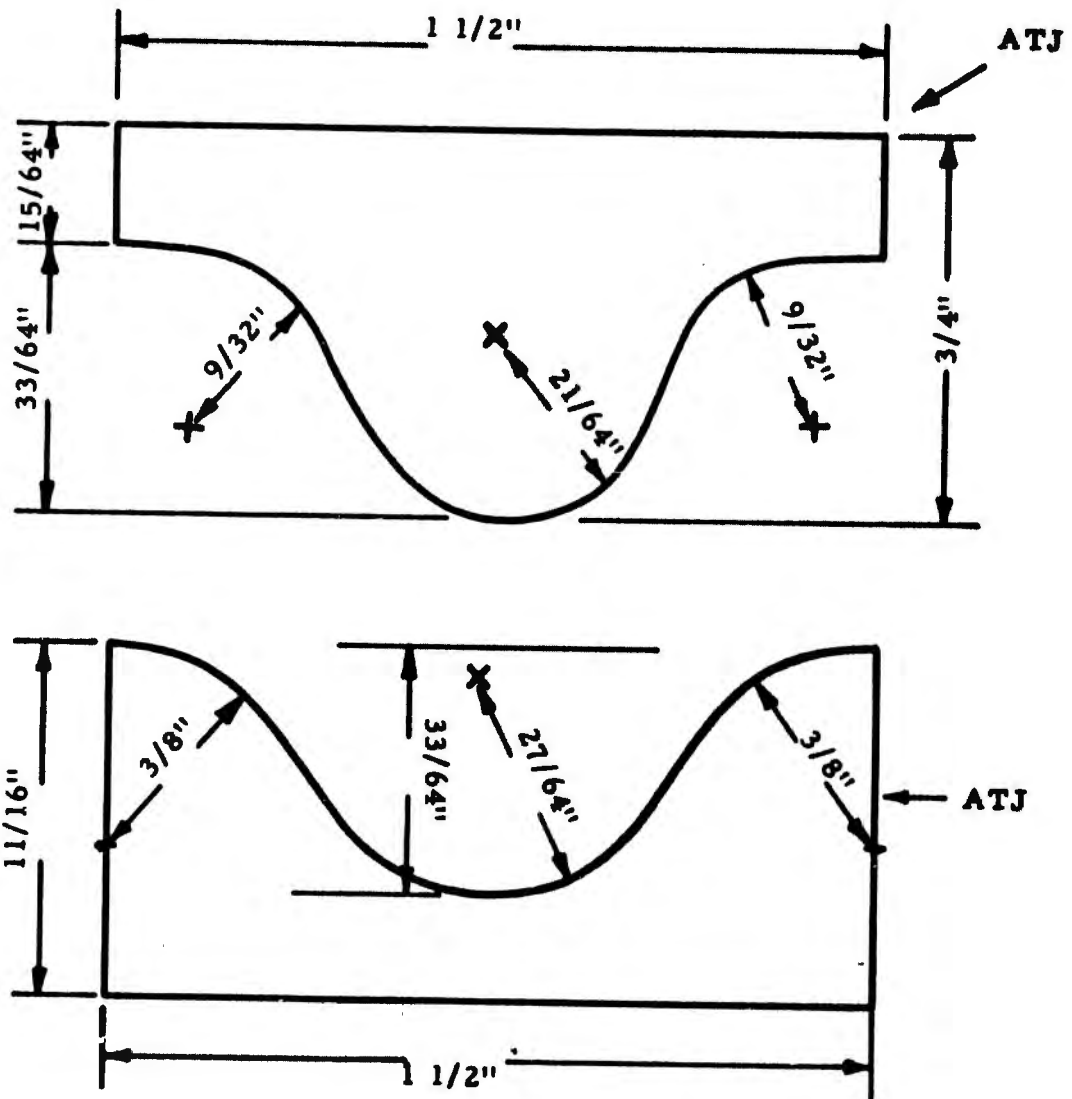


Figure 15. Male and Female Rams for Hot-Pressing Grade JTA to Shape.

N-16852



Figure 16. Hot-Pressed to Shape JTA.

N-11513

C. Grade JTA Bending

Attempts to bend Grade JTA graphite composite material by reheating the sample to a temperature near the eutectic point and applying bending forces were unsuccessful. Grade JTA samples 1 3/4 in. by 1 3/4 in. by 1 1/4 in. were first prepared by hot-pressing to a bulk density greater than 3.0 g/cc. In each bending trial, one of the Grade JTA samples was placed in a Grade ATJ graphite mold and positioned between male and female graphite plungers. A 1/4-in. nose radius on the male plunger and half-angles of 30° provided the bending moment for the sample.

The assembly was resistance heated in a graphite tube furnace at a rate of 740°C per hour. A minimum amount of pressure was applied to the specimen prior to heating--just enough to hold the specimen between the rams.

Expansion and contraction of the system during heating was measured with a dilatometer. Expansion of the graphite components occurred during the heating until a temperature of approximately 2200°C was reached. After a one-half hour hold at temperature, pressure was increased slowly.

Three bending temperatures slightly below the composite eutectic temperature of 2260°C were selected for the trials. The first attempt at bending prepressed Grade JTA was made at a temperature of $2220 \pm 10^\circ\text{C}$, 40°C below the eutectic temperature. The specimen fractured as pressure was applied. Very little plasticity was observed in the sample at this temperature. The temperature of the second bending experiment was increased to $2255 \pm 10^\circ\text{C}$. Fracture occurred again as pressure was applied and very little plasticity was observed. Liquid runout observed in the fractured specimen is shown in Figure 17. The runout material indicates that the Grade JTA composite eutectic temperature was exceeded.



Figure 17. Fractured Bend Specimen Depicting Runout at a Maximum Temperature of $2255 \pm 10^\circ\text{C}$.

N-17533

The bending experiments at 2220°C and 2255°C were made with the Grade JTA samples positioned so that the bending force was applied in the with-grain direction. To assure that sample fracture was not related to grain direction, an additional bending experiment was performed at a temperature of 2245 ± 10°C with the bending force applied in the against-grain direction. Fracture occurred as pressure was applied, and very little plasticity was observed prior to failure. Liquid runoff from the specimen was not observed during this trial which indicates that the maximum temperature in the sample was slightly below the composite eutectic temperature.

Based on the results of the three bending experiments, the investigation of this method for Grade JTA fabrication was discontinued.

D. Leading Edge Fabrication

1. Design

The Air Force Technical Contract Monitor was consulted and a leading edge design for scale-up was suggested. The design of the full-size leading edge was a split cylinder with an end radius of 2 inches, a length of 8 inches, and a wall thickness of approximately 3/8 inch.

2. Warm-Pressing

A mold assembly prepared from Grade ATJ graphite was used to warm-press the full-size split cylinders of Grade JTA. During warm-pressing experiments, small cracks were noted in some of the warm-pressed leading edges. These cracks were eliminated by lowering the warm-pressing temperature from 250°C to 180°C, the lower temperature reduced the differential contraction between the JTA material and the male mandrel. The warm-pressed leading edges had sufficient strength for normal handling and could be loaded in the hot-pressing mold without difficulty. A warm-pressed split cylinder leading edge is shown in Figure 18.

3. Hot-Pressing in a Confined Mold Assembly

The mold assembly for hot-pressing, also prepared from Grade ATJ graphite, consisted of three parts: 1) a cylindrical 14 1/2-in. outside diameter mold with a 4-in. by 8-in. rectangular cavity, 2) a 4-in. by 8-in. rectangular ram with an end radius of 1 5/8 in., and 3) a corresponding female base with a 2-in. end radius.

The mold assembly was centered in a series of ceramic rings on a graphite pedestal and packed with thermax insulation powder. The hot-pressing assembly was heated inductively, and pressure was provided by a 117-ton capacity hydraulic press.

The first leading edge was heated with only the weight of the upper ram acting on the Grade JTA preform. At a temperature of 1800°C, the pressure was increased in increments of 250 psi. A maximum temperature of 2200 ± 30°C was maintained as pressure was being increased. Ram travel was measured in millimeters, and a predetermined total travel was calculated that would yield the maximum leading edge density. The predetermined total travel was obtained after a holding period of 30 minutes at

2200 \pm 30°C and a maximum pressure of 1750 psi. The hot-pressing was discontinued at this point to permit evaluation and also as a safety precaution to prevent damage to the mold assembly. During cooling, maximum pressure was maintained until the temperature fell below 1700°C; then all pressure was removed.

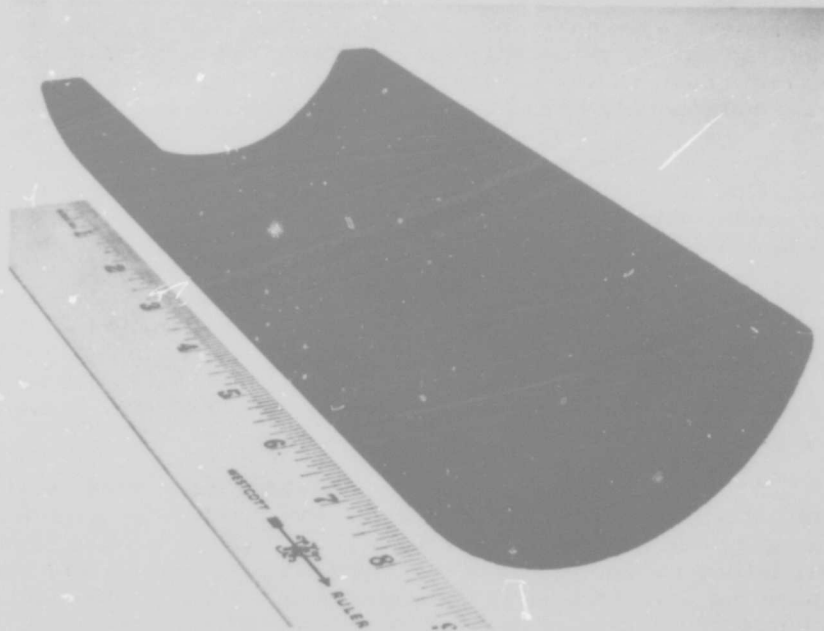


Figure 18. Split Cylinder Leading Edge After Warm-Pressing.
N-17532

The general appearance of the leading edge was good, and no cracks or flaws were observed. Bulk density, determined by water immersion techniques, was 2.5 g/cc. The resulting density of the Grade JTA leading edge indicated that higher pressures would be required to obtain densities in excess of 3.0 g/cc. Examination of the leading edge has shown that the predetermined total travel was not obtained. The discrepancy between measured total travel and actual total travel was related to expansion and densification of the graphite components in the assembly.

A second Grade JTA warm-pressed leading edge was hot-pressed, and the same process procedures were used. The maximum pressing temperature was 2200 \pm 30°C, and the pressure was increased from 1750 psi to 2575 psi. The leading edge was held at maximum temperature and pressure for a period of 30 minutes.

No cracks were observed in the leading edge after hot-pressing and the mold assembly was in good condition. A bulk density of 2.6 g/cc was measured on the Grade JTA leading edge.

A third pressing was prepared, and pressing parameters were selected at 2250°C and 4500 psi. Unfortunately, at a temperature of 2240°C and a pressure of 3900 psi, the mold assembly failed. Since all graphite components of the assembly, the Grade JTA leading edge, and the pedestal fractured severely, it could not be determined where the initial failure occurred. Segments of the fractured leading edge were retrieved and an average bulk density of 2.9 g/cc was measured on four pieces.

A new graphite mold assembly was prepared. The applied load during hot-pressing was reduced from 90 tons to 78 tons in an attempt to prevent further mold breakage. The load reduction was made by changing the length of the leading edge shape from 8 inches to 6 inches.

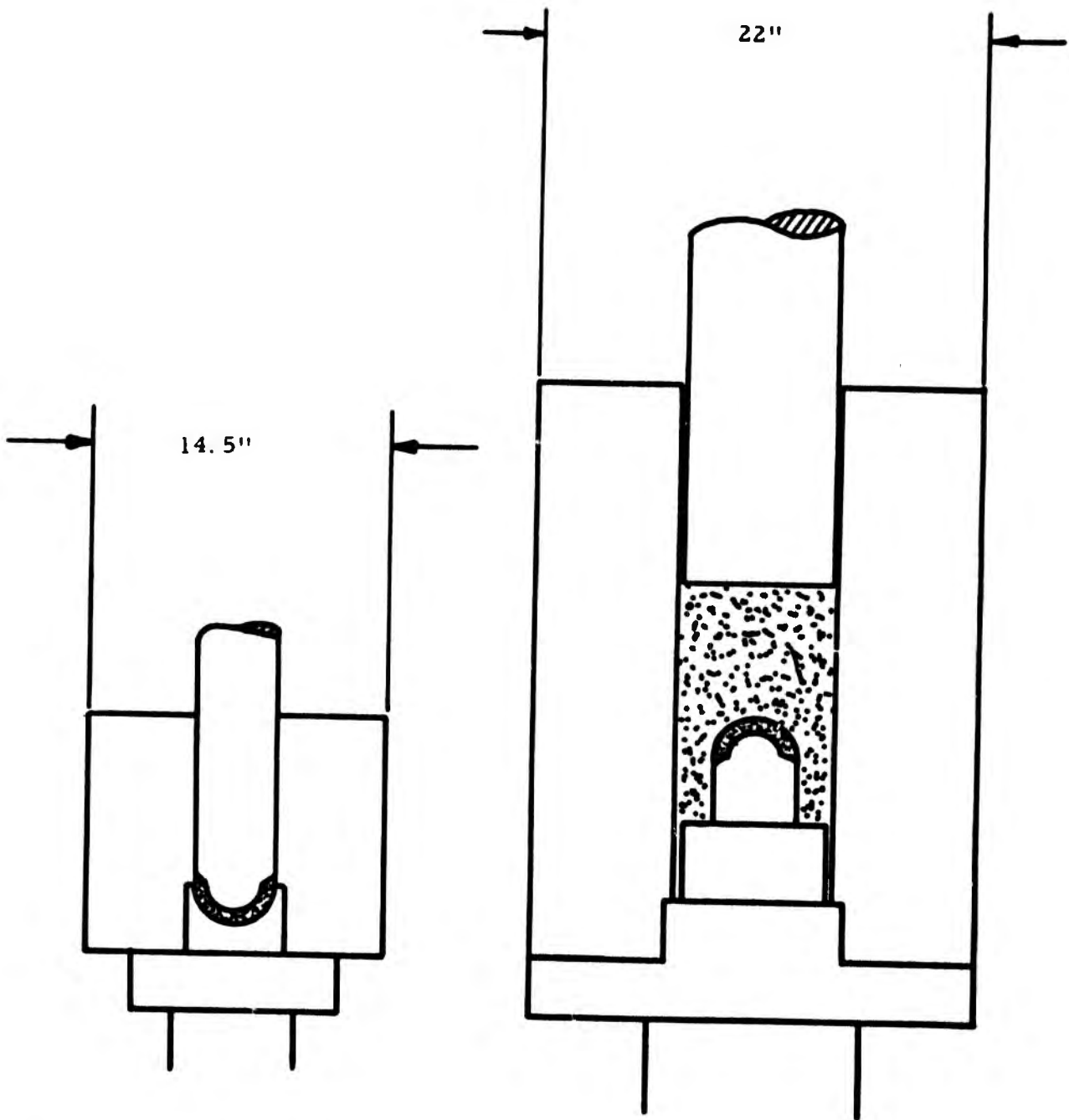
This time Grade JTA blend was hand pressed in the mold. Thus, the hot-pressing procedure was modified slightly to combine warm-pressing and hot-pressing in a single operation. An initial pressure of 1000 psi was applied to the blend prior to heating, and was increased gradually after a temperature of 1800°C was reached. At a temperature of 1900°C and a pressure of 3200 psi, the mold assembly failed.

Once again it was impossible to determine exactly which component failed first; however, the failures were related to the female base section of the assembly. The base section adjacent to the leading edge nose was evidently failing in tension. The tensile strength of Grade ATJ graphite used to prepare the base section was being exceeded when the vertical pressure exceeded 3000 psi.

So that additional failures in the mold assemblies would not occur, the female base section was eliminated. Warm-pressed preforms were again made and inserted and supported on the male mandrel. Pressure was applied by using gas black between the flat plunger and the Grade JTA preform.

4. Isostatic Hot-Pressing - 600-Ton Press

Hot-pressing trials were now shifted from the 117-ton capacity press to a 600-ton press, so that a thicker walled graphite mold could be utilized to better resist the high forming pressures. The new mold was 22-in. o. d. by 8-in. i. d. The large inner diameter allowed the male mandrel to be unrestricted by the mold wall and thus, help eliminate mold breakage. Figure 19 shows a schematic drawing of the hot-pressing assembly for the restricted mandrel (117-ton press) and unrestricted mandrel (600-ton press). The female base section employed in the early trials was eliminated. Pressure was applied to the warm-pressed preform using gas black carbon as the pressing media. The first hot-pressing trial using the assembly (shown in Figure 25b) was made at a pressure of 5000 psi and a mold outer diameter temperature of 2100°C. Maximum pressure was maintained during cooling to 1700°C, at which time the pressure was released. Examination of the Grade JTA leading edge shape after hot-pressing showed that the eutectic temperature (2260°C) was exceeded during pressing. The temperature correction between the mold wall and the leading edge in the cavity was evidently greater than 160°C.



(a) Previously Used Assembly
in 117-Ton Press

(b) New Assembly for 600-Ton Press

Figure 19. Hot-Pressing Assemblies for Press-to-Shape Leading Edge Trials.

N-19526

In the second hot-pressing, the maximum temperature was reduced from an observed temperature of 2100°C to 2000°C. At maximum pressure of 5000 psi and a temperature of 2000°C, the mold failed. The cause of the mold failure was believed to be fatigue, since the mold had been used several times before for other hot-pressing applications.

The leading edge was cracked but the mandrel was not damaged during the failure. No melting was observed in the Grade JTA leading edge, indicating that the eutectic temperature was not exceeded at 2000°C.

Another hot-pressing was made at 4000 psi pressure and 2050°C (observed) temperature. Small amounts of liquid runout were observed in the leading edge. A water immersion density of 2.5 g/cc indicated that higher pressures would be required to achieve a density in excess of 3.0 g/cc.

In the next hot-pressing, the pressure was increased from 4000 psi to 5200 psi and the maximum temperature was held at 2020°C. A 15-minute hold time at maximum temperature and pressure was used to reduce the possibility of exceeding the eutectic temperature. The appearance of the hot-pressed leading edge was good and no cracks or flaws were observed. A water immersion density of only 2.4 g/cc suggests that still higher pressures are required to achieve a 3.0 g/cc density.

Two minor modifications were made in the hot-pressing procedure for the last 6-in. long leading edge. The graphite mandrel supporting Grade JTA preform was raised 6 inches higher in the mold from that used in previous pressings to reduce any bridging effect which may occur in the gas black pressing medium. The second modification was the addition of "Grafoil" foam between the mandrel and mold wall; this change was made to eliminate or reduce high stress concentrations at the square corners and thus reduce the possibility of mold breakage.

Previous hot-pressing procedures were duplicated in that the pressure was increased gradually when the mold temperature exceeded 1800°C. A maximum pressure of 7000 psi was applied at the final pressing temperature of 2020°C. Full pressure was maintained for 30 minutes, and the mold temperature was cycled between 1990°C and 2020°C. The leading edge was cooled under pressure to a temperature of 1700°C, at which point all pressure was released.

When cool, the leading edge was removed from the mold and was found to be broken in several pieces. No metal runout was observed in the mold, indicating that the eutectic temperature was not exceeded. However, the leading edge evidently broke in the early stages of pressing. The top, middle section of the leading edge was missing, indicating that, as the pressure was increased, the broken leading edge was spread farther apart.

The cross-section of the broken leading edge had a highly polished appearance, a condition usually observed on the outside surface of previously hot-pressed edges or at the leading edge-gas black interface.

A density of 2.72 g/cc was measured on a fractured piece of the leading edge. It is difficult to judge if the increased pressure would have been sufficient to produce a high-density leading edge.

SECTION V PHYSICAL PROPERTIES

The 14-in. solid billet, the 30-in. by 15-in. by 3-in. plate, and the 29-in. o. d. by 15-in. high solid billet, hot-pressed with modified Grade JTA blend, were diamond sawed in a manner to yield physical property samples representative of the entire billet. Bulk density, sonic modulus, and flexural strength were run on a sufficient number of samples to calculate meaningful standard deviations. Sample size was 1/2-inch square and varied from 3 inches to 5 inches long depending on location. Side faces of the samples were ground true and parallel with an aluminum oxide wheel on a horizontal surface grinder. End faces were trued with the diamond saw and not ground.

Bulk density was calculated from volumes measured to the nearest 0.001 cm with hand micrometers, and weights were determined on gravimetric balances to the nearest 0.01 gram.

Young's modulus was based upon sample natural frequency determined by the sonic method.

Flexural strengths were determined from four-point loading with standard ASTM procedures. No corrections were made for frictional forces at the loading and supporting edges.

Compressive strength, tensile strength, thermal expansion, and thermal conductivity tests were run on selected samples randomly cut from the whole billet.

Compressive strength was determined from 1-in. o. d. by 1-in. high cylinders, crushed between parallel steel plates. No potting compound was used on the sample faces.

Thermal conductivity testing was run on 0.500 ± .002-in. o. d. by 3-in. long cylinders by the Meers Method, using Armco Steel as the standard.

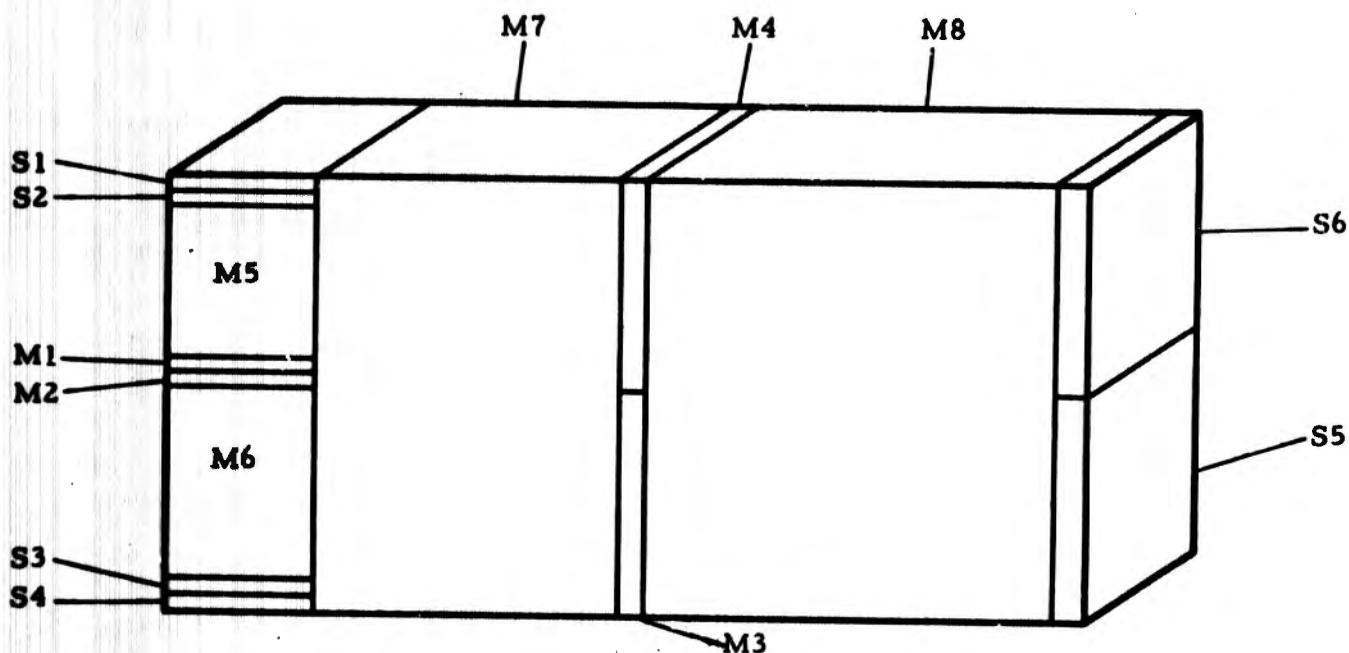
Tensile strength was run on "dog bones" machined from 1 1/8-in. o. d. by 5 1/8-in. long cylinders, per ASTM 565-65T.

Coefficient of thermal expansion was run on 1/4-in. by 1/4-in. by 2 1/2-in. long specimens to 1600°C in a graphite tube furnace. The free ends of the samples were continuously measured with optical micrometers. The low temperature CTE samples were 0.3 in. by 0.75 in. by 6 in. long. They were heated by steam from 30°C to 100°C and measurements taken by an optical lever technique.

A. Large Flat Plate

The 30-in. by 15-in. by 3-in. thick flat plate was the highest density, full scale Grade JTA material made under this program. Its large surface area-to-volume ratio allowed easy densification. Figure 20 schematically shows the sample plan of this piece. Analysis of the density data shows evidence of a slight "skin effect." A small improvement in with-grain flexural strength and a drop in density variations occur if the data are recalculated eliminating the 1/2 in. sample which had been taken from the surface. This difference is not particularly surprising and its magnitude is summarized in Table II. Since the differences in properties resulting from discounting the first 1/2-in. samples was slight, it is doubtful that this "skin effect" could be much deeper than 3/32 of an inch.

Overall physical property uniformity in this large plate is considered good. Based on standard deviations, this uniformity is equal to, or better than, data reported previously on 5-in. o. d. commercial blanks. No visual flaws were apparent on any of the cut surfaces. There were no very-low-strength samples which would have indicated hidden flaws.



S1, M1, S4, M4, S5 - cut into 1/2" x 1/2" x 3"-5" for with-grain samples
S2, M2, S3, M3, S6 - cut into 1/2" x 1/2" x 3"-5" for against-grain samples
M5, M6 - cut for CTE, K, compressive strength, and tensile strength
M7, M8 - radiographed for flaws

Figure 20. Sampling of 30-in. by 15-in. by 4-in. Thick Modified JTA Plate.
N-20934

TABLE II

Modified JTA 30-in. by 15-in. by 3-in. Plate
Room Temperature Physical Properties

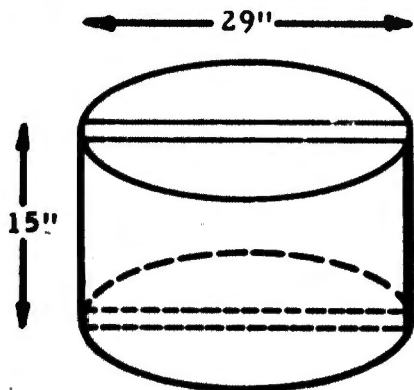
	All Samples			Without Samples From 1/2" Outside Skin						
	\bar{X}	Min.	Max.	\bar{X}	Min.	Max.				
Bulk density, g/cc	3.16	3.11	3.22	.019	86	3.17	3.12	3.20	.013	44
Young's modulus, 10 ⁶ psi	17.1	12.2	21.1	2.6	33	18.0	14.9	21.0	2.2	15
with-grain	8.4	6.3	10.8	1.3	53	8.2	6.3	10.8	1.4	29
against-grain										
Flexural strength, psi	18,230	15,300	20,980	1,530	33	18,721	15,540	20,980	1,620	12
with-grain	9,380	7,050	10,750	820	53	9,390	7,980	10,680	680	29
against-grain										
Compressive strength, psi	34,010	29,160	39,320	--	6	--	--	--	--	--
with-grain	33,170	23,020	36,350	--	6	--	--	--	--	--
against-grain										
Tensile strength, psi	15,860	15,410	16,490	--	6	--	--	--	--	--
with-grain	--	--	--	--	--	--	--	--	--	--
against-grain										
Thermal expansion, 10 ⁻⁷ / °C (1)	59	58	62	--	6	--	--	--	--	--
with-grain	69	67	72	--	6	--	--	--	--	--
against-grain										
Thermal conductivity, BTU hr ⁻¹ Ft ⁻¹ °F ⁻¹	80	71	97	--	6	--	--	--	--	--
with-grain	45	41	54	--	6	--	--	--	--	--
against-grain										

(1) 25°C-1600°C

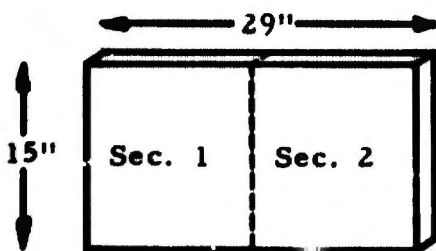
B. Solid 29-in. o. d. Billet

The overall density of this large, 1090 pound hot-pressing was very slightly higher than minimum acceptable value. Calculations of the allowable forming pressure, based on mold strength and dimensions, allowed only 2600 psi on the billet. This experiment is the first time that any billet of Grade JTA has been brought to acceptable density with such a low pressure.

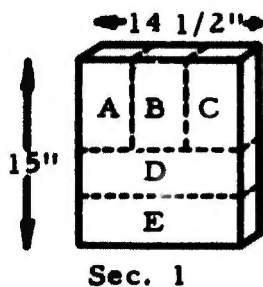
A 5/8-in. thick plate was cut from the center of the billet. This plate, 29 in. wide by 15 in. high, was cut in half. One half was diamond sawed into 1/2-in. by 1/2-in. samples for a complete density, flexural, and sonic modulus, profile. The other half was randomly sampled for CTE, thermal conductivity, and tensile strength (see Figure 21).



Remove 5/8-in. thick by 29-in. by 15-in. plate from center of billet



The 5/8-in. center plate was cut into two equal sections



Section 1 was completely cut into 1/2-in. by 1/2-in. by 3-in. to 5-in. samples. Subsections A, B, C were cut with-grain; subsections D, E were cut against-grain

Section 2 was radiographed and cut into CTE, thermal conductivity, and tensile samples

Figure 21. Sampling of 29-in. o. d. Modified JTA Billet.
N-20935

Again, uniformity of physical properties, based on standard deviations, was equal to or better than previously reported data on 5-in. billets. A slight "skin effect" also occurred in this large billet. The higher density samples were very often in the outer 1/2 inch of the end faces and side. However, when the data were recalculated by removing these outer samples, no significant improvement in uniformity was noted (see Table III).

No visible flaws were apparent on any of the cut surfaces of this billet, and no very low strength samples were encountered which would indicate hidden flaws.

C. Solid 14-in. o. d. Grade JTA Billet

The first solid 14 inch billet made with the modified Grade JTA formula was sampled and some physical properties determined. These are summarized in Table IV. No large sampling program was undertaken for this billet, and, consequently, the standard deviations may not be representative of the piece. Again, no flaws, visible or hidden, were detected.

D. Nondestructive Testing

1. Physical Properties Versus Density

Like most hot-pressed ceramic bodies, the physical properties of Grade JTA are dependent upon porosity. Figures 22 and 23 illustrate the apparent straight-line effect of density on Young's modulus and flexural strength for modified Grade JTA. Density dependence for regular Grade JTA has been previously reported.⁽¹⁾ The uniformity of these large billets and agreement of data indicate that quite accurate physical properties can be predicted from bulk densities.

2. Ultrasonic Testing of Grade JTA

A number of Grade JTA billets have been examined by ultrasonic techniques. The method is rapid, nondestructive, and very sensitive to small inconsistencies in structure. Two ultrasonic measurements, velocity and attenuation coefficient, are in common use. Two 14-in. o. d. by 7-in. regular Grade JTA solid billets were ultrasonically scanned and then cut into 1-in. by 1-in. by 7-in. samples at the scan sites. Density and Young's modulus tests were run on the samples and compared with the velocity and attenuation values (see Figures 24 and 25).

The attenuation coefficient values followed the apparent density and the sonic modulus values except near the billet edges. The sound velocity measurements exhibited wide scatter and did not appear to be a useful measure of billet quality.

In other billets and plates, density differences of 2-3%, which were revealed by X-rays, were also detected with the ultrasonic probe.

⁽¹⁾ Integrated Research on Carbon Composite Materials, AFML-TR-66-310, Part II, Union Carbide Corporation, December, 1967.

TABLE III

Modified JTA 29-in. o. d. by 15 in. High Billet
Room Temperature Physical Properties

	All Samples			Without Samples From 5/8" Outside Skin				
	\bar{X}	Min.	Max.	\bar{X}	Min.	Max.		
Bulk Density, g/cc	3.01	2.98	3.05	3.01	2.98	3.05	.017	56
Young's modulus, 10 ⁶ psi								
with-grain	8.3	7.1	10.1	8.3	7.1	9.9	0.9	24
against-grain	4.1	3.3	5.3	4.1	3.3	5.1	0.5	32
Flexural strength, psi								
with-grain	11,610	10,240	13,110	11,610	10,240	13,110	875	24
against-grain	7,020	5,630	9,430	6,880	5,630	8,310	730	32
Compressive strength, psi								
with-grain	25,600	20,450	29,210	--	--	--	--	--
against-grain	24,660	19,300	28,580	--	--	--	--	--
Tensile strength, psi								
with-grain	6,980	4,110	8,530	--	--	--	--	--
against-grain	4,810	4,440	5,390	--	--	--	--	--
Thermal expansion, 10 ⁻⁷ /°C (1)								
with-grain	42	41	42	--	--	--	--	--
against-grain	52	52	52	--	--	--	--	--
Thermal conductivity, BTU hr ⁻¹ Ft ⁻¹ °F ⁻¹								
with-grain	55	49	61	--	--	--	--	--
against-grain	47	--	--	--	--	--	--	--

(1) 30°C-100°C

TABLE IV
Modified JTA Piece 14-15 Room Temperature Physical Properties

	With-Grain				Against-Grain					
	\bar{X}	Max.	Min.	σ	n	\bar{X}	Max.	Min.	σ	n
Bulk density, g/cc	3.06	3.09	3.02	.018	20	--	--	--	--	--
Young's modulus, 10 ⁶ psi	11.4	12.3	10.5	.45	9	5.5	6.6	5.0	.45	11
Flexural strength, psi	14,000	15,900	11,500	455	9	7,300	7,800	6,550	420	11
Compressive strength, psi	21,500	23,310	19,720	--	3	18,840	20,830	15,440	--	3

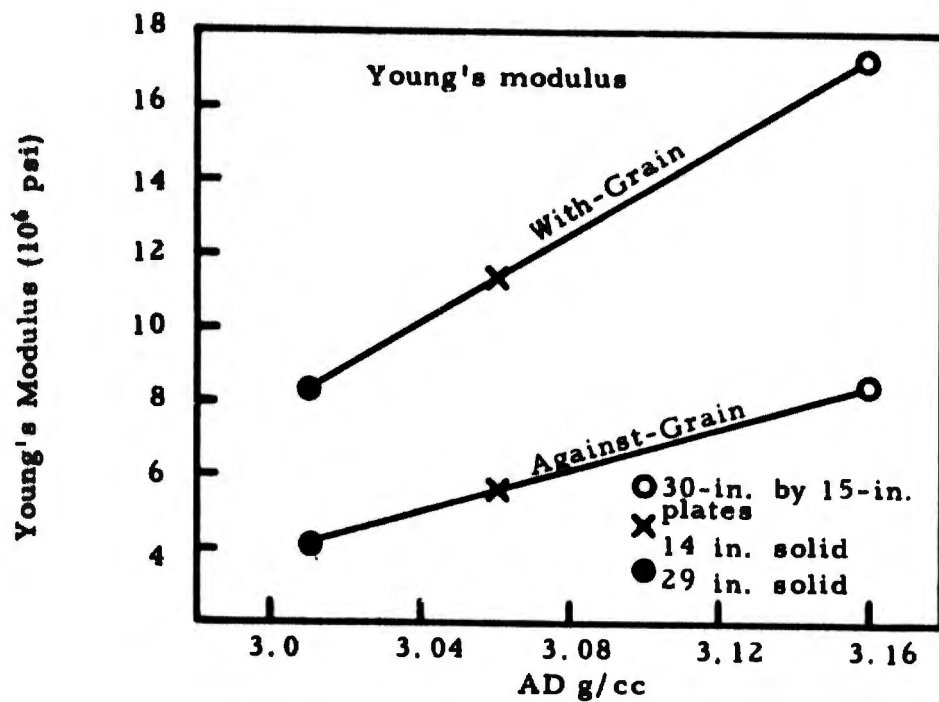


Figure 22. Dependence of Young's Modulus on Bulk Density. N-21196

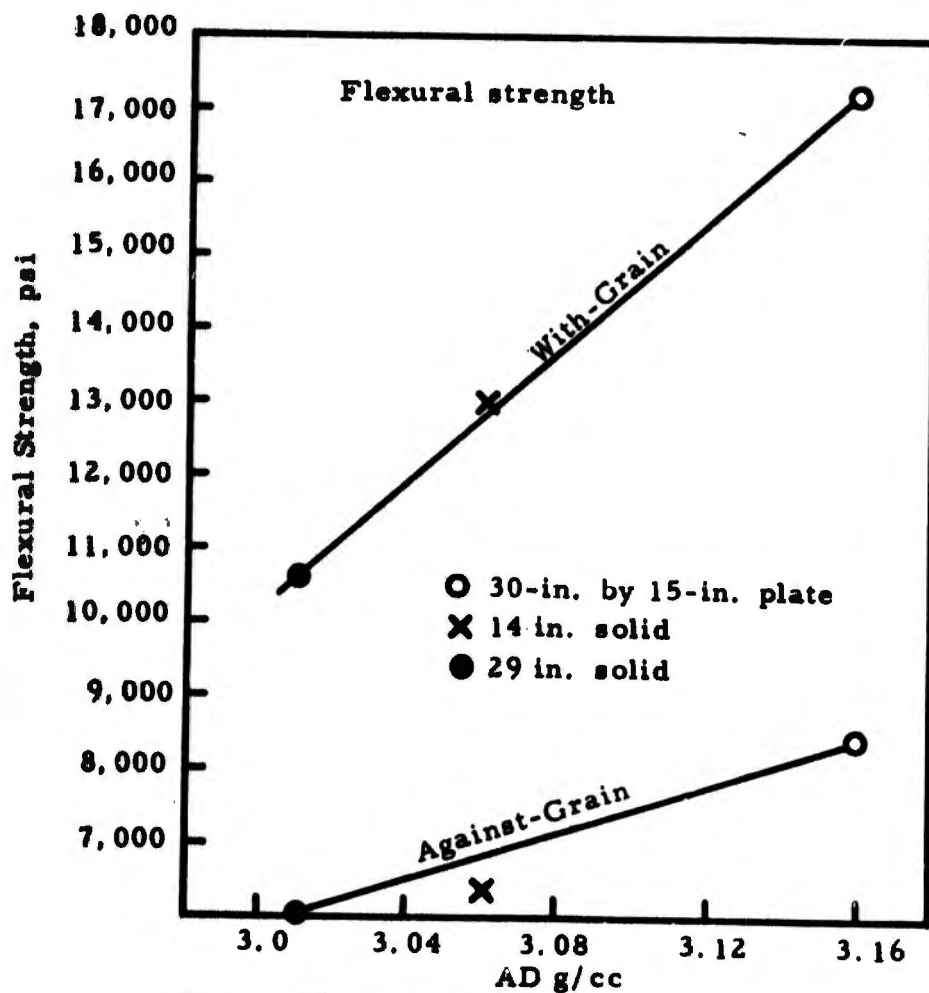


Figure 23. Dependence of Flexural Strength on Bulk Density. N-20936

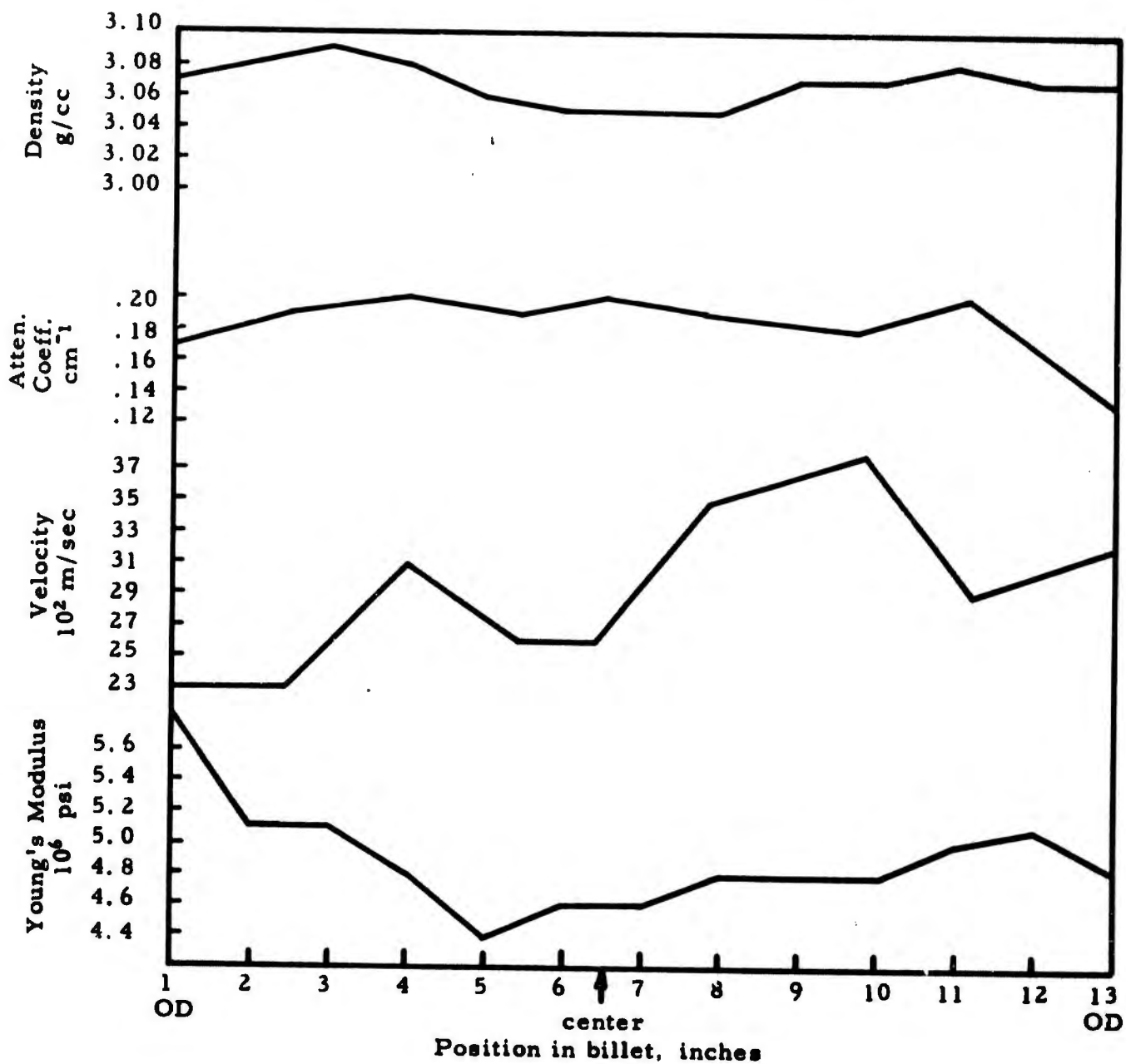


Figure 24. Property Variations in JTA 14-4.

N-19678

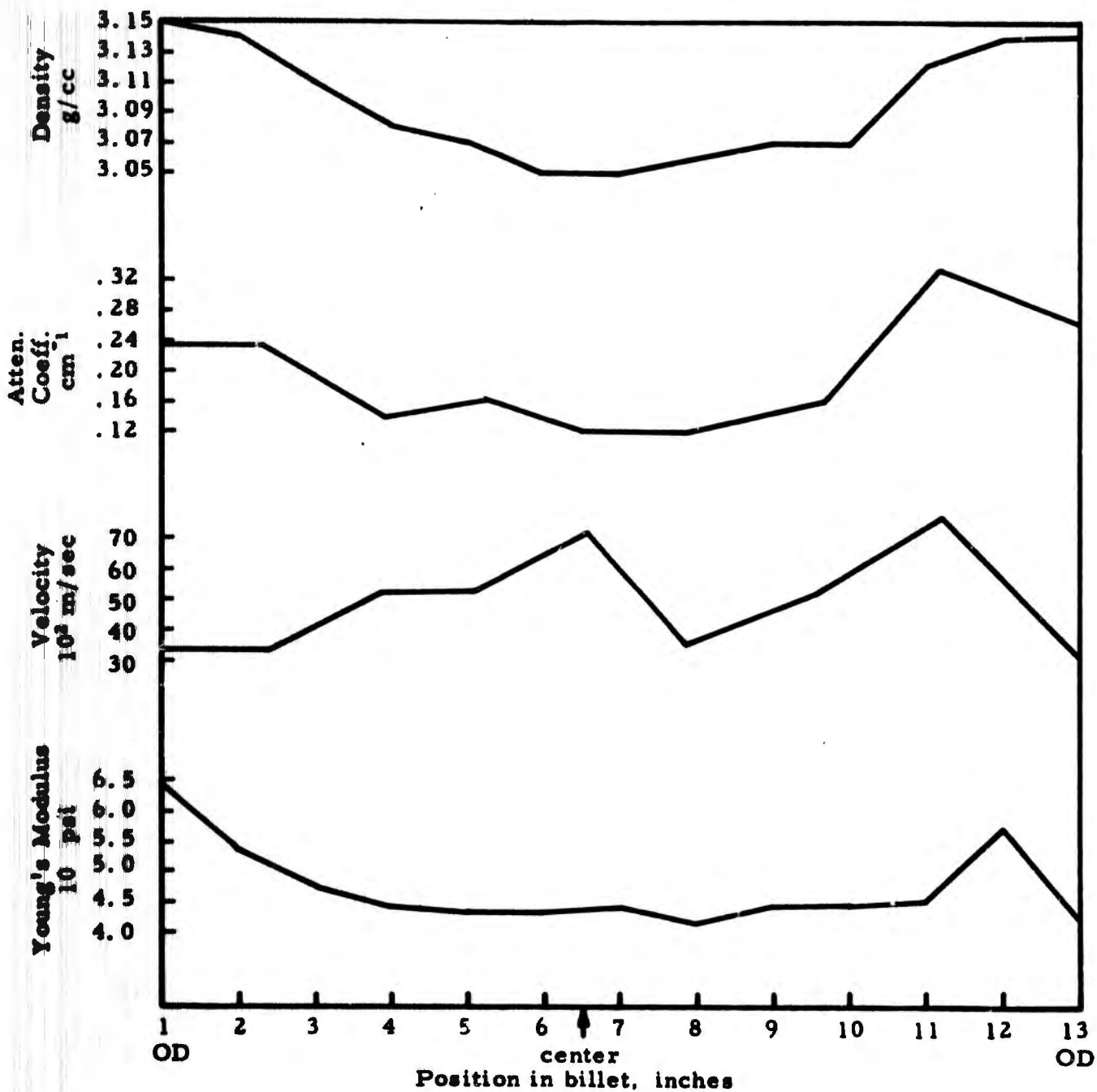


Figure 25. Property Variations in JTA 14-5.

N-19679

In general, ultrasonic techniques appear to be quite sensitive to hidden flaws, and the measurements of attenuation coefficients apparently can be used as an index of property uniformity. More work is needed in these areas to remove billet edge effects and to determine if absolute values of attenuation can be converted into density or Young's modulus values.

3. X-ray Examination

All JTA plates and 14-in. solid billets were X-rayed for hidden flaws. No attempt was made to X-ray through the 29-in. o. d. billet because its large mass and thickness would have presented formidable problems. Peak voltage varied from 200 kv for 5/8-in. thick to 300 kv for 6-in. thick Grade JTA. Type M film with lead screens was used in all exposures. Porter-Bucky grids were also used when the Grade JTA thickness exceeded 1 inch. The X-ray sensitivity was such that a 0.005-in. deep scratch on the surface of a 6-in. thick Grade JTA billet was readily seen. Thus very small flaws, as well as density variations within the stock, could be easily detected. The method appears to be very sensitive for nondestructive flaw detection, at least through 6-in. thicknesses.

4. High Temperature Properties

The only elevated temperature physical property determination was thermal expansion. It must be cautioned that while the modified Grade JTA physical properties are essentially equal to or better than properties reported on 5-in. and 3-in. developmental billets, they are all room temperature measurements. It is not known at this time if removal of the carbon bond will affect oxidation resistance or strength at elevated temperatures.

APPENDIX A

WORKING STRESS IN GRAPHITE MOLDS

The use of graphite as a containment vessel in hot-pressing operations has increased significantly in recent years. Most such processes require high pressures as well as high temperatures. Since graphite is relatively weak compared to more common pressure vessels such as metals, it often must be used at pressures approaching its ultimate strength. The difficulty faced by the innovator of a hot-molding process is; how can the working strength of graphite under the conditions of actual use be determined?

Based upon the room temperature tensile strength, an empirical formula has been developed to calculate the maximum permissible applied pressure. The formula, of course, can only be a guide. The tensile strength variations within graphite pieces are commonly $\pm 25\%$. The presence of hidden flaws, a jammed ram, a tilted mold, will cause failures that cannot be calculated. Thus, the use of such a formula must be with caution. The values produced by the formula seem reasonable in the light of limited experience, but have not been proven under controlled conditions.

SIMPLE GRAPHITE CYLINDER

The following discussion applies to regular, right-circular cylinders. These normally have a straight-through or tapered hole in a solid graphite cylinder. Stress is from applied internal pressure only.

We believe the stress formula (1) that most closely approaches conditions in graphite is:

$$S = P \frac{(b^2 + a^2)}{(b^2 - a^2)}$$

where S = the circumferential wall stress, a = inner radius, P = tensile strength of the graphite, b = outer radius.

This formula assumes uniform loading over the entire internal length of the mold with a hot-pressed body that acts as a liquid. Such is not usually the case in practice. Most ceramics act as semi-plastic solids during hot pressing. Pressure transmittal through such bodies is not uniform. In addition, as the hot-worked body compresses and increases in density, its height in the mold decreases. Less and less total side wall is under load. In very thin pieces, hardly any pressure is on the side wall, but is instead held by the rams. The load can be safely increased in such circumstances. It has been observed that a factor in the form of:

$$\sqrt{\frac{L}{l}}$$

where L is the total length of mold, l is the length of the hot-worked body in the mold, can express a fraction to modify the stress.

(1) Roark, Formulas for Stress and Strain, McGraw Hill, Third Edition.

Graphite has the unusual property of increasing in strength with temperature. The increase, however, is not linear. A graph (Figure A-1) has been prepared indicating a factor (T_f) that can be used to adjust the allowable pressure versus temperature.

Rearranging these factors, an empirical formula for maximum allowable working pressure can be calculated, thus:

$$P = \frac{(b^2 - a^2) S_t \cdot T_f \cdot \sqrt{L/l}}{(b^2 + a^2)}$$

where P = allowable working pressure, psi; S_t = room temperature tensile strength of mold graphite, psi; T_f = temperature factor from chart; a = internal radius of mold; b = external radius of mold; L = length of mold; l = length of billet in mold.

MOLD DEFORMATION

Another, sometimes unrecognized source of stress in a graphite mold is caused by stress deformation. Even at room temperature graphite will not return to its original dimensions after loading to more than 10% of its ultimate strength.

The greatest deformation in a mold will occur the first time it is used. Work by others (2) has shown about 60% of the total deformation, caused by multiple cycling of graphite to constant loads, occurred on the first cycle. After each cycle, a diminishing, but cumulative "set" occurred, even though the load in each case was the same.

We have observed graphite molds becoming "barrel" shaped after a single usage. Not only was the hot-pressing wall area expanded as one would expect, but both top and bottom openings slightly closed. Thus, tolerances that were very carefully machined into the rams and mold, no longer existed. If such a situation is allowed to persist, ill-fitting parts could possibly break a mold. This situation could be the cause of "mold fatigue" failures observed by some operators after multiple uses of a hot-pressing assembly.

(2) Arragon & Berthier, Caractérisation Mécanique Du Graphite, Paper presented at London Industrial Carbon and Graphite Conference, 1957.

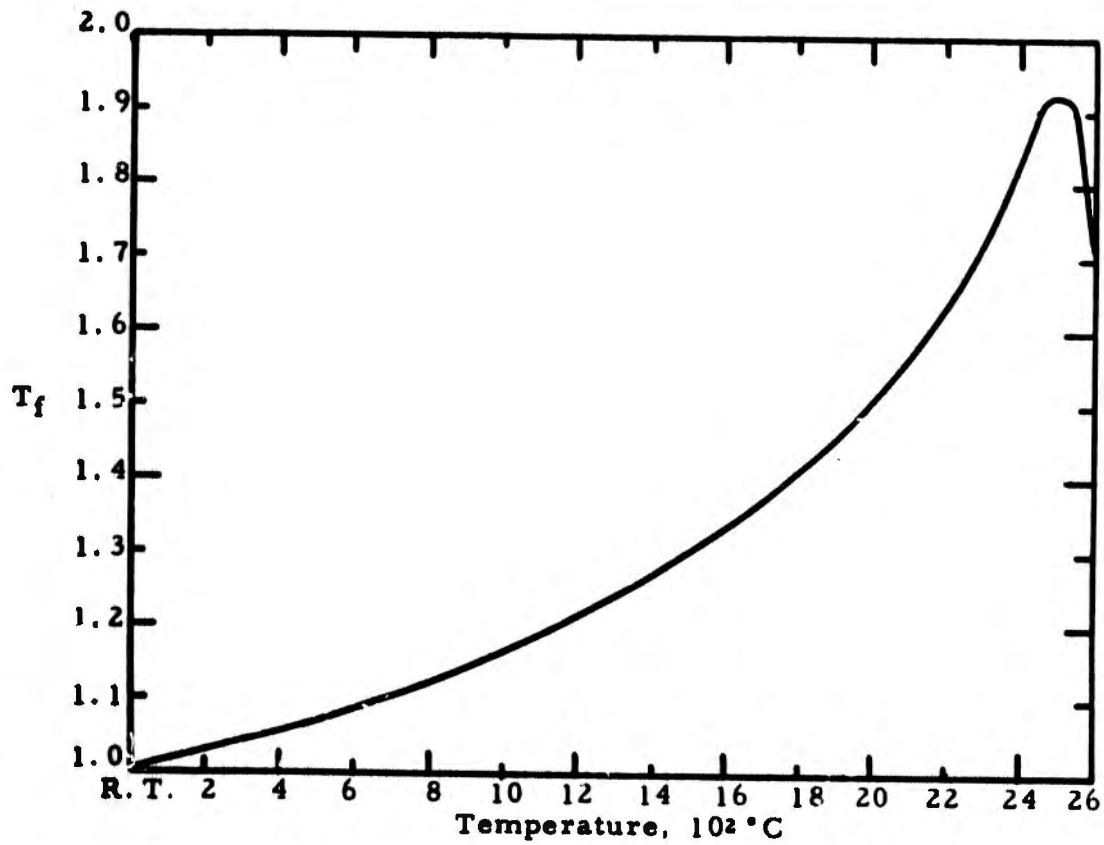


Figure A-1. Graph* of Strength Multiplier (T_f) Versus Temperature.

N-21201

* Adapted from data in "The Industrial Graphite Engineering Handbook" Union Carbide Corporation, Carbon Products Division, p. 5A.02.03, Figure 5A.02.02.

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Manufacturing techniques were developed for handling, firing, and hot-pressing graphite composite materials in 57-in. o. d. by 40-in. high graphite molds. Consumable wooden supports were used to achieve almost perfect float molding conditions. Forming parameters were established for manufacture of Grade JTA plates 30 in. by 15 in. by 3 in. thick, and solid billets 29-in. o. d. by 15 in. high. The solid billet weighed 1090 pounds and is believed to be the largest ceramic billet ever hot-pressed. Hollow cylinders up to 14-in. o. d. were also hot-pressed. Cracking was eliminated in large Grade JTA composites by removing the pitch binder from the formulation. Limited progress was achieved in pressing Grade JTA composites into small leading edge shapes.

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14.	KEY WORDS	LINK A		LINK B		LINK C	
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