FOREWORD

This is a supplement to Volume VII of the WADD Technical Report 61-72 series describing various phases of research and development on advanced graphite materials conducted by National Carbon Company, a Division of Union Carbide Corporation, under USAF Contract AF 33(616)-6915.

The work covered in this report was conducted from September 1961 through May 1962 at the Advanced Materials Laboratory of National Carbon Company, Lawrenceburg, Tennessee, under the management of R. M. Bushong, Director of the Advanced Materials Project, and of R. C. Stroup, Manager of the Advanced Materials Laboratory.

The contract for this R & D program was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials, "Task No. 735002, "Refractory Inorganic Non-Metallic Materials: Graphitic," Project No. 7381, "Materials Application," Task No. 738102, "Materials Processes," and Project No. 7-817, "Process Development for Graphite Materials." The work was administrated by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Captain R. H. Wilson, L. J. Conlon, and W. P. Conrardy as Project Engineers.

Other volumes in this WADD Technical Report 61-72 series are:

Volume I - Observations by Electron Microscopy of Dislocations Graphite, by R. Sprague

Volume II - Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence

Volume III - Decorations of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague

Volume IV - Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch

Volume V - Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.

Volume VI - Creep of Carbons and Graphites in Flexure at High Temperature, by E. J. Seldin

Volume VII - High Density Recrystallized Graphite by Hot Forming, by E. A. Neel, A. A. Kellar, and K. J. Zeitsch

ABSTRACT

This report describes the development and fabrication techniques utilized in the scale-up of grades ZTE and ZTF graphite to 30-inch diameter sizes. Grades ZTE and ZTF graphite which are normally characterized by a bulk density range of 1.92 to 1.97 g/cc and 1.97 to 2.02 g/cc, respectively, are manufactured by hot working grade RVA graphite which is characterized by a bulk density of 1.84 g/cc under pressures as high as 3500 lbs./in.^{2} and temperatures up to 3000°C. The physical properties of a 30-inch diameter ZTE graphite billet are tabulated along with the properties of RVA graphite.

This report has been reviewed and is approved.

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1. INTRODUCTION

The process for the fabrication of high-density ZT graphites can be stated very simply. Graphite bodies are heated to a temperature at which they become plastic and then are compressed by the application of hydraulic pressure.[1] Specifically, a graphite billet is heated to 2400°C at which point hydraulic pressure is applied. Heating of the graphite body continues to approximately 3000°C while the application of hydraulic pressure is uniformly increased at a rate that is determined by the creep rate of the specific graphite billet being hot worked. The creep properties of graphite as they apply to the hot working process were discussed in the original ZT graphite report.[1] The knowledge of the creep or plasticity of graphite at elevated temperatures provided the background for hot working graphite billets into high-density graphite.[2]

Hot working of graphite produces a volume reduction that is not accompanied by a weight loss and the overall result is a mass densification of the graphite body. The increase in bulk density leads to property characteristics which are not otherwise obtained in artificial graphites. Physical properties of high-density graphite have been reviewed.[1] In practice, the process for fabricating ZT graphite is complicated because of the 3000°C working temperature and attendant tooling and containment problems. The problems are compounded further during the process by the addition of compressive forces to the hot components.

Prior to the work discussed in this report, National Carbon Company had successfully developed a process capable of producing 14-inch diameter by 10-inch length high-density ZT graphite billets. Two restrictions confined the maximum size to these dimensions. One was the lack of a suitable starting material in larger diameters and the other was the lack of the tooling necessary for hot working a large-diameter, fine-grain graphite billet. Both restrictions were eliminated by the development of advanced graphite materials under the present program. A large-diameter, fine-grain graphite, grade RVA, was developed[3] and equipment has been provided at the Advanced Materials Laboratory for the purpose of developing a hot working process capable of fabricating ZT graphite billets as large as 30 inches in diameter.

The object of this report is to describe the development of the process for producing 30-inch diameter billets of high-density ZT graphite with physical properties comparable to the 14-inch diameter billets.

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2. EQUIPMENT

2.1. Electrical

A 500-kw static frequency convertor with an output frequency of 180 cps was utilized as the power source in the development of the process for fabricating 30-inch diameter ZT graphite. The power unit was capable of delivering 700 kw to the induction coil that heated the graphite billet. An induction coil, with the electrical and mechanical characteristics shown in Figure 1, provided the electro-magnetic field necessary for heating the graphite billet.

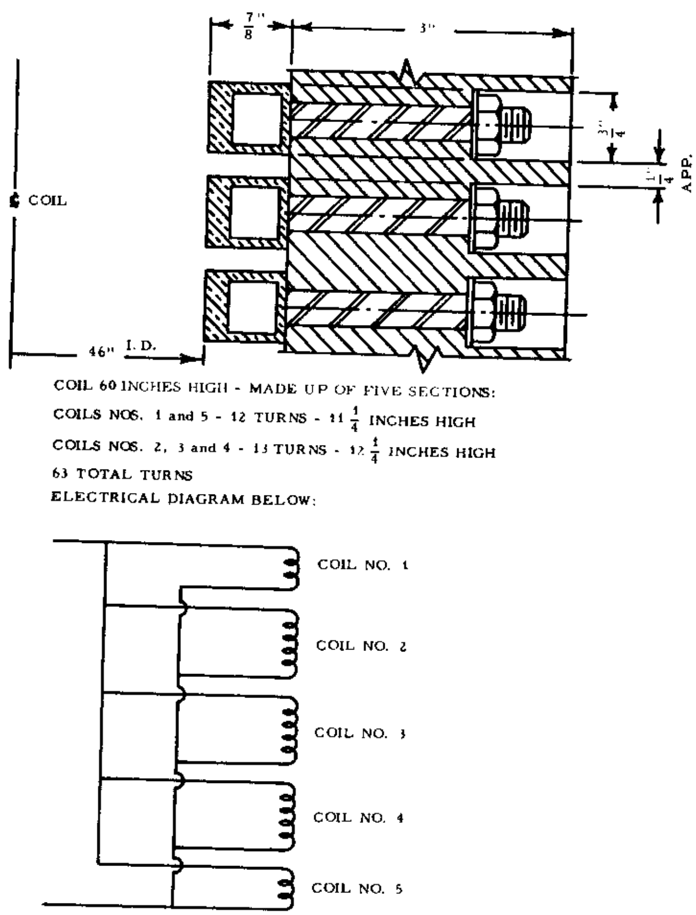

Figure 1. Schematic Drawing of Induction Coil Used in Hot Working Process

2.2. Press

A 2500-ton hydraulic press with a single-action ram, shown in Figure 2, was utilized for all the 30-inch diameter hot working trials.

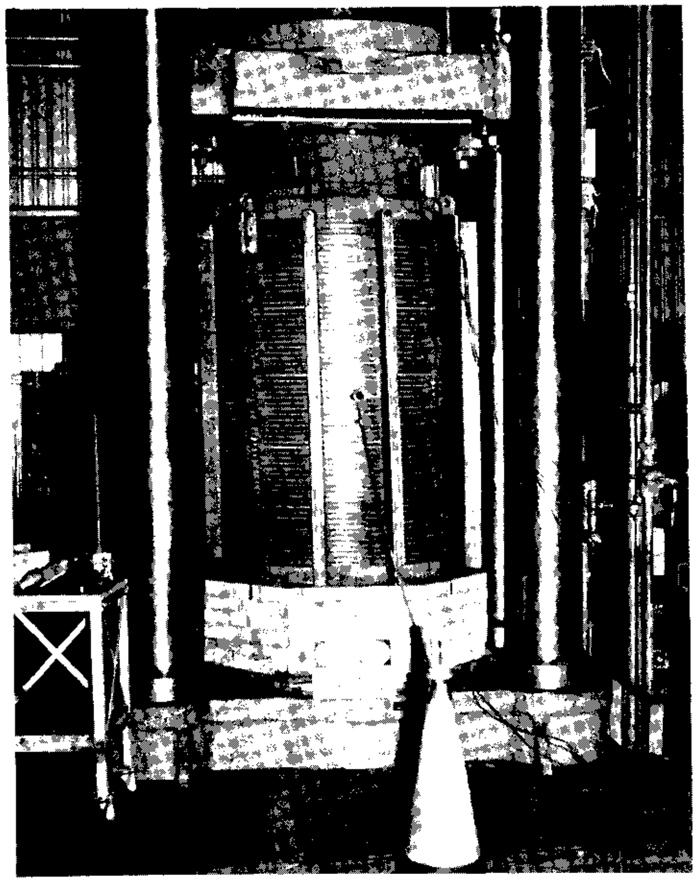

Figure 2. Front View of 2500-Ton Press, Completed Assembly

2.3. Miscellaneous Tooling

Two water-cooled platens were required to reduce the temperature at the ends of the graphite column which is discussed in Section 3 of this report. Both the top and the bottom water-cooled platens were cast from an aluminum bronze alloy. Ceramic rings were used to contain the 30-inch diameter graphite billet along with the necessary insulating medium.

3. CARBON AND GRAPHITE MATERIALS

3.1. Material for Hot Working

Two grades of graphite, ATL and RVA, were selected for the 30-inch diameter hot working trials. Grade ATL graphite was utilized in only the initial trial which was designed primarily for equipment break-in. The remaining two trials used grade RVA graphite which was the only premium grade of graphite available in the required 30-inch diameter.

3.2. Material for Punches

A punch, capable of transmitting pressure loads of 3500 lbs/in^2 at approximately 3000°C, was developed from carbon and graphite materials. By constructing the punch of several sections (bolsters) of graphite, as shown in Figure 3, two important characteristics were developed. First, and most important, the thermal stresses derived from extreme temperature gradients were greatly minimized. Second, it was possible to reduce the heat flow from the column to a minimum by using layers of carbon felt between the bolsters.

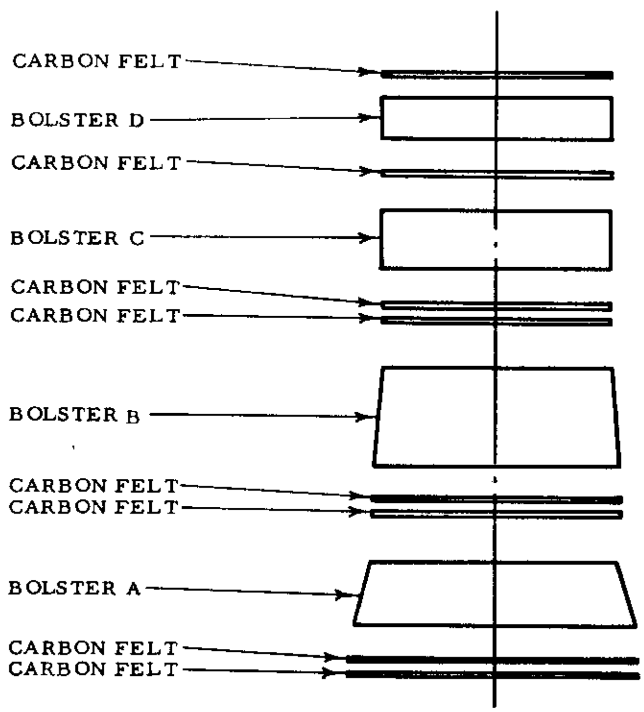

Figure 3. Graphite Punch Configuration for Hot Working Process

3.3. Insulation

Thermatomic black was used as insulation around the graphite billet. The low thermal conductivity of this black prevented excessive heat losses from the assembly. In each hot working trial there was approximately 5 1/2 inches of thermatomic black around the graphite billet.

4. HOT FORMING TRIALS 30-INCH DIAMETER ZT GRAPHITE

4.1. Trial Number 1

Figures 4, 5, and 6 show progressive steps to completion of the assembly for the first 30-inch diameter hot working trial. Although the resulting product was of importance, this initial trial was primarily for evaluation of equipment and design concepts. Consequently, grade ATL graphite was used for the product billet instead of the premium grade RVA graphite which was ultimately selected as the starting material in the hot working process for large diameters.

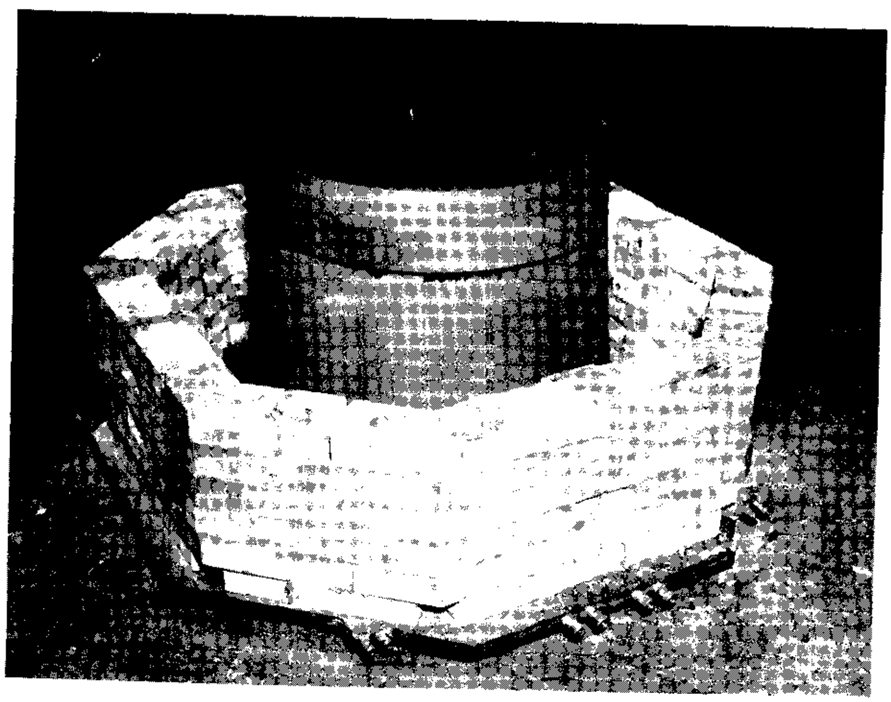

Figure 4. Partial Assembly for Hot Working, Bottom Punch, Bottom Platen and Brick Foundation

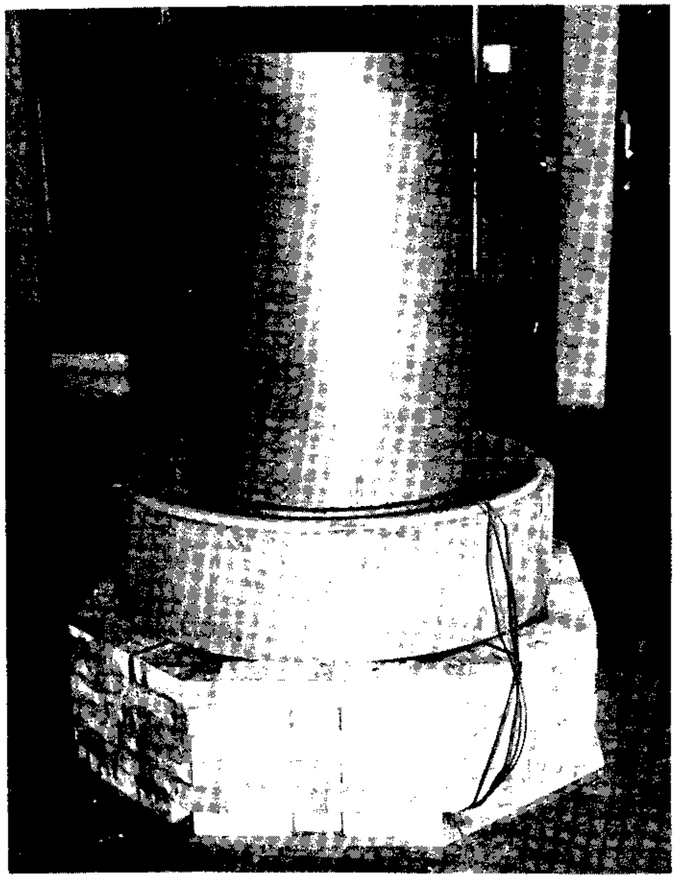

Figure 5. Grade ATL Graphite Billet Assembled on Bottom Punch, Prior to Hot Working

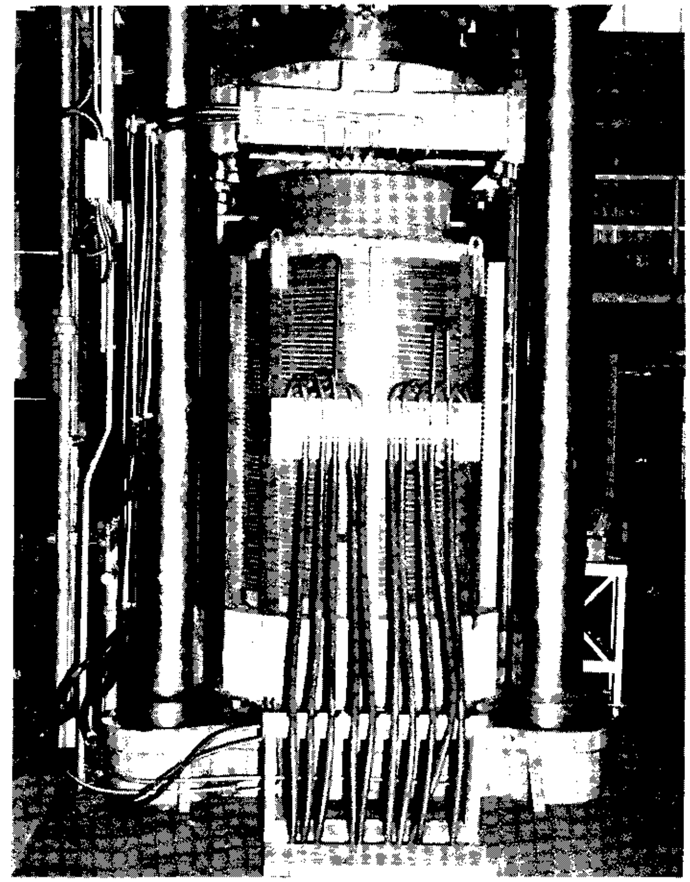

Figure 6. Rear View of Completed Assembly for Hot Working Process

In each trial reported herein a product analysis was made both before and after hot working. Table 1 presents the basic dimensions of the ATL billet before and after hot working, and shows that the bulk density of the hot worked billet was much less than the 1.92 g/cc density established as a minimum for ZT graphite.

Table 1. Graphite Dimensions and Bulk Density, Hot Working Trial Number 1

Property	Before Hot Working	After Hot Working
Diameter, Inches	28.00	29.97 (Ave.)
Length, Inches	40.00	32.31 (Ave.)
Weight, Pounds	1505	1502
Bulk Density, g/cc	1.69	1.82 (Estimated)

Sketches of the cross section of the assembly for the first trial, both before and after hot working, are presented in Figures 7 and 8 and illustrate the effect of hot working on the graphite. The graphite punches, responsible to a large degree for the successful hot working trial, also are illustrated in these figures.

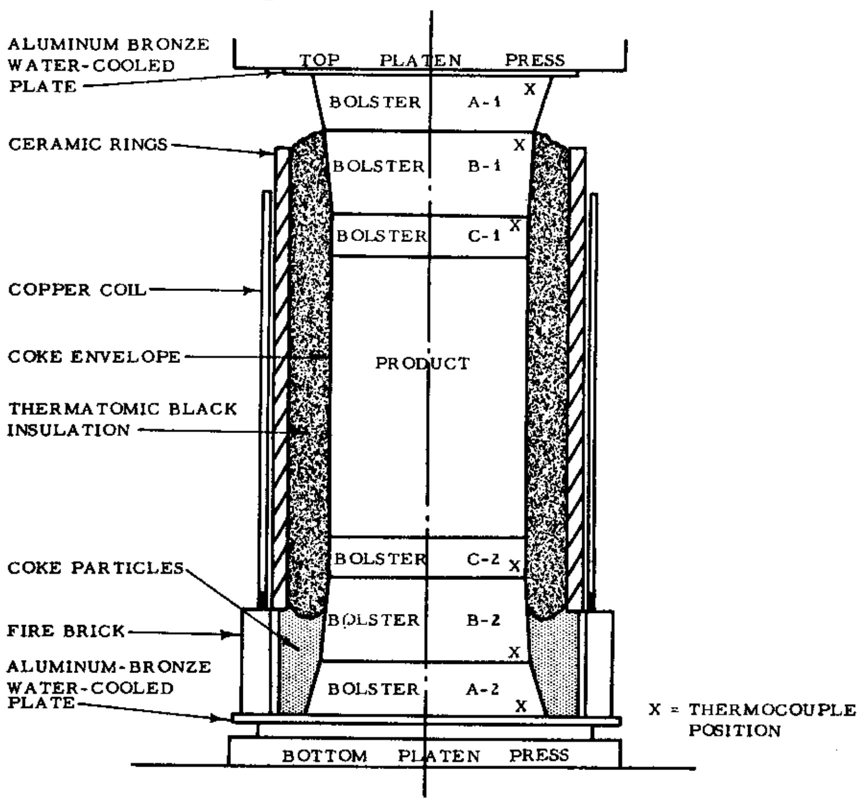

Figure 7. Sketch of Hot Working Assembly Before Pressing

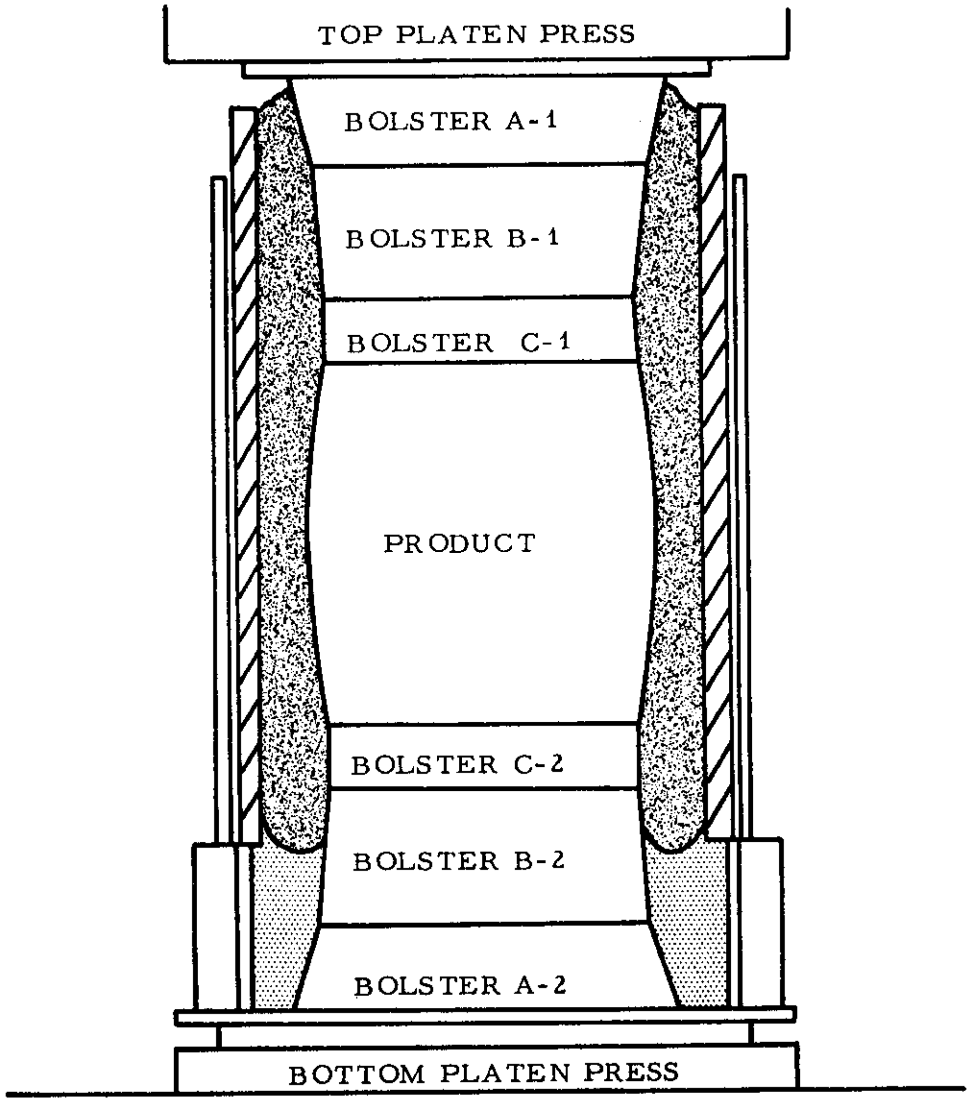

Figure 8. Sketch of Hot Working Assembly After Pressing

The thermal conductivities of ATL and RVA graphite are relatively high (69.7 and 57.6 BTU ft/ft^2 hr °F, respectively)[4] and, thus, some means of insulating the graphite column was required to prevent excessive heat losses. National Carbon grade VDF carbon felt, having a thermal conductivity of 0.023 BTU ft/ft^2 hr °F, was placed between each bolster. Table 3 shows the temperature of each bolster in the column as the product was heated to 3000°C.

Table 2. Temperature Characteristics of Graphite Components, Hot Working Trial Number 1

Time			Bolsters				Approximate Product-
Minutes	A-1[1]	A-2	B-1	B-2	C-1	C-2	Temperature, °C
0	26	26	26	26	26	26	26
90	82	88	158	192	492	307	530
120	90	98	175	140	550	369	620
240	102	150	273	230	820	610	1090
300	110	210	340	320	1040	815	1340
450	130	428	610	600	x	x	2400
500	205	470	730	700	x	x	2700
600	140	490	x[2]	x	x	x	2900
615	140	490	x	x	x	x	3000

(1) Refer to Figure 7 for thermocouple placement.

(2) x - thermocouple failed at this point.

The hot working parameters, temperature, pressure, slump, and kw output, for Trial Number 1 are presented in graphical form in Figure 9. Although this data indicated a highly successful initial trial, the product density was considerably less than the 1.92 g/cc which represents the minimum for ZT graphite. Despite the low bulk density, analysis of the billet provided the information necessary for design changes in succeeding trials. During Trial Number 1 the ends of the billet were at a significantly lower temperature than the middle of the billet. Figure 10, which compares the billet before and after hot working, shows the effect of the temperature gradient. The ends of the billet were less plastic than the middle and, therefore experienced less creep which explains the 3.5-inch difference between the maximum and minimum diameters of the billet. Corroboration of the temperature gradient was obtained from the bulk density profile, Figure 11, which indicated a variation in bulk density of 0.15 g/cc from the middle to the ends of the billet.

With the above knowledge, three changes were made in the physical assembly for succeeding trials which reduced the temperature gradient appreciably and allowed the successful fabrication of 30-inch diameter ZT graphite.

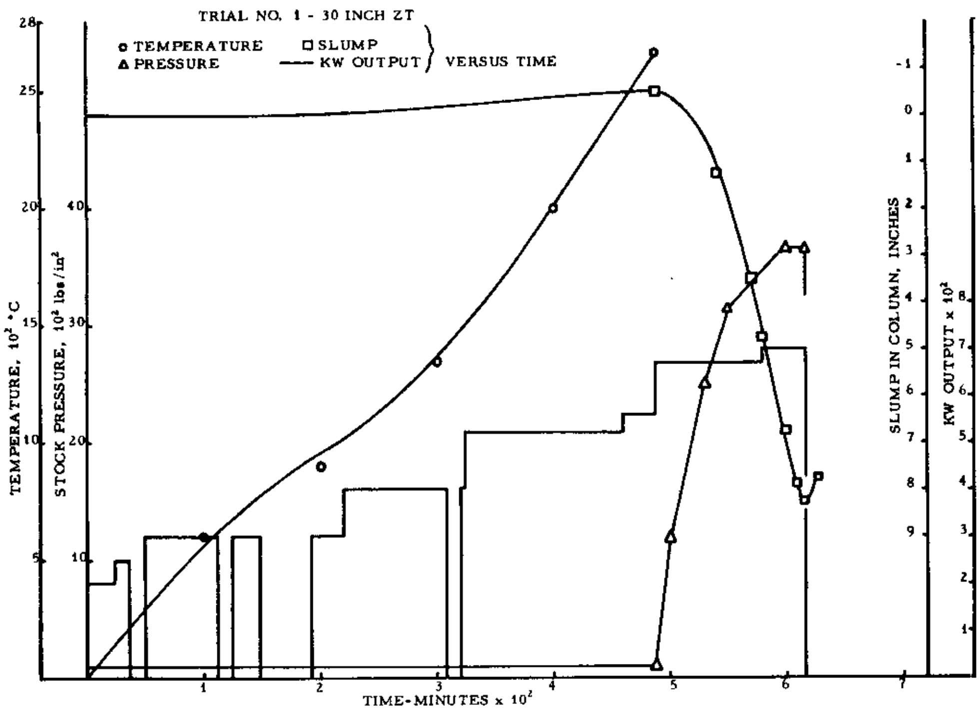

Figure 9. Temperature, Pressure, Slump, and Power Output versus Time, Hot Working Trial Number 1

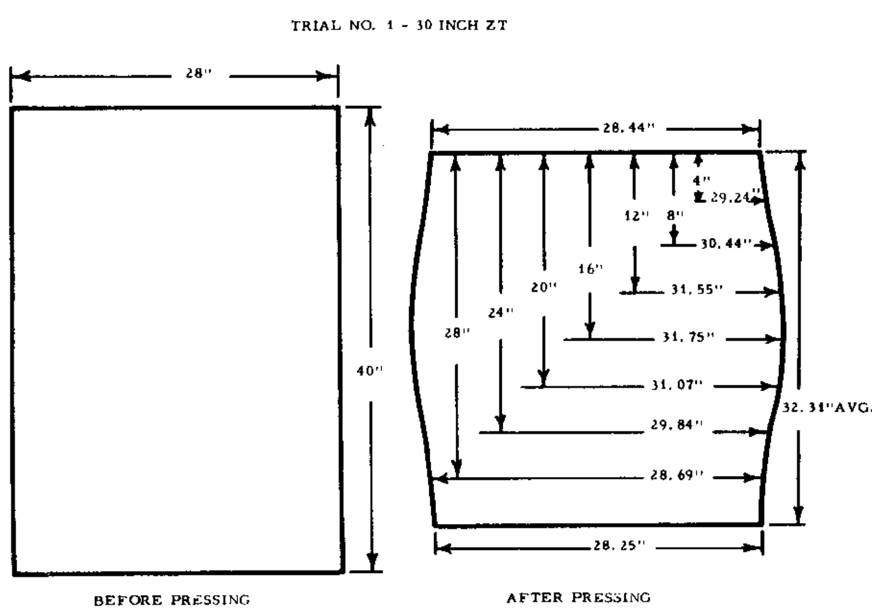

Figure 10. Dimensions of Grade ATL Graphite Billet Before and After Hot Working

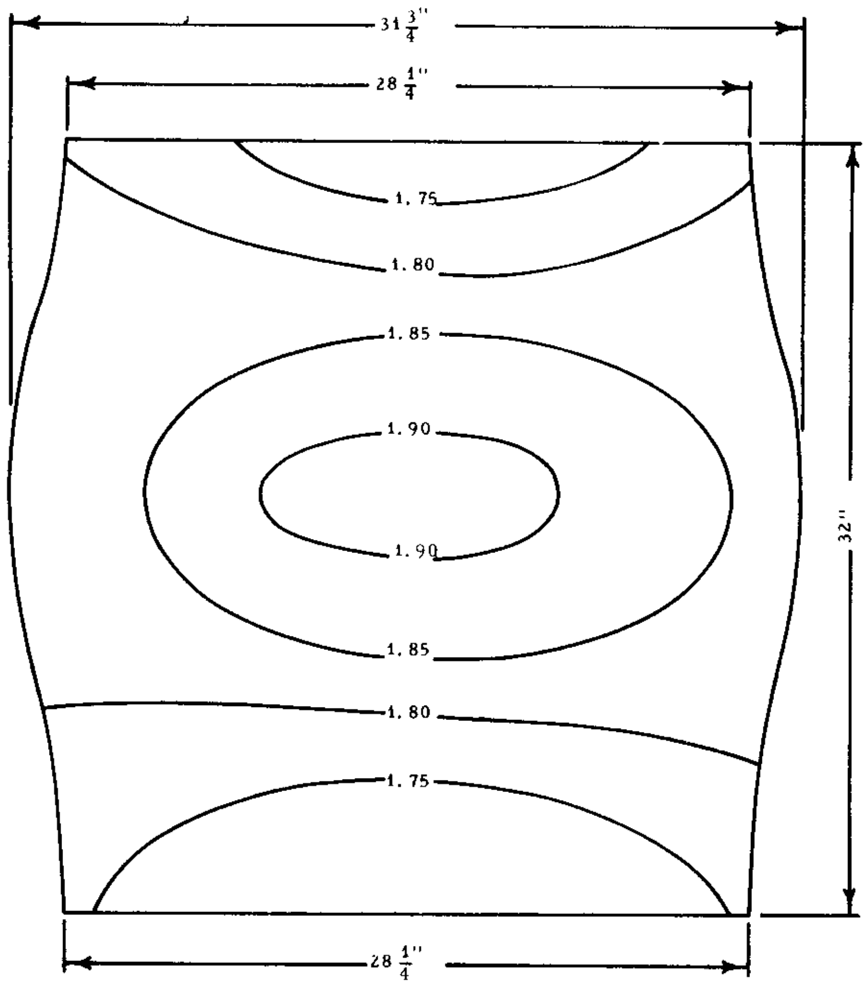

Figure 11. Bulk Density Profile, Hot Worked Grade ATL Graphite Billet

4.2. Trial Number 2

The second hot working trial produced the first 30-inch diameter graphite with a bulk density in the ZT range, which is 1.92 to 2.10 g/cc. This graphite, designated as ZTE, had a bulk density of 1.96 g/cc. Table 3 presents the dimensions and density of the billet for Trial Number 2 and Figure 12 illustrates the machined ZTE billet.

Table 3. Graphite Dimensions and Bulk Density, Hot Working Trial Number 2

Property	Before Hot Working	After Hot Working	Machined
Diameter, Inches	27.94	29.86 (ave.)	29.00
Length, Inches	31.92	25.62 (ave.)	23.50
Weight, Pounds	1296	1273	1099
Bulk Density, g/cc	1.835	1.96 (estimated)	1.96

Figure 12. Machined Grade ZTE Graphite Billet

Three major changes made in the hot working assembly accounted for the successful fabrication of the 29-inch diameter ZTE billet in the second trial. The most important change in the assembly was the substitution of the premium grade RVA graphite for the product billet. The RVA graphite had a bulk density of 1.835 g/cc which was higher than the final bulk density (1.82 g/cc) of the hot worked ATL billet from Trial Number 1. The second change was also related to the starting product and amounted to a decrease in the length of the billet from 40 inches to 32 inches. Additional insulation placed between the bolsters in the second trial constituted the third change in the assembly.

Although the column for Trial Number 2 did have additional insulation with respect to Trial Number 1, the temperature gradient in the billet was reduced primarily by the configuration change in the starting product.

After decreasing the billet length, the graphite column was increased in length by the addition of bolsters D-1 and D-2 shown in the cross sectional drawing of the assembly for Trial Number 2 (Figure 13). These bolsters helped to reduce the temperature gradient of any component of the column in two ways. Firstly, the additional graphite sections brought the total number of components in the column to nine. These nine sections were exposed to the same temperature extremes as the seven sections in the column of Trial Number 1. Secondly, two more interfaces were made available for the insertion of the carbon felt heat dam which reduced the heat loss from the column. Table 4 presents the temperature characteristics of the graphite column components for hot working Trial Number 2.

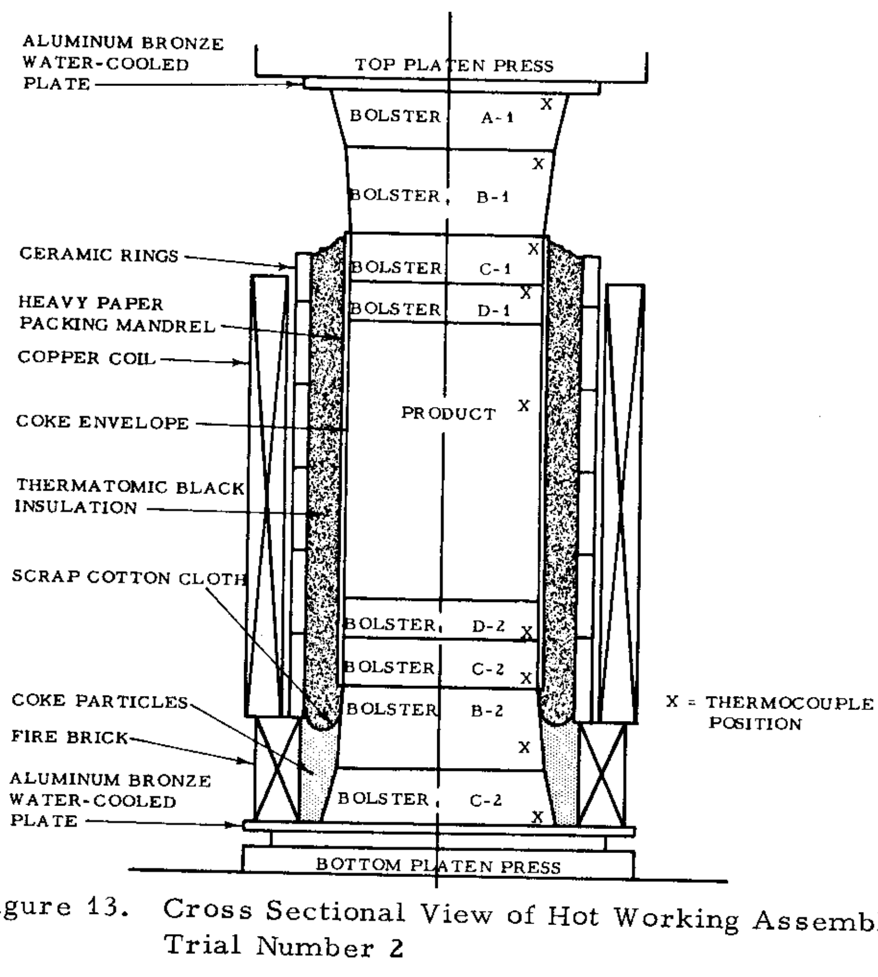

Figure 13. Cross Sectional View of Hot Working Assembly, Trial Number 2

Table 4. Temperature Characteristics of Graphite Components, Hot Working Trial Number 2

Time	Bolsters				Temperature °C (1)				Product	Temp. °C
Minutes	A-1	A-2	B-1	B-2	C-1	C-2	D-1	D-2	T. C.	Optical
0	22	22	22	22	22	22	22	22	22	
60	48	41	142	137	277	269	315	339	327	
120	77	91	273	271	529	533	633	641	658	
180	111	152	437	421	788	802	895	942	x	1050
240	152	230	612	582	1031	1029	1131	1139	x	1395
300	168	318	800	729	1140	1152	x	x	x	1800
360	185	431	x (2)	862	x	x	x	x	x	2220
420	230	482	x	x	x	x	x	x	x	2500
480	260	510	x	x	x	x	x	x	x	y (3)
540	285	550	x	x	x	x	x	x	x	y

(1) Refer to Figure 14

(2) x - indicated thermocouple failure

(3) y - sight tube failure

The hot working cycle for Trial Number 2 presented little difficulty; however, at 535 minutes of the cycle, bolster A-1 developed a vertical fracture that originated at the cold face and the trial was terminated. It was felt, after examination of bolster A-1, that the fracture was developed by a combination of thermal and mechanical stresses which exceeded the strength of the ATL graphite. The above parameters are presented graphically in Figure 14. Although Trial Number 2 was terminated early, the bulk density of the billet was increased from 1.835 to 1.960 g/cc, which placed the billet within the bulk density range of ZTE graphite, 1.92 to 1.97 g/cc.

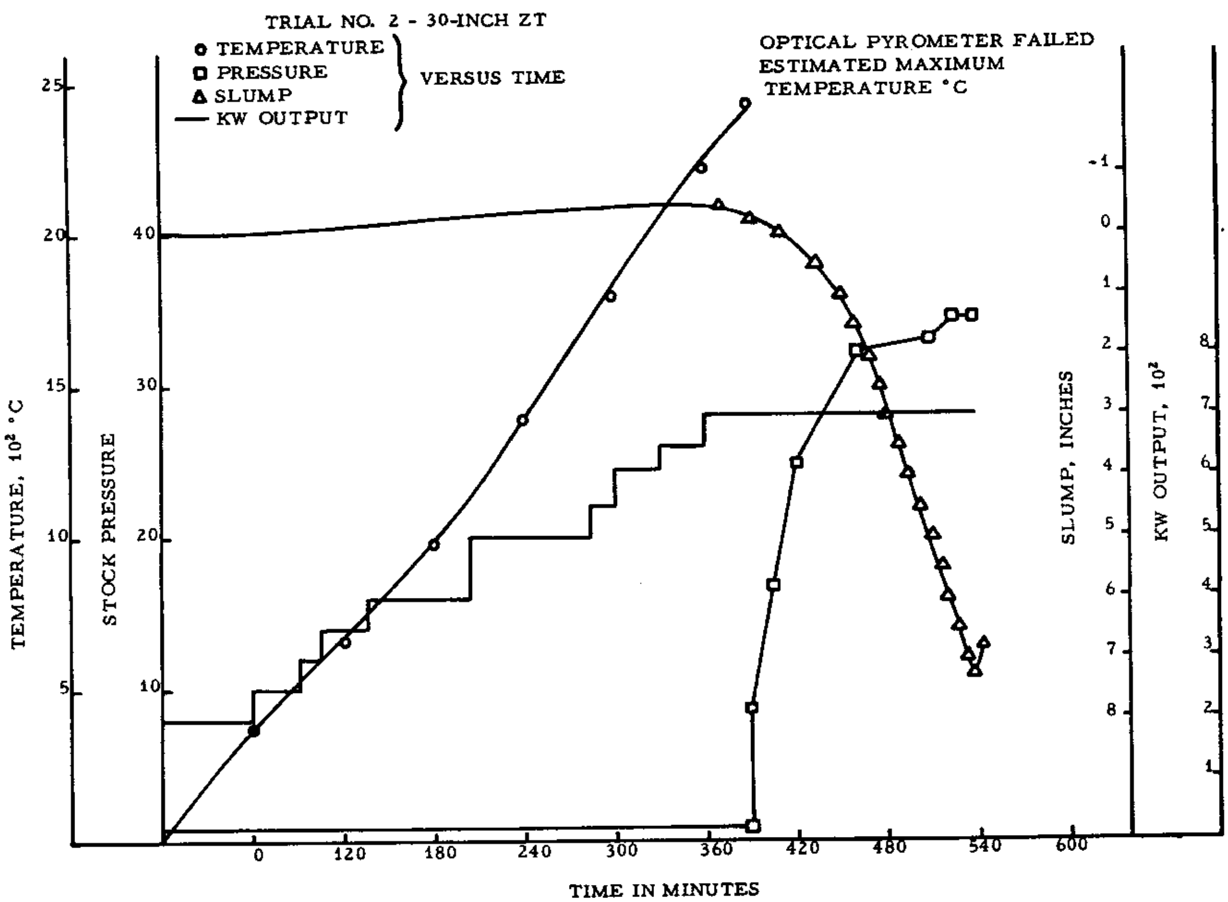

Figure 14. Temperature, Pressure, Slump and KW Output versus Time for Hot Work Trial Number 2

A view of the ZTE billet is presented in Figure 15. The billet was appreciably hotter than the other components of the column as is reflected by the comparison of the different diameters. Bolsters D-1 and D-2 show diametrical growth at the hot faces but very little if any at the cold faces which indicated a substantial temperature gradient.

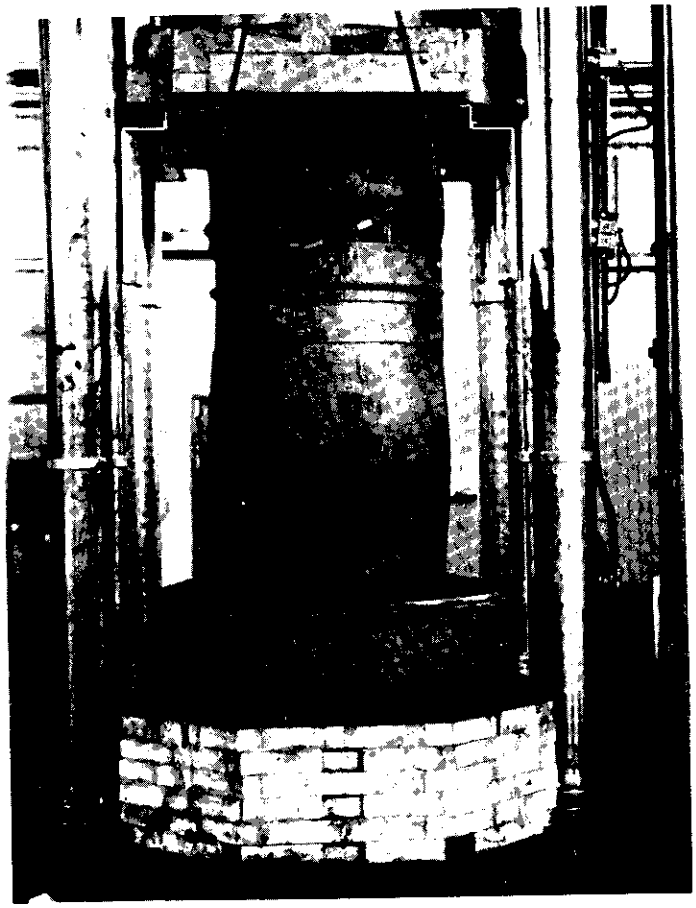

Figure 15. Graphite Column After Hot Working, Trial Number 2

The dimensions of the billet before and after hot working are presented in Figure 16 and show the flow changes in the graphite. This figure also shows the improvement in temperature uniformity and the resulting small difference between the maximum and minimum diameters. Although the ends of the billet were still colder than the middle, they did exhibit an increase in diameter of over one inch whereas the ATL billet of the first trial experienced a diametrical growth at each end of only 0.25 inch.

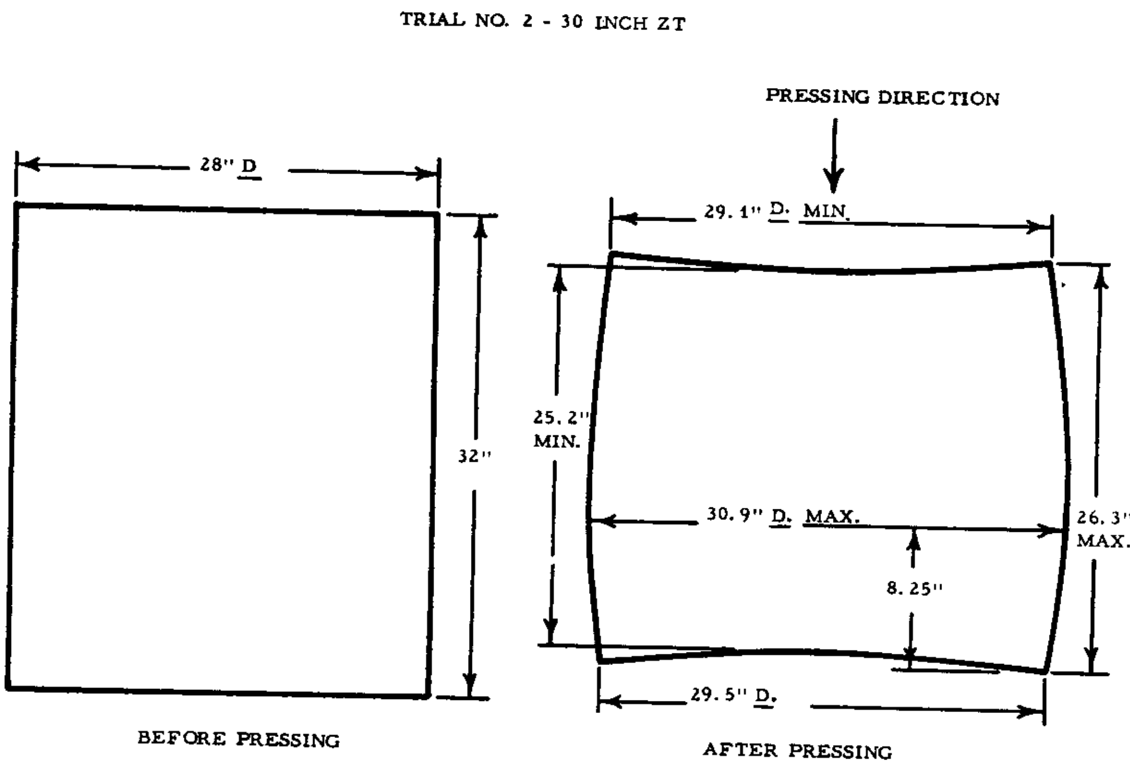

Figure 16. Dimensions of Grade RVA Graphite Billet Before and After Hot Working

A density profile, Figure 17, of the machined ZTE billet also shows the effect of the reduction in the temperature gradient. The hot worked ATL billet of Trial Number 1 had a variation in bulk density of 0. 150 g/cc whereas the maximum variation of the ZTE billet of Trial Number 2 was 0. 064 g/cc.

1. 950	1. 951	1. 947	1. 949	1. 953
1. 947	1. 975	1. 981	0. 982	0. 979
1. 948	1. 949	1. 945	1. 946	1. 948

Figure 17. Bulk Density Profile, Grade ZTE Graphite Billet 30-Inch Diameter by 23 1/2 -Inch Length

4.3. Trial Number 3

A ZTF graphite billet with a bulk density of 1.99 g/cc was produced in Trial Number 3. Table 5 lists the dimensions and bulk density of the graphite before and after the hot working process.

Table 5. Graphite Dimensions and Bulk Density, Hot Working Trial Number 3

Property	Before Hot Working	After Hot Working	Machined
Diameter, Inches	29.0	30.2 (min.) 32.3 (max.)	30.0
Length, Inches	34.3	26.9 (min.) 28.1 (max.) 27.3 (ave.)	24.0
Weight, Pounds	1511	1505.5	1215.3
Bulk Density, g/cc	1.85	1.98	1.99

The construction of the physical assembly for Trial Number 3 is shown in Figure 18. Steel plates were inserted between the first bolster and the water cooled platen at both ends of the graphite column in an attempt to reduce or eliminate the fractures in the cold ends of bolsters A-1 and A-2. Although bolsters A-1 and A-2 again fractured at the cold face, the fractures were not enough to terminate the trial.

A further design change was to increase the size of the starting material from 28-inch to 29-inch diameter which, from previous experience, would insure a machined piece of 30-inch diameter. This proved to be the case since the ZTF billet from Trial Number 3 machined to a diameter of 30 inches. Another change was the addition of low thermal conductivity thermatomic black to the carbon felt and resin heat dams for increased insulation between the graphite sections of the column. Heating data of the billets from Trials Numbers 2 and

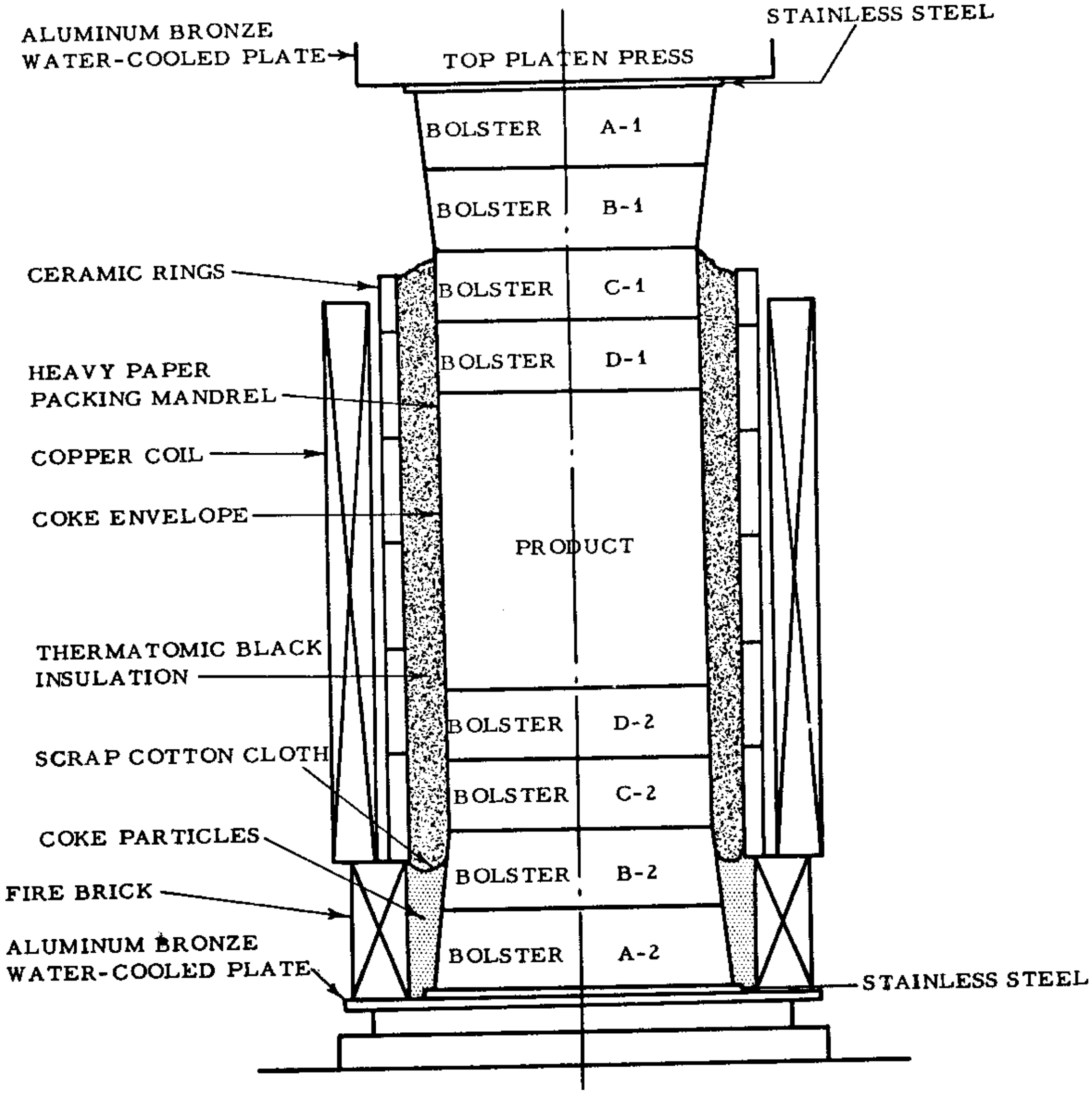

Figure 18. Cross Sectional View of Hot Working Assembly, Trial Number 3

and 3 given in Table 6 show that, over the same time interval, the RVA billet of Trial Number 3 was heated to a higher temperature at a lower power input. Although the magnitude of difference was not great, it indicated that the thermatomic black did decrease the heat loss from the column.

With the exception of a somewhat slower slump rate, the hot working cycle of Trial Number 3 nearly duplicated Trial Number 2.

Table 6. Comparison of Bolster Temperatures, Hot Working Trials Numbers 2 and 3

Bolster * Temperature, °C

Time,	A				B				C				D				Product	
Min.	1	1'	2	2'	1	1'	2	2'	1	1'	2	2'	1	1'	2	2'	1	2'
0	22	25	22	25	22	25	22	25	22	25	22	25	22	25	22	25	22	25
60	58	40	41	54	142	152	137	132	277	277	282	312	315	378	339	392	327	330
120	77	50	91	111	273	268	271	262	529	557	533	577	633	710	641	738	658	680
180	111	62	152	202	437	442	421	409	788	820	802	851	895	998	942	1075	1014	1175
240	152	78	230	309	612	592	582	578	1031	1100	1029	1109	1092	---	1139	----	1395	1575
300	168	92	318	418	800	765	729	740	----	----	----	----	----	---	----	----	1800	1910
360	185	109	431	527	940	920	862	876	----	----	----	----	----	---	----		2220	2310

* Refer to Figure 18
1 and 2 are related to Trial 2
1' and 2' are related to Trial 3

Firing Data

	Trial 2	Trial 3
Time, Minutes	360	360
KWH	2760	2930
Product Weight, Pounds	1296	1511
Product Temperature, °C	2220	2310
KWH/lb.	2.13	1.94

Figure 19, a graphical presentation of the change in length of the graphite column for Trial Number 3, illustrates the variation in the across grain coefficient of thermal expansion of the graphite billet. The maximum accumulated expansion prior to application of pressure was 0.44 inch. Upon completion of the hot working cycle, the pressure was decreased to the normal 43 lbs/in² and the assembly was allowed to cool to room temperature in the press. From the point of spring back, which occurred in the vicinity of 3000°C, to the final temperature of approximately 20°C, the length of the column was reduced an additional 1.55 inches as a function of the coefficient of thermal expansion (CTE). The ratio of contraction to expansion was nearly 3.5 to 1 which was quite indicative of the amount of grain re-orientation that occurred during the hot working process. The billet from Trial Number 3 was held for disposition and properties were not obtained.

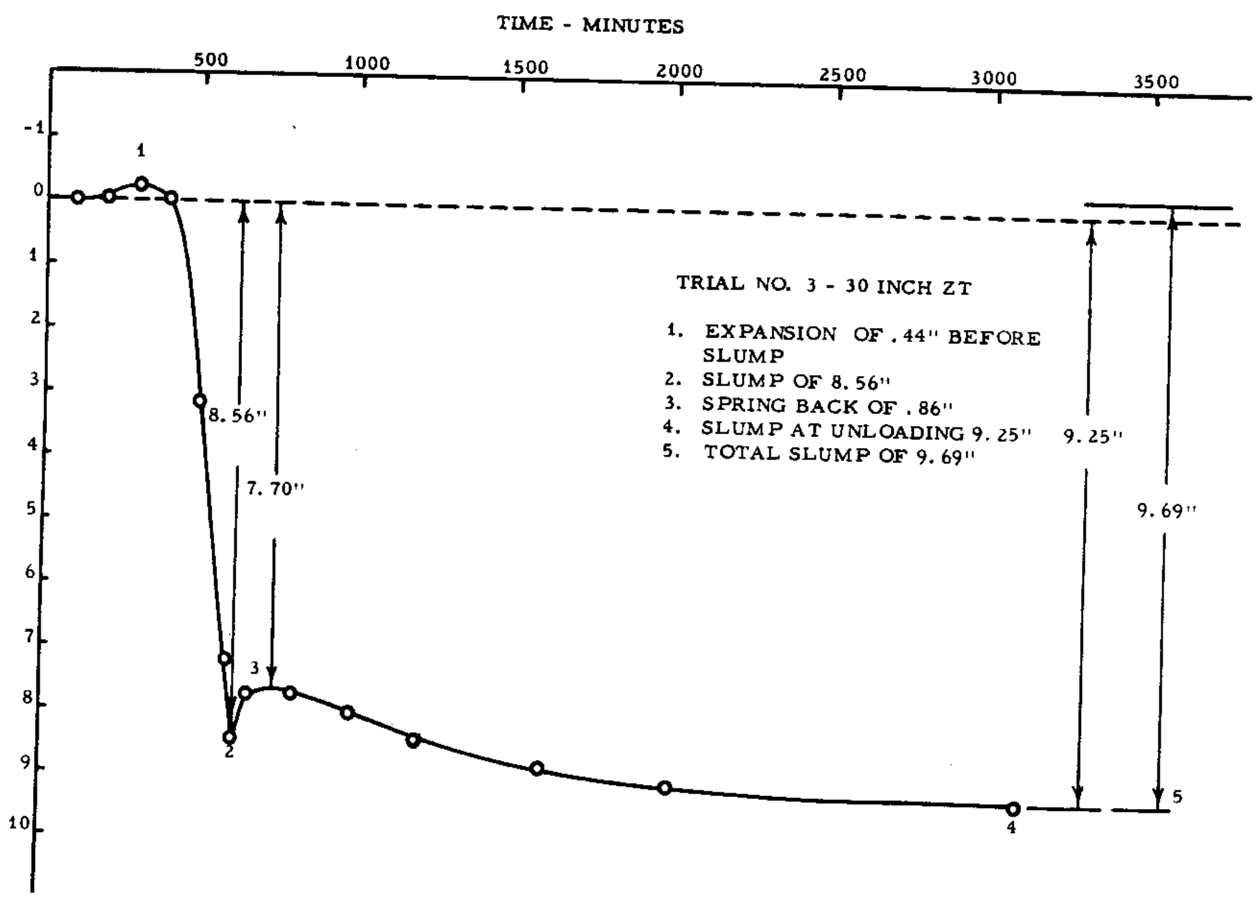

Figure 19. Slump versus Time, From Start of Hot Working Cycle to Unloading, Trial Number 3

A summary of the data for the second and third hot working trials is presented in Table 7.

Table 7. Summary of Data, Hot Working Trials Numbers 2 and 3

	Trial No. 2	Trial No. 3
Before Hot Working		
Grade	RVA	RVA
Diameter, Inches	27.94	29.00
Length, Inches	31.92	34.30
Weight, Pounds	1296	1511
Bulk Density, g/cc	1.835	1.848
After Hot Working		
Grade	ZTE	ZTF
Diameter, Inches		
Maximum	30.90	32.30
Minimum	29.10	30.20
Length, Inches		
Maximum	26.30	28.10
Minimum	25.20	26.90
Average	25.62	27.30
Bulk Density, g/cc (estimated)	1.95	1.98
Machined		
Grade	ZTE	ZTF
Diameter, Inches	29.00	30.00
Length, Inches	23.50	24.00
Weight, Pounds	1099	1215.3
Bulk Density, g/cc	1.96	1.99
Total Slump, Column, Inches	7.75	9.25
Billet Slump, Per Cent	19.7	20.4
Increase in Bulk Density, Per Cent	6.9	7.5
Total Fire Time, Minutes	537	613
Pressing Cycle, Minutes	145	238
Maximum Pressure, lbs/in^2	3470	3500
Maximum Slump Rate, Inches/hour	5.10	3.25
KWH/lb of Product	3.83	3.42

5. PHYSICAL PROPERTIES OF 30-INCH DIAMETER GRADE ZTE GRAPHITE, TRIAL NUMBER 2

5.1. Microstructure

The most significant of the property changes resulting from hot working RVA graphite is probably the change in microstructure. Figures 20 and 21 show photomicrographs of RVA and ZTE (hot worked RVA) graphites, respectively. The decreased porosity of the ZTE if quite evident from these photomicrographs.

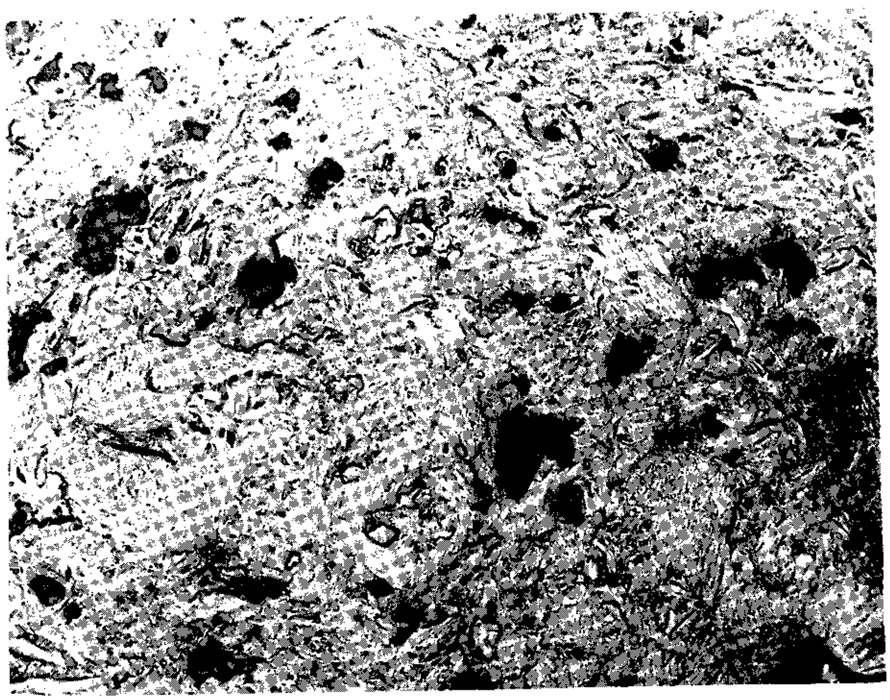

Figure 20. Photomicrograph of Grade RVA Graphite, Across Grain, 100X

Figure 21. Photomicrograph of Grade ZTE Graphite, Across Grain, 100X

5.2. Room Temperature Properties

The ZTE billet fabricated in Trial Number 2 was cut into samples for physical property measurement and the results are presented in Table 8. For comparison purposes the physical properties of RVA graphite are also included in Table 8.

Table 8. Room Temperature Properties, 30-Inch Diameter Grade ZTE Graphite, Trial Number 2

	ZTE			RVA*		
Property	N	Ave.	Std. Dev.	N	Ave.	Std. Dev.
Bulk Density, g/cc						
w. g.	108	1.96	0.015	117	1.84	0.016
a. g.	-	-	-	-	-	-
Electrical Resistivity, 10^{-4} ohm-cm						
w. g.	65	8.94	0.59	55	12.06	0.34
a. g.	41	20.40	0.25	62	15.65	0.66
Young's Modulus, 10^6 lbs/in^2						
w. g.	65	2.444	0.205	39	1.878	0.0070
a. g.	41	0.800	0.280	62	1.349	0.092
Flexural Strength, lbs/in^2						
w. g.	64	4335	264	44	3735	301
a. g.	41	2316	278	42	2925	276
Compressive Strength, lbs/in^2 ($^1/_2$-inch diameter by $^1/_2$-inch length)						
w. g.	10	8350	482	10	10420	491
a. g.	10	12035	460	10	10505	680
Thermal Expansion, 20 to 100°C, $\frac{\Delta L}{L}$ x 100						
w. g.	4	0.006	-	4	0.013	-
a. g.	4	0.054	-	4	0.022	-

* Block A-24 [5]

6. LIST OF REFERENCES

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