NAA-SR-2293
COPY

SOME PHYSICAL PROPERTIES OF HIGH DENSITY GRAPHITES

ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.

NAA-SR-2293
METALLURGY AND CERAMICS
26 PAGES

SOME PHYSICAL PROPERTIES OF HIGH DENSITY GRAPHITES

BY

A.E. MILLER

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8
ISSUED: MAY 15, 1958

DISTRIBUTION

This report has been distributed according to the category "Metallurgy and Ceramics" as given in "Standard Distribution Lists for Unclassified Research and Development Reports" TID-4500 (13th Edition), January 15, 1957. A total of 580 copies was printed.

TABLE OF CONTENTS

		Page No.
	Abstract	4
I.	Introduction	5
II.	Apparatus and Procedure	5
III.	Discussions and Results	16
IV.	Conclusions	23
	References	26

LIST OF FIGURES

1. Permeability Test Apparatus 8
2. High Temperature Tensile Test Apparatus 9
3. Graphite Helix Heating Element 11
4. Graphite Tensile Specimen 13
5. Hydraulic Circuit for Tensile Test Apparatus 14
6. Short-time Breaking Strength of Various Grades of Graphite as a Function of Temperature 20
7. Short-time Breaking Strength of AUF Graphite. 21
8. A Typical Density Profile of Extruded AUF Rod 22
9. Typical Tensile Failure of Graphite 24

ABSTRACT

The short-time tensile strength of a number of grades of special high density graphite was measured at room temperature and at 2000° C. Measurements of density and fluid permeability were made at room temperature. Included for comparison are the values of these properties obtained on one of the better commercially available graphites before and after a furfural polymerization treatment.

The characteristic increase in strength with temperature was exhibited by all grades and, in general, the high density graphites were stronger and exhibited lower permeability than the commercial grade. Furfural treatment of the commercial grade significantly increased its strength so that it exceeded the strength of the high density grades. In addition this treatment increased the density and improved the permeability of this grade.

This work was completed early in 1953. Data are still of interest, although superior graphites are now available.

I. INTRODUCTION

Applications of artificial graphite as a refractory material in high-temperature heat-transfer systems as well as a moderating material in nuclear reactors has encouraged the development of artificial graphites posessing improved physical properties. In particular, attempts have been made to increase density and to reduce permeability. It is expected that higher density would be accompanied by decreased porosity, increased strength, and probably decreased permeability. Low permeability and high strength are of major importance when graphite is used as a piping and structural material in high-temperature liquid-metal heat-transfer systems. At the same time high density, with its associated decreased diffusion lengths, is directly applicable in improving the performance of graphite as a reactor moderating material.

Appreciable effort has been expended at Atomics International in the past, on all phases of graphite technology including the measurements of physical properties and the development of methods for improving physical properties of commercial graphites. One of the most promising methods thus far developed for improving density and permeability characteristics consists of impregnating graphite with furfural, polymerizing the furfural, and baking to convert the resin to a carbonaceous material within the pores of the graphite.

Measurements are reported here of the density, permeability, and short-time tensile strength of a selected series of some promising special high density graphites available commercially. Also included for comparison are the values of these properties, before and after furfural polymerization treatment, obtained on one of the better commercial graphites.

II. APPARATUS AND PROCEDURE

A. DENSITY

Apparent or bulk density was calculated after weighing on an analytical balance accurately machined specimens of known volumes. The specimens were either small cylinders or tubes. This method has proved to be more satisfactory than the displacement-of-water method where partial filling of the pores decreased the accuracy obtainable or the displacement-of-mercury method where non-wetting of the surfaces also decreased accuracy obtainable.

B. PERMEABILITY

The use of graphite for pipes and other components in high-temperature liquid-metal heat-exchange systems requires that the graphite contain the liquid metal without leaking. Permeability, which is a measure of the ease with which a fluid will flow through a porous medium, is a function of the structure of the porous medium only and is independent of the nature of the flowing fluid. Derivation of the permeability equation, sometimes known as Darcy's Law, is presented in detail by Muskat.[1] For the flow of an ideal gas through a porous medium the permeability is given by the following relationship:

$$K = \frac{U\bar{Q}L}{A\,(P_1 - P_2)}$$

or for radial flow

$$K = \frac{UQ\text{Ln}\,\frac{D_o}{D_i}}{2h\,(P_1 - P_2)}$$

where:

K = permeability in Darcys

U = viscosity in centipoise

$\bar{Q}$ = flow rate of dry gas at average pressure $\left[\frac{P_1 + P_2}{2}\right]$ in $\frac{cm^3}{sec}$

A = area normal to flow direction in cm^2

P_1 = absolute inlet pressure in atmospheres

P_2 = absolute outlet pressure in atmospheres

D_o = outside diameter in cm

D_i = inside diameter in cm

L = length parallel to flow direction in cm

h = length of tube in cm

These equations are valid only in the region of viscous flow where pressure drop is directly proportional to the gas velocity in the flow passages (connecting pores). If the velocity is such that the flow is turbulent the pressure drop becomes proportional to some other power of the velocity. Under such conditions the permeability appears to vary with changes in velocity when the above equations are used. In these experiments the possibility of obtaining erroneous results, by taking measurements in the turbulent region, was eliminated by using low flow rates and repeating the test on each specimen at not less than three different rates of flow.

Permeability was determined by measuring pressures and flow rates and utilizing the above equations. The equipment was arranged as shown in Fig. 1. Inlet air, controlled by a diaphragm-type pressure regulator, was dried by a desiccant before it passed through the specimen. The absolute pressure of the inlet air was obtained by adding to the atmospheric pressure, measured with an aneroid barometer, the inlet pressure measured by a test quality bourdon type pressure gage (U.S. Gage, 0-1550 mm, accuracy: ± 1/2 of 1% of indicated reading). Because of the low flow rates and therefore the small pressure drops in the connecting tubes, it was not necessary to measure the outlet air pressure. An insignificant error was introduced by considering this to be atmospheric pressure. Flow rate was determined by measuring the time required for the air to displace a known volume of water. This vapor saturated volume was then corrected to an equivalent volume of dry gas at the mean pressure. Both cylindrical and tubular specimens were tested. The cylinders, 0.82 inch-diameter and 0.50 inch-length, were mounted in tight fitting rubber hose. The tube specimens, 1.18-inch OD x 0.88 inch ID x 3.63 inch long, were sealed by "O" rings within a short length of pipe. Air was passed radially through the tubes from their inside to their outside surfaces.

C. TENSILE STRENGTH

Due to the limited quantity of the special grades of graphite available, short-time tensile strength tests were made at only two temperatures. Six specimens of each grade were tested at both 20° C and 2000° C.

The general arrangement of the tensile test equipment is shown in Fig. 2. This equipment with minor modifications can also be used for creep and

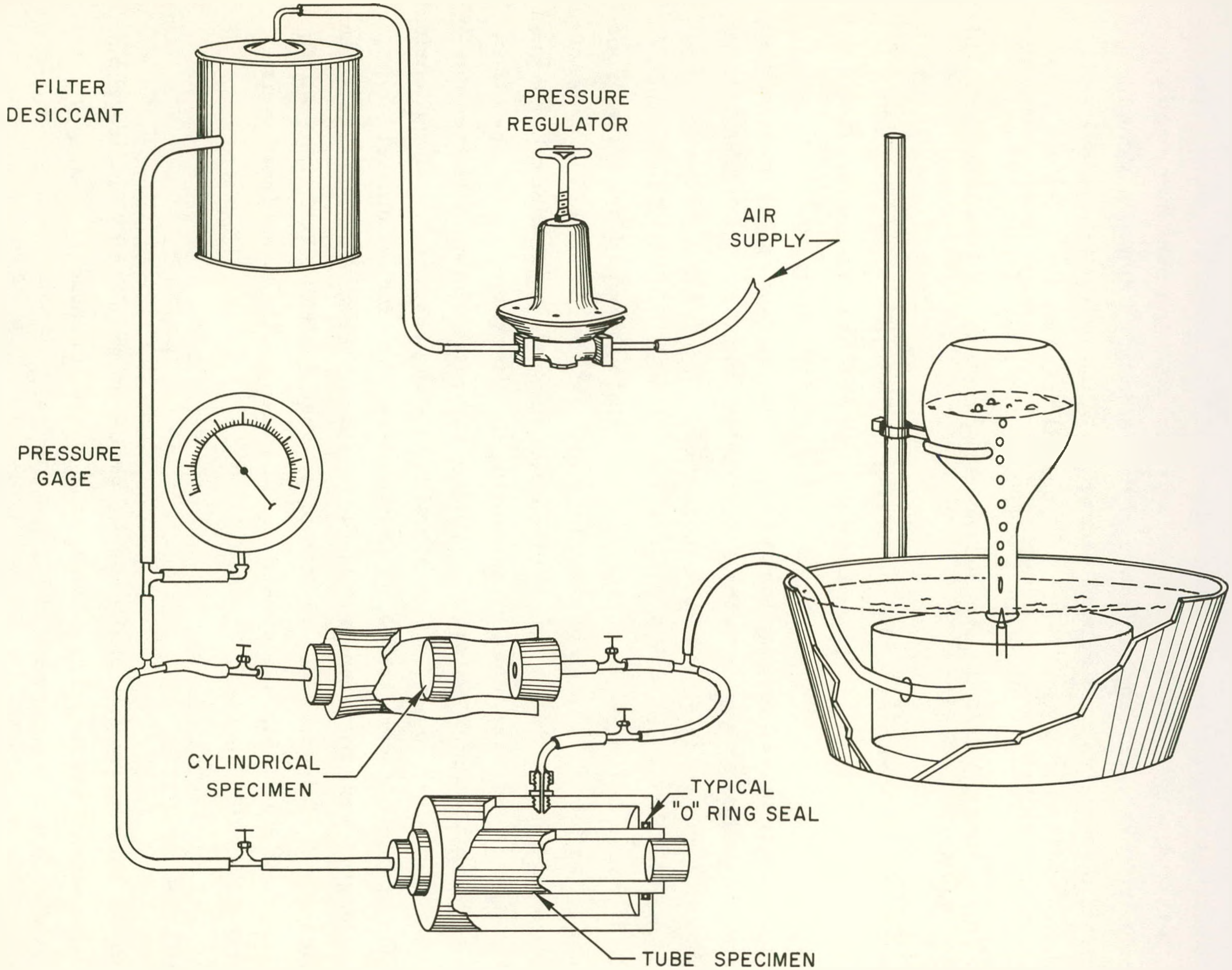

Fig. 1. Permeability Test Apparatus

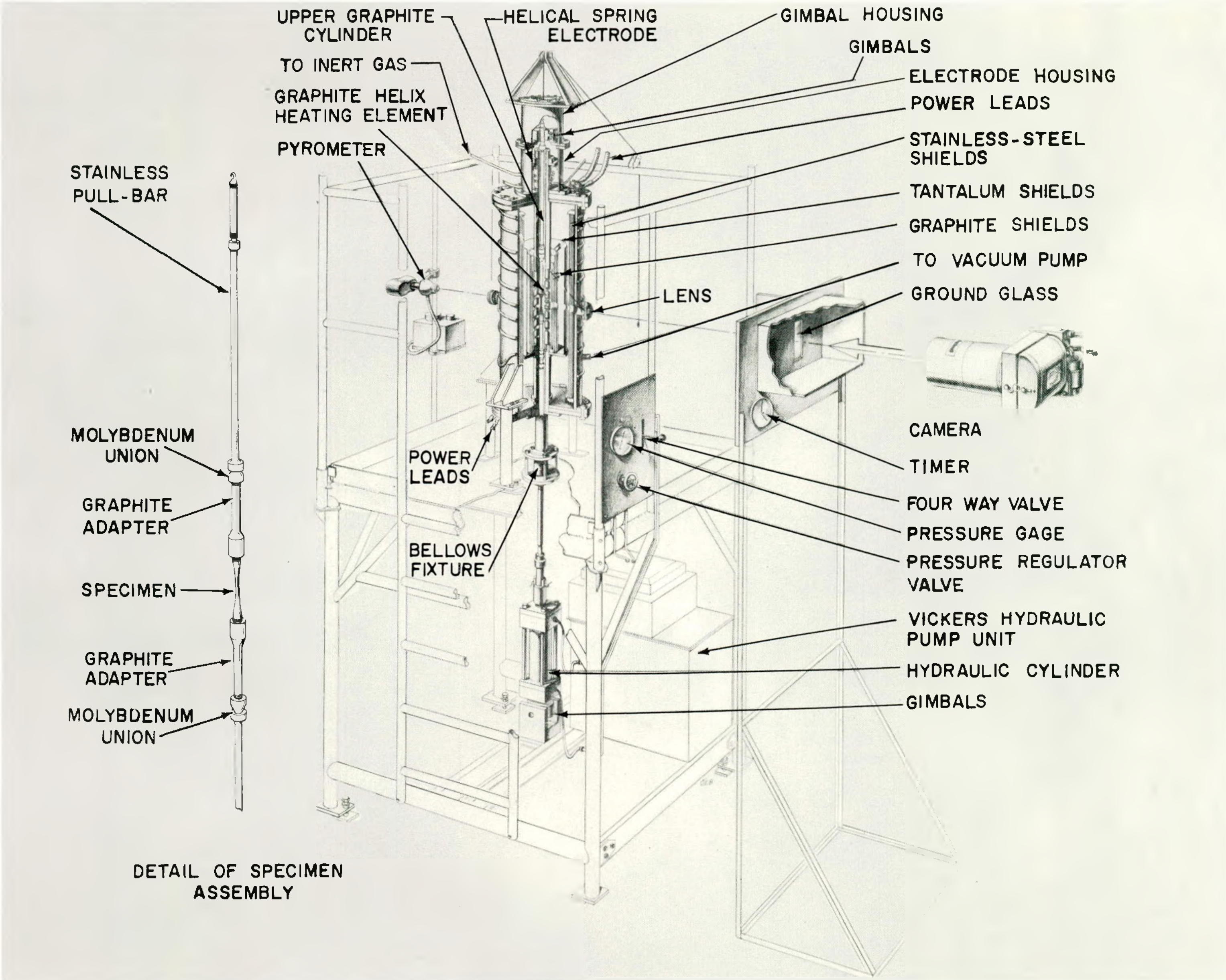

Fig. 2. High Temperature Tensile Test Assembly

stress-stain measurements. Tests may be made under vacuum, static inert gas, or dynamic inert gas atmospheres.

The furnace shell is a water-cooled, 12 inch-diameter steel pipe closed at each end with a water-cooled flange. Two diametrically opposed windows permit observation of the test section of the specimen. Attached to the top flange is the electrode housing in which the upper electrode is mounted. The water cooled electrode is made of copper tubing wound in the form of a helical spring and has a brass disk brazed to one end. A graphite nut screwed onto the top of the upper graphite cylinder bears against this disk compressing the spring electrode. A graphite helix heating element is threaded into the bottom of the upper graphite cylinder and into the top of the lower graphite cylinder which in turn is threaded into the bottom flange. This flange serves as the second electrode.

Heating is accomplished by passing direct current from a 36 kw (30 volts, 1200 amperes) motor generator set through the graphite cylinders to the helix heating element. This element, Fig. 3, which has a lead of 2/3 of a thread per inch and is 12-1/2 inches long, requires 22 kw (22 volts, 1000 amperes) to maintain the specimen at 2000° C. The helix has an outside diameter of 2-1/4 inches and an inside diameter of 1-3/16 inches. Drilled through one side of the helix in line with the pyrometer window is a 3/8 inch-diameter hole. Facing the opposite window is a 1-1/4 inch by 1/2 inch slot in the helix. The helical shape for the heater was chosen, after other shapes were considered, because it best fulfilled the severe requirements of strength, size, and flexibility, and because it permits the specimen to be observed for temperature and strain measurements.

A concentric arrangement of two graphite, three tantalum, and four stainless-steel, thin-wall tubes provides radiation shielding. Shield material was chosen on the basis of estimated shield temperatures. These concentric shields, which contain 1-1/4 inch-diameter holes in line with the windows, comprise the only thermal insulation in the furnace.

Directly above the electrode housing but electrically insulated from it is another housing which contains the top gimbals. The top of this housing can be removed, as shown in Fig. 2, to permit placing the specimen into the furnace. In order to assemble, it is first necessary to lower the upper stainless-steel

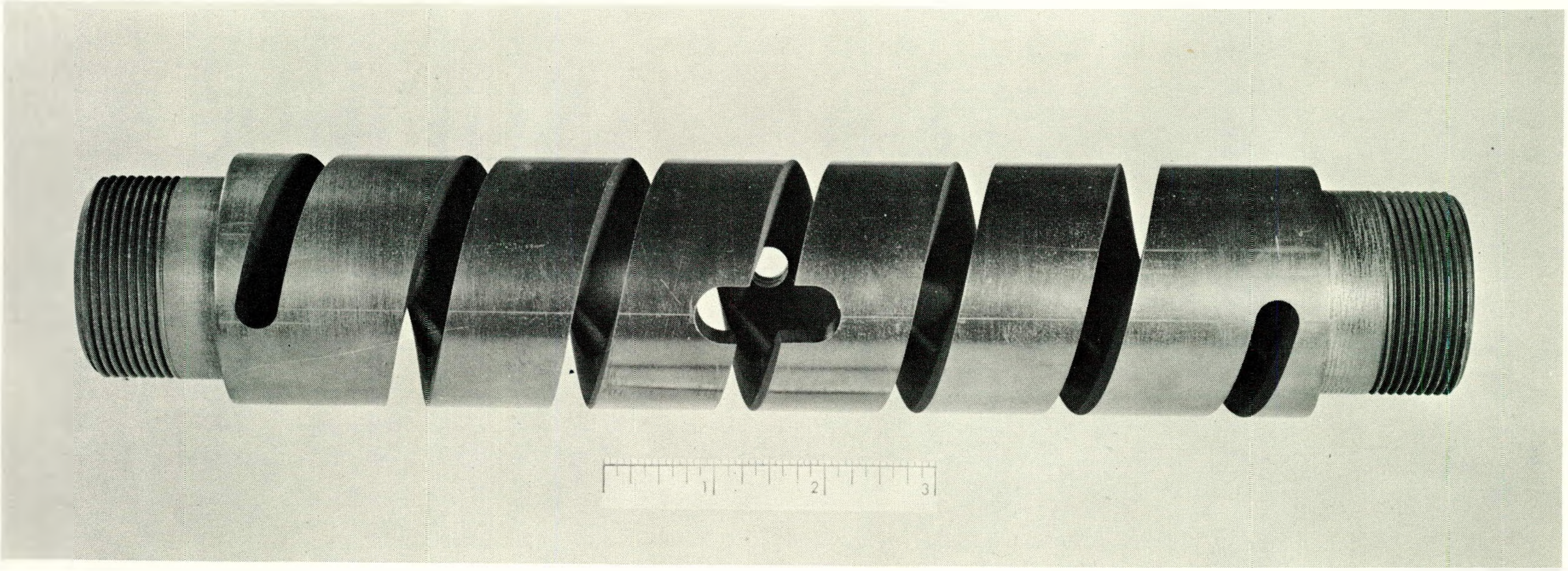

Fig. 3. Graphite Helix Heating Element

pull-bar,* with its attached graphite adapter, down through the core of the furnace by means of a flexible steel cable which runs up over a pulley and down under the stand. The specimen, Fig. 4, whose diameter and cross-sectional area in the test sections is 0.2523 ± 0.0005 inches and 0.050 square inches respectively, is screwed into the top graphite adapter which is now extending out through the bottom of the furnace. Next the lower graphite adapter with its attached stainless-steel pull-bar is attached to the specimen. The whole assembly is then pulled up through the furnace and attached to the top gimbals. At this time the center of the specimen is directly opposite the windows. When it is desired to perform the test under vacuum or under a static inert atmosphere a bellows fixture containing a sliding seal is attached to the bottom of the furnace with the lower pull-bar passing through the seal. This step is eliminated when the test is to be made under a flowing inert atmosphere. The hydraulic cylinder, already secured to the bottom gimbals,† is swung into position and attached to the specimen assembly.

A schematic representation of the hydraulic circuit is shown in Fig. 5. The essential components of this circuit are as follows:

1) 0-1000 psi, 3 gpm - Vickers Hydraulic Motor & Pump Unit

2) 0-100 psi, Hannifin Pressure Regulator Valve

3) 0-100 psi, ± 1/2 of 1%, 8-1/2 inch-Helicord Test Quality Pressure Gage.

4) 3-1/4 inch-bore, 6 inch-stroke, Miller Low Fiction Cylinder

With the specimen assembly supported by the top gimbals and attached at the bottom to the hydraulic cylinder, as described above, a tare load of 40 pounds was applied to the assembly in order to prevent warping while the specimen was being heated. When the test temperature was reached, as determined with a Leeds and Northrup disappearing-filament optical pyrometer, the assembly was loaded by manually adjusting the Hannifin pressure regulator valve. The apparent temperature indicated by the optical pyrometer was corrected for the emissivity of the graphite and the transmissivity of the window glass. A detailed development of these corrections is made by Malmstrom.[2]

---

*Both the upper and lower steel pull-bars are tubular in cross-section to minimize axial heat flow from the furnace.

†One side of the bottom gimbals housing is hinged to allow the cylinder to rotate out of the way to facilitate assembly.

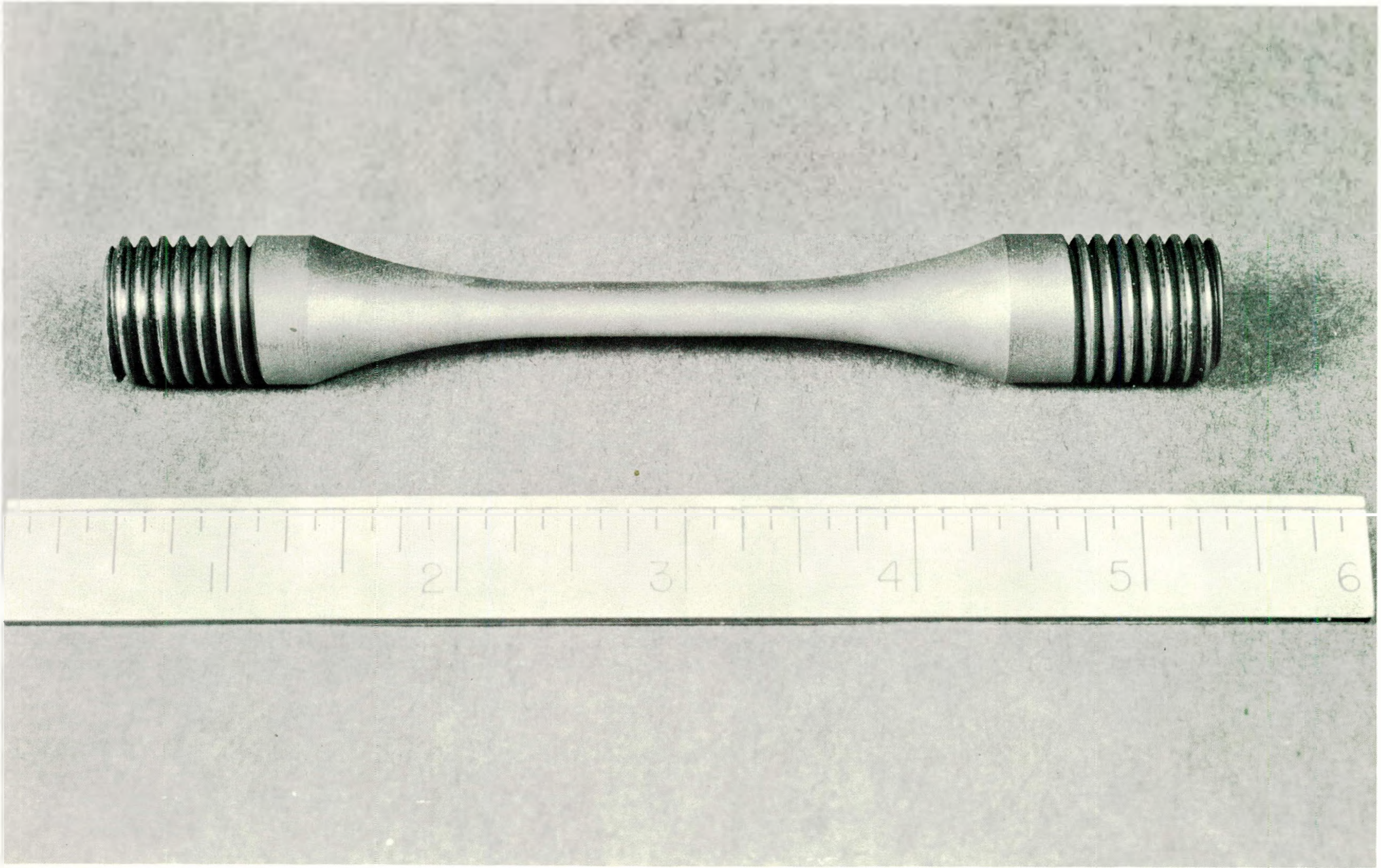

Fig. 4. Graphite Tensile Specimen

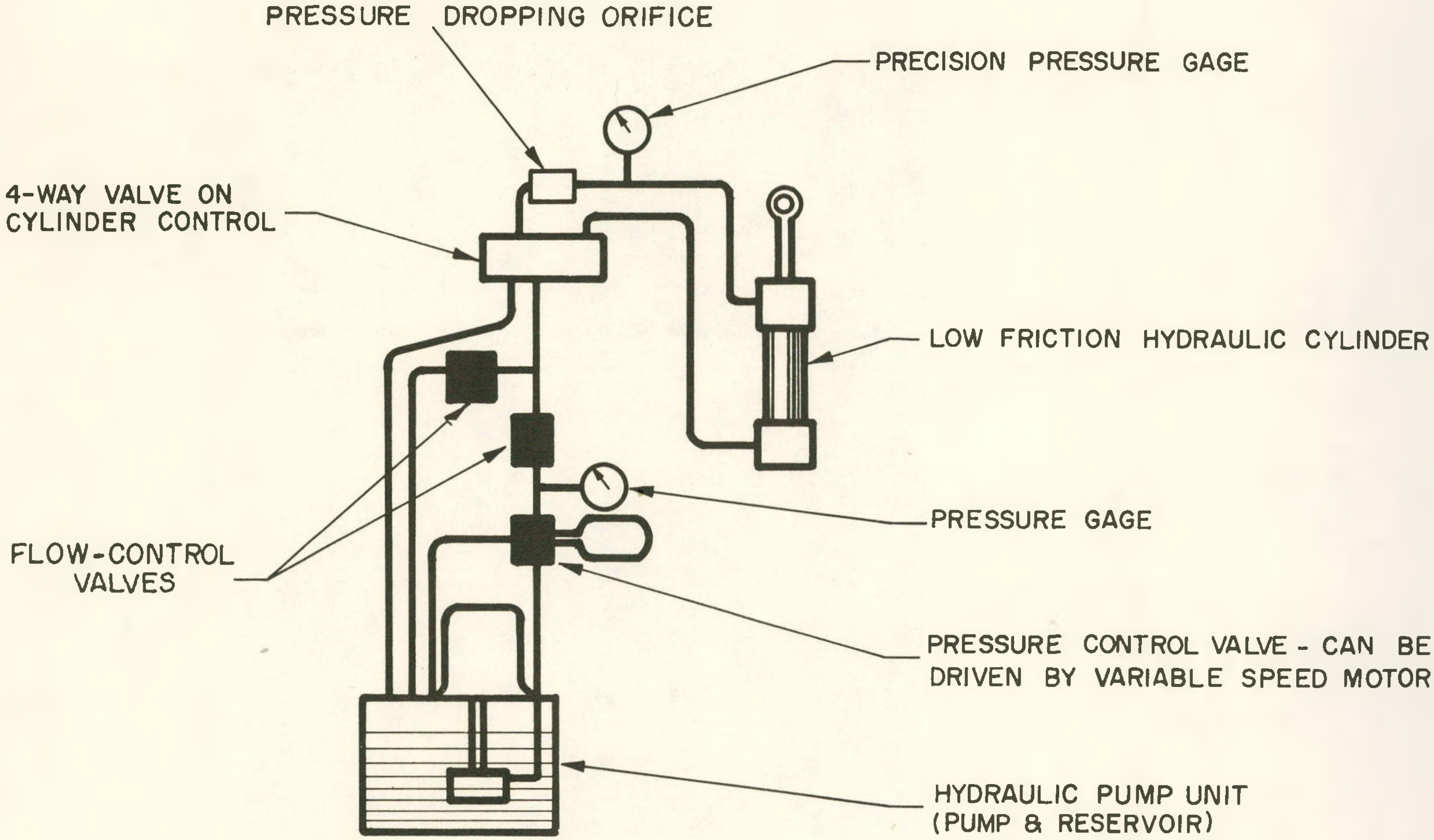

Fig. 5. Hydraulic Circuit for Tensile Test Apparatus

A stress loading rate of 3500 ± 350 psi per minute was used in these experiments. Tests performed with loading rates of 3000 and 4000 psi per minute showed no detectable difference in ultimate strength. Other factors causing spread in the strength data masked any difference due to loading rates in this range.

Ultimate strength was determined by converting the maximum gage reading, recorded by a maximum pointer, to load on the specimen. From this value cylinder friction was subtracted and the dead weight of the pull-bar assembly was added. Considering gage tolerance, variation in cylinder friction, and machining errors the maximum strength error is estimated to be ± 100 psi.

As mentioned previously, the furnace can be used for high temperature creep and stress-strain experiments, as well as for tensile strength measurements. With one of the windows replaced by a lens, an image of the specimens gage length can be projected on a ground glass screen. By simultaneously photographing the screen and an illuminated timer, creep information is recorded. Stress-strain measurements may be made by replacing the timer with a pressure gage that indicates the tensile load. The camera intended for use in conjunction with this equipment is a modified Air Force K-24 Aerial Camera with a 7-inch f2.3 lens. Although no creep measurements have as yet been made with this particular equipment, it is expected that it will operate satisfactorily as other somewhat similiar apparatus has previously been used successfully at this laboratory.[2,3]

In its original design the current-carrying circuit was different from that described above. Originally, both the upper and lower graphite cylinders were fixed to their respective flanges. The heating element fitted into tapered holes in each of the cylinders and depended upon pressure between the element and cylinders to maintain electrical contact. The element was compressed in assembly and it was expected that elongation due to thermal expansion would maintain good contact. It was found that the additional compression at high temperatures caused the heater to creep to the extent that contact was broken upon cooling. To remedy this, the heater and cylinders were threaded together and the top graphite cylinder was lengthened and attached to a helical copper tube electrode. Thus, electrical contact was assured, and the stress in the heater was decreased by the flexibility of the electrode.

During the course of the experiment, it was found that a considerable number of failures occured in the graphite adapters. These failures took place in the threads which connected the adapters to the stainless-steel pull-bars. The failures were caused by the difference in thermal expansion of the graphite and the stainless steel. To overcome this difficulty, it was necessary to connect the stainless-steel pull-bars to the graphite adapters with molybdenum unions whose thermal expansion coefficient is between that of graphite and stainless-steel.

III. DISCUSSION AND RESULTS

Tensile strength, permeability, and density measurements were made on all special grades supplied as 1 inch-diameter rods. Permeability and density measurements were made on the other four grades obtained as tubes. The following is a list of the grades tested and of the manufacturers of these grades:

1) Experimental Grade 43051-1, National Carbon Company Research Laboratories, Cleveland, Ohio.

2) Experimental Grade 43051-3, National Carbon Company.

3) AUF, National Carbon Company.

4) Experimental Grade MGH,* Great Lakes Carbon Company, Morton Grove, Illinois.

5) Experimental Grade MGR,* Great Lakes Carbon Company.

6) Graphitar #2215, U.S. Graphite Company, Saginaw, Michigan.

7) Graphitar #48, U.S. Graphite Company.

8) Graphitite, Graphite Specialties Corporation, Niagara Falls, New York.

9) Regraphitized Graphitite, Graphite Specialties Corporation.

10) Multiple-treated Regraphitized Graphitite, Graphite Specialties Corporation.

11) P.M. Type 02-A-142 Untreated, National Carbon Company.

---

*The grades designated as MGH and MGR were developed by Great Lakes Carbon under a subcontract from this laboratory.

A method of decreasing the permeability of small pieces (sections less than 3/4 of an inch in diameter) of graphite by impregnating it with furfural ($C_2H_5O_2$) and subsequently polymerizing the furfural was utilized by Bennett and Pearlman.[4] Tensile specimens of grade AUF were impregnated under vacuum, polymerized with mineral acid, and then baked at 1000° C in a hydrogen atmosphere.* It was felt that if this impregnated material bonded to the original graphite, instead of just filling the voids, an increase in strength as well as the reported decrease in permeability would be found. For this reason a set of AUF specimens were machined, treated, and tested. Untreated specimens from the same batch of 1 inch-diameter AUF were also tested as a control. (This grade had previously been tested by Miller and Malmstrom.[5])

The results of the strength measurements are presented in Table I. In Table II, the density and permeability of these grades as well as the four other special grades are shown. Strength characteristics of a number of commercially available National Carbon Company graphites, previously reported by this laboratory[5,6] are shown in Fig. 6 and 7 for comparison. The characteristic increase in strength with temperature is exhibited by these experimental grades. Grades 43053-1, MGH, Graphitar 2215, and AUF are stronger than ECA which was the strongest grade previously tested. Grade ECA is no longer manufactured and has been replaced by the manufacturer by grade AUF, stated to be of similar quality.

The difference in the strength of AUF, as shown in Fig. 7 and in Table I is attributed to the difference in density of the material used in the two tests. For the data presented in Table I the tensile specimens were made from 1 inch-diameter rods with an average bulk density of 1.70 g/cc. The specimens used in the plot shown in Fig. 7 were machined from a 12 inch-diameter cylinder with an average density of 1.62 g/cc. A typical density profile in a 12 inch-diameter cylinder, shown in Fig. 8, indicates that the density difference was to be expected. Evidently in the extruded grades the greatest density and strength is attained near the walls of the extrusion mold.

It is interesting to note that the furfural treatment increased the strength of AUF (16.5% at room temperature and 20.8% at 2000° C) to a point beyond that of any of the high density or special grades. In addition the treatment appreciably

*It was found during the course of this series of tests that firing in a hydrogen atmosphere increased the carbon yield and reduced oxidation.

TABLE I

TENSILE STRENGTH

Grade	Temperature °C	Minimum psi	Average psi	Spread psi
43051-1	20	2933	3175	506
	2000	3534	4133	1028
43051-3	20	4239	4510	605
	2000	5703	6423	1362
MGH	20	1189	3540	3443
	2000	5678	6484	1581
MGR	20	1642	2757	3057
	2000	5451	6177	2896
Graphitar-2215	20	4318	4628	652
	2000	5780	6369	1276
Graphitar-48	20	2933	3243	572
	2000	3800	4370	1357
AUF	20	4017	4112	207
	2000	6004	6081	131
Furfural-treated AUF	20	4491	4797	444
	2000	6860	7346	775

TABLE II

DENSITY AND PERMEABILITY

Grade	Density g/cc	Shape	Permeability millidarcys
43051-1	1.92	Cylinder	0.17 to 1.64
43051-3	1.94	Cylinder	0.20 to 0.90
MGH	1.91	Cylinder	0.73 to 10.77
MGR	1.78	Cylinder	0.33 to 29.50
Graphitar 2215	1.84	Cylinder	0.67*
Graphitar 48	1.84	Cylinder	1.27*
AUF	1.70	Cylinder	3.98†
Furfural-treated AUF	1.77	Cylinder	0.35*
02-A-142 Untreated	1.85	Tube	0.051 to 0.054
Graphitite	1.84	Tube	0.2073*
Regraphitized Graphitite	1.82	Tube	0.012*
Multiple-treated & Regraphitized Graphitite	1.84	Tube	0.0039*

*Only one sample tested.
†AUF is known to vary between 3.98 and 10.0 millidarcys depending on the size of the original blocks and the position in blocks from which it is taken.

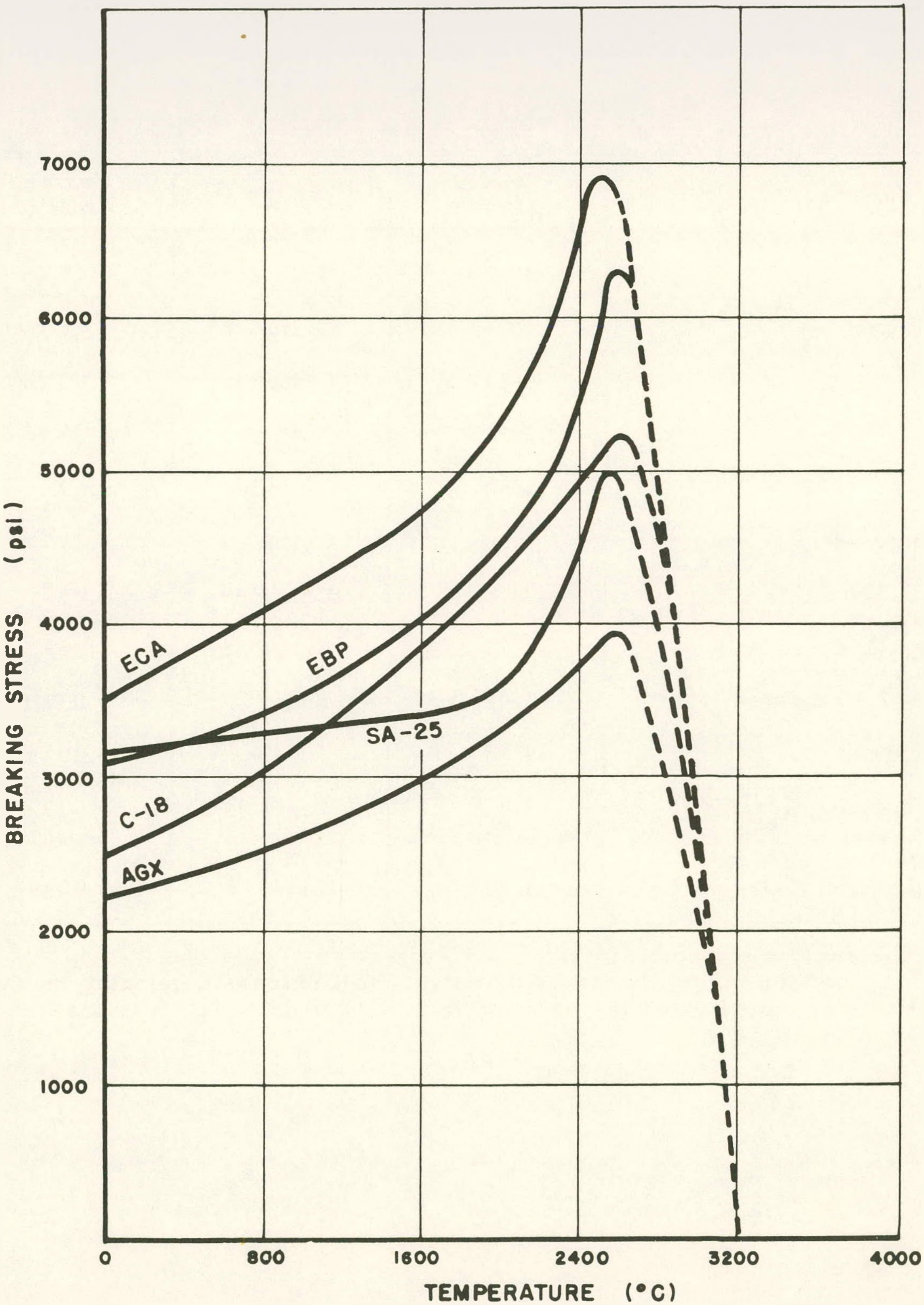

Fig. 6. Short-time Breaking Strength of Various Grades of Graphite as a Function of Temperature

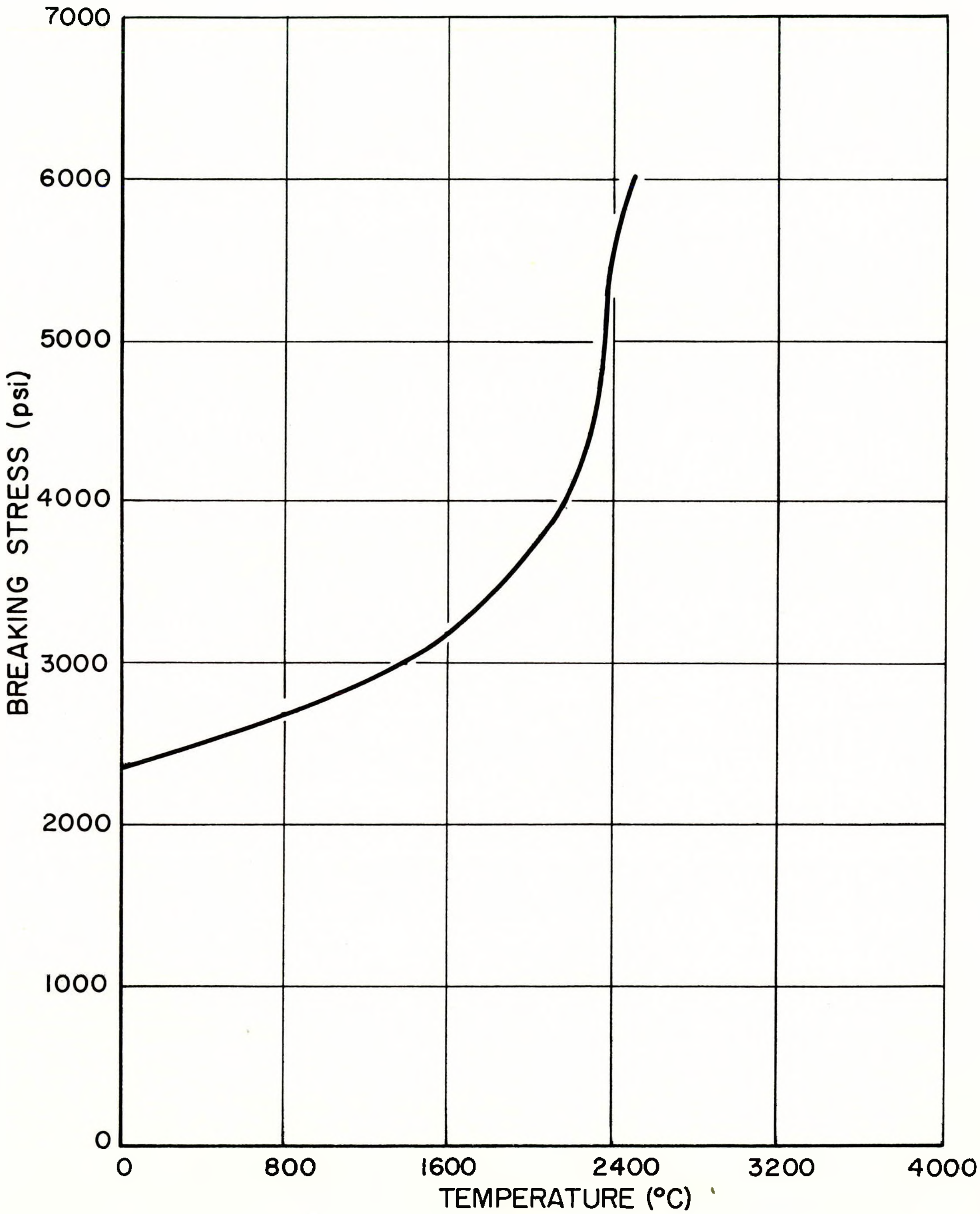

Fig. 7. Short-time Breaking Strength of AUF Graphite

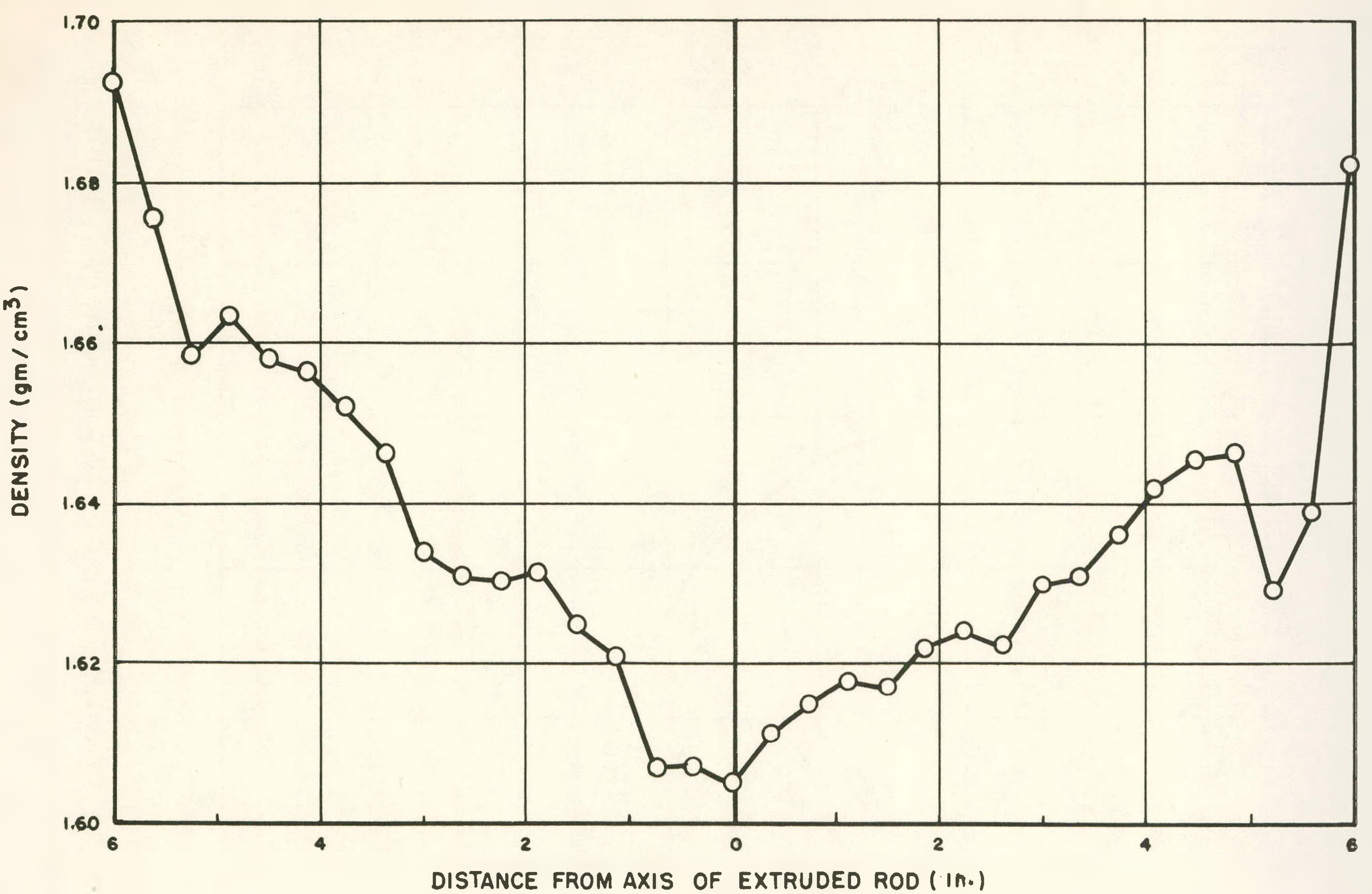

Fig. 8. A Typical Density Profile of Extruded AUF Rod

improved the density and permeability of AUF. The increased strength spread of the furfural treated AUF is attributed to variations in effectiveness of the treatment.

Laminations or cracks, see Fig. 9, which are characteristic of high density graphites manufactured in any but the smallest solid shapes, were exhibited in considerable quantities by the high density grades tested (43051-1, 43051-3, MGH, and MGR). The number and size of these flaws varied greatly throughout each grade and are believed to be a major cause of the large spread in the permeability and strength data obtained. The unusual nature of the tensile fracture of these grades as compared to what previously had come to be considered "normal" (Fig. 9) graphite fracture was also due to these imperfections. Failure occurred across the planes of minimum area between the cracks.

Communication with National Carbon Research Laboratories indicated that they were not able to fabricate solid sections of high density graphite free of such laminations but probably could extrude tubes of this material with improved properties.[7] Assuming that the other manufacturers can also obtain better properties when extruding tubes, the permeability of the four grades received as tubes should have been superior to that of the rod shaped grades. Examination of Table II shows this to be the case. Conversely, it might be expected that if these four grades were available in solid shapes, their permeability would increase.

IV. CONCLUSIONS

Some of the experimental grades which are as yet available only in small sizes, are superior in average strength to the majority of the more standard commercial graphites. How the properties of these grades will be affected by size is unknown. High density graphites exhibit laminations or cracks which account for large variations in strength. Considering average strength as well as spread in the breaking strength, grades 43051-3 and Graphitar 2215 are by far the best of the special graphites. AUF graphite in 1 inch-diameter specimen size is about equal to the two above mentioned grades and is available in commercial quantities.

The furfural treatment increased the strength of 1 inch-diameter AUF to where it is definitely stronger than any graphite tested to date. It is felt that this improvement warrants continuation of the development work on this process.

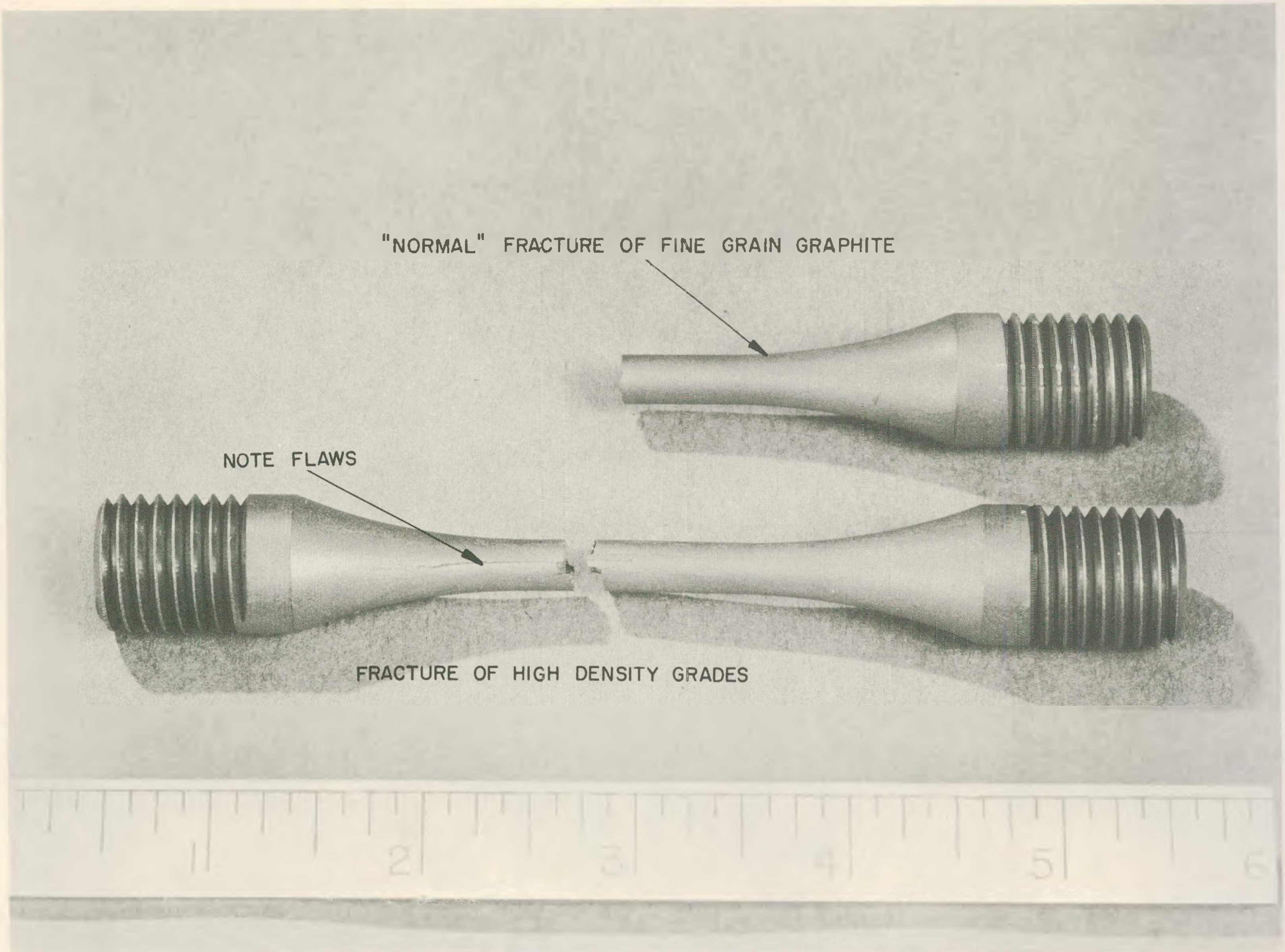

Fig. 9. Typical Tensile Failure of Graphite

The four grades thus far available only in the shape of tubes have the lowest permeability of all grades tested. It would be desirable to obtain these in the form of rods to permit strength measurements. There is the likelihood that if these grades were made in solid bars, their permeability would be greater. Permeability of furfural-treated AUF is as good as any of the special grades with the exception of these four grades.

When considering only those graphites for which strength, permeability, and density information is available, it appears that furfural-treated AUF is most suitable for use as piping and heat exchangers in high-temperature liquid-metal systems. It is possible, however, that the four grades which have lower permeability, and for which no strength data is available may be superior. In applications where density is of major importance and the other properties secondary, one of the higher density grades may be more suitable.

REFERENCES

1. M. Muskat, Flow of Homogeneous Fluids, Chapter II, (J. W. Edwards, Inc., Ann Arbor, Michigan, 1946),
2. C. R. Malmstrom, "Tensile Strength and Creep of Graphite up to the Sublimation Point," NAA-SR-2, December 1, 1947
3. R. Keen, "The Creep Characteristics of ECA Graphite," NAA-SR-51, January 26, 1950
4. G. A. Bennett and H. Pearlman, "Experiments on Graphites of High Density and Low Permeability," NAA-SR-22, April 13, 1953
5. A. E. Miller and C. R. Malmstrom, "Tensile Strength of Uranium-Impregnated Graphite," NAA-SR-151, September 14, 1951
6. L. Green Jr., "Measurement of Young's Modulus on Grade AUF Graphite at Elevated Temperatures," NAA-SR-98, December 7, 1950
7. Private Communication from M. T. Jones, National Carbon Research Laboratories, to H. Pearlman, North American Aviation (unpublished, July 23, 1951)
8. C. R. Malmstrom, R. D. Keen and L. Green, Jr., "Some Mechanical Properties of Graphite at Elevated Temperatures," J. Appl. Phys. 22, 593, (1951)