IITRI Project G6003

Quarterly Report No. 1

GRAPHITE-METAL COMPOSITES

National Aeronautics and
Space Administration
Washington, D.C.

IIT RESEARCH INSTITUTE
10 West 35th Street
Chicago, Illinois 60616

Contract No. NASr-65(09)
IITRI Project No. G6003

GRAPHITE-METAL COMPOSITES

IITRI-G6003-1

Quarterly Report
for the period
August 1 to November 1, 1965

Prepared for

National Aeronautics and Space Administration
Washington, D.C. 20546

October 18, 1965

GRAPHITE-METAL COMPOSITES

I INTRODUCTION

This program was originally conceived to investigate liquid phase sintering in graphite-metal composites during hot pressing at elevated (2800°-3000°C) temperatures. The results of the first year's studies[1] have shown that a strong bond is obtained by formation, diffusion, and subsequent recrystallization of a carbide-carbon eutectic phase in selected compositions. Flexural strengths of greater than 10,000 psi at 2000°C were exhibited by graphite systems containing niobium, hafnium, or molybdenum.

The purpose of this year's work is to extend the compositional studies and to fully characterize the more interesting composites and their properties. The guest metal phases with which we will be most concerned are niobium, hafnium, molybdenum and tantalum. In addition, systems incorporating zirconium, titanium, boron and uranium will be examined. Two metal additives which have not received previous study, vanadium and tungsten, will also be investigated.

During this period, modifications have been introduced into the fabrication equipment for more precise control over the hot pressing technique. Attempts have been made to prepare graphite bodies using no metal additive in order to establish the properties available without guest carbide phases. In addition, different compositions have been evaluated for density and microstructure to assess the degree of uniformity in a pressed billet.

---

(1) Y. Harada, "Graphite-Metal Composites," IITRI-G6003-F-4, July 28, 1965 (Contract No. NASr-65(09).

II. RESULTS AND DISCUSSION

A. Equipment

Certain refinements have been made and others will be incorporated into the hot pressing apparatus for closer control of variables. A difficulty encountered in the past has been the presence of volatiles in the sight tube at elevated temperatures. The resulting attenuation of transmittance has caused problems in accurate pyrometry. This handicap has been virtually eliminated by building in an improved venting system for the gas purge in the sight tube which rapidly sweeps away the error-inducing vapors.

Our pyrometry has been calibrated closely using an NBS calibrated pyrometer. Experiments have shown that some deviation occurs at the higher temperatures commencing at about 2500°C with increasing departure up to about 70°C at 3100°C. The proper corrections will be incorporated into all future runs, and calibration will be conducted periodically.

Other studies have been conducted to determine more precisely the temperature of a sample during processing. As shown in Figure 1, a run was conducted in which temperature indicated in the sight tube (T_1) and in the actual sample locale (T_2) were monitored simultaneously. The "sample" was a graphite mold plunger with the desired optical and purge gas paths drilled in. A graph (Figure 2) showing the comparative temperatures reveals a lag in T_2 at the lower temperature during heating. This is to be expected since induction heating occurs from the outside, or skin of the susceptor, inward. At higher temperatures in excess of 2500°C, the lag is less evident and equilibrium seems to maintain throughout the system for the remainder of the heating cycle. During cooling, it would appear that the "sample" loses heat at a slightly more rapid rate than indicated through the sight tube. Thus, our method for measuring temperature appears quite valid.

Application of pressure during processing has been done manually to date. The apparatus is now being equipped with a constant pressure device for more uniform, continuous pressing. Other anticipated modifications in processing procedure include soaking at ~2000°C for 30 min and periodic release of pressure during heating to permit easier escape of volatiles, both from the mold and from the raw coke mixture being pressed.

B. Petroleum Coke Studies

The direct relationship between increasing metal content and improved strengths has been shown for a variety of graphite-metal composites. The present experiments were conducted to determine the densification and strengths obtainable by hot pressing the raw petroleum coke (-325 mesh, <44 microns) alone with no metal additives. Two tests were conducted in which the samples were heated to 3000°C at 3000 psi in 1 hr and 15 min, at which time the runs were concluded.

In both runs, shear failure occurred in the billet sample during hot pressing. Examination of a sample after sectioning the mold in half revealed gross extrusion of material around the punches as shown in Figure 3. The same sample is shown with the fractured conical section removed in Figure 4. In addition, it was observed that the mold wall had undergone deformation to accommodate bulging of the sample in a direction perpendicular to the force applied during the hot pressing. It was also observed that the two punches were no longer in a uniaxal relationship to each other.

The flow of material around the punches was due not only to the high plasticity of coke at these temperatures, but also to differential thermal expansion between the mold and punch materials. Apparently the misalignment of punches was aggravated by the extrusion, and the resulting non-uniaxial loading gave rise to shear failure along slip planes.

Samples were sectioned from the pieces of the two billets for property measurements. The geometry of the fractured pieces precluded obtaining of samples in the across grain direction. Some of the properties are presented in Table I, for the two runs are designated CPC-A and CPC-B.

TABLE I

PROPERTIES OF HOT PRESSED PETROLEUM COKE

Run	Density, g/cc	Flexural Strength, psi	Lattice Parameters a_o	Lattice Parameters c_o
CPC-A	1.89	970	2.46	6.74
CPC-B	1.96	1170	2.47	6.76

Although fairly high densities were exhibited by the samples from both experiments, the strengths were quite low, showing poor bonding. This is in agreement with the findings in an earlier program at IITRI[(2)] in which extensive laminations and poor bonding were encountered in the hot pressing of coke. Their work also showed that good densification and high flexural strengths (2.05 g/cc, 5500 psi) were obtained only when a furfuryl alcohol binder was incorporated with the raw petroleum coke.

In examination by x-ray diffraction, an indication of graphitization is modulation of the (hk) 2-dimensional reflections. When the (10) and (11) reflections start to split into (100)-(112) respectively, it indicates that the parallel layer groups are beginning to assume ordered or graphitic relationship. Both CPC-A and CPC-B specimens exhibited sharp

(2) Y. Baskin et. al., "Study of the Mechanism of Failure of Rocket Materials and Materials Research," ASD-TDR-62-314, May 1962.

resolution of the 2-dimensional reflections into the (100)-(101) and (110)-(112) reflections. This coupled with nearly ideal graphite lattice parameters suggests a high degree of graphitization.

This experiment will be repeated using mold-plunger assemblies of closer tolerances to minimize misalignment of plungers and extension of material around the plungers. These results show, however, that although petroleum coke can be highly graphitized by this operation, C-C bonding is quite poor and additives such as metals are clearly necessary to provide good bonding.

C. Compositional Studies

In order for a graphite-metal composite to be of maximum utility, uniformity in properties must prevail throughout the body. Analyses of density versus location in the processed sample have been made for the three systems which have shown the highest flexural strengths, i.e., Nb-C, Hf-C and Mo-C. Density profiles were determined from samples sectioned in the with grain direction as illustrated in Figure 5. Thus the grids presented for the various compositions represent densities of ¼ x ¼ x 1¼-2 in. specimens.

1. Nb-C System

Among the Nb-C compositions, the only system which exhibited significant heterogeneity was the 50 wt% Nb system pressed at 3000°C. The grid of densities for this composition appears in Table II. Two trends are evident: density increases toward the bottom of the sample and also toward the central axis.

TABLE II

DENSITY PROFILE OF 50 WT% Nb-GRAPHITE PRESSED AT 3000°C

	Row A	Row B	Row C
Top layer	3.18 g/cc	-	-
	3.26	-	-
	3.33	-	3.06
	3.39	3.25	-
	3.47	-	3.31
	3.51	-	3.46
Bottom layer	3.54	-	-

The relationships between strength and density are quite interesting. Data for individual specimens appear in Table III. The figures suggest an inverse relationship which

TABLE III

PROPERTIES OF SAMPLES OF 50 WT% Nb-GRAPHITE PRESSED AT 3000°C

Sample	Density, g/cc	Flexural Strength, psi
T1	3.18	16,870
T2	3.26	16,500
T4	3.39	15,660
T6	3.51	10,240

is the reverse of the usual case. These data indicate that the higher density samples are not as well bonded as those of lower density.

Microstructures of a sample in the top layer of Row A (sample T1, 3.18 g/cc) and of a sample near the bottom (T6, 3.51 g/cc) appear in Figure 6 and 7. It is quite clear that the "denser" piece has larger carbide particles which occupy a greater volume percent, thus yielding the higher density due to the additional weight. In other words, the 3.51 g/cc density sample probably contains more than 50 wt% metal and the 3.18 g/cc density specimen, less than the experimental 50 wt% niobium. This segregation may have been caused during loading of the mold prior to pressing. This operation involves tamping of the mixture plus vibration of the mold, and this could result in the heavier, or larger carbide particles migrating toward the bottom of the mix.

It may be argued that the upper, or lower density samples show smaller carbide grains due to greater carbide solution into the graphite matrix and have actually densified to a greater extent. This is probably correct in view of the strength data. However, if carbide distribution were uniform throughout the complete composite, the specimens from the upper portions of the billet should exhibit higher densities than the lower sections; since the opposite is true, it is quite apparent that segregation of carbide grains has occurred.

It is apparent from this analysis that carbide segregation can occur, and density measurements alone can be misleading. Thus, higher density values do not necessarily mean higher densification, and other evaluations such as microstructural studies and strength measurements are necessary for an accurate picture of the conditions which prevail.

Density profiles were also obtained for 2¼ in. diameter x 3/4 in. disc specimens of 50 wt% Nb pressed at 3000°C. Sectioning along the plane perpendicular to the pressing direction yielded six samples each for composite A (using Nb as the raw material) and composite B (using NbC in the raw mix). Density and strength

data are presented in Table IV; sample numbers represent the position in the disc, i.e., A-1 and A-6 are the sections near the edges whereas A-4 and A-5 represent the center. The higher

TABLE IV
PROPERTIES OF SAMPLES OF 50 WT% Nb-GRAPHITE DISCS PRESSED AT 3000°C

Sample	Density, g/cc	Flexural Strength, psi
A-1	2.75	12,340
A-2	2.85	-
A-3	2.90	-
A-4	2.89	11,780
A-5	2.85	12,020
A-6	2.75	-
B-1	3.05	11,460
B-2	3.24	-
B-3	3.35	-
B-4	3.37	9,470
B-5	3.31	9,810
B-6	3.16	-

densities toward the center of these disc samples correspond to the data for the larger billets. The inverse relationship between density and flexural strength is again evident.

Micrographs of samples A-1 and A-4 appear in Figures 8 and 9, and samples B-1 and B-4 in Figures 10 and 11. In both composites, the "denser" center sections (A-4 and B-4) contain larger carbide grains which probably influence the density values.

2. Hf-C System

In general, hafnium carbide containing systems displayed greater density variations within individual billets, among the various metal-graphite systems studied. Compositions containing 50 wt% hafnium showed the following density profiles as outlined in Tables V and VI. The same general trends in

TABLE V
DENSITY PROFILE OF 50 WT% Hf-GRAPHITE
PRESSED AT 3000°C

	Row A	Row B	Row C
Top layer	2.84 g/cc	-	2.78
	2.81	-	2.82
	2.82	-	2.79
	2.87	2.86	2.86
	3.18	3.12	3.07
Bottom layer	3.59	-	3.38

TABLE VI
DENSITY PROFILE OF 50 WT% Hf-GRAPHITE
PRESSED AT 2800°C

	Row A	Row B	Row C	Row D
Top layer	2.87 g/cc	2.76	2.51	2.33
	3.17	3.13	2.97	2.49
	-	3.29	3.14	2.65
	-	3.45	3.30	2.84
	-	3.65	3.50	3.19
	3.68	3.74	3.71	-
	3.63	3.66	3.68	-
Bottom layer	3.63	3.71	3.71	-

density profiles are seen for these samples as were observed for niobium containing bodies. However, flexural strength values showed no definite correlation with density as indicated by the data in Table VII.

TABLE VII
PROPERTIES OF SAMPLES OF 50 WT% Hf-GRAPHITE PRESSED AT 3000°C

Sample	Density, g/cc	Flexural Strength, psi
T1	2.84	12,220
T3	2.82	11,180
T5	3.59	13,280

Although somewhat lesser non-uniformity were exhibited by bodies incorporating 30 wt% Hf, the trends in density profile were the same and still in evidence.

Experiments will be conducted to determine if this lack of uniformity can be minimized by simple mechanical modifications in mixing and loading. It is felt that in all cases, the higher densities are a result of disproportionate carbide segregation rather than actual densification to a higher degree in localized areas. This has been borne out both by microstructural studies and strength measurements.

3. Mo-C System

In contrast to the Nb and Hf systems, samples containing molybdenum showed relatively good uniformity at all levels of metal addition. A grid for a 50 wt% molybdenum system pressed at 3000°C appears in Table VIII. The higher densities toward the central axis and bottom of the processed billet is still apparent, although to a much lesser degree. Furthermore, strength data also showed good uniformity.

TABLE VIII

DENSITY PROFILE OF 50 WT% Mo-GRAPHITE PRESSED AT 3000°C

	Row A	Row B	Row C
Top layer	2.92 g/cc	-	2.82
	2.99	2.93	2.83
	2.93	-	-
	2.91	-	2.82
	2.96	2.92	2.84
	3.00	2.98	2.88
Bottom layer	3.00	-	2.89

4. Other Systems

Systems incorporating the other metal additives, i.e., tantalum, zirconium, titanium, boron, beryllium, uranium and thorium, all exhibited density ranges which were relatively homogeneous. Variations were approximately ± 3% or less which can be considered within experimental error. Good uniformity was also observed in flexural strength data.

It has been observed that with increasing amounts of metal (in particular for the Nb-C and Hf-C systems) heterogeneity in the properties within a single composite can occur. It would appear that this lack of uniformity can be minimized with proper care in mixing and loading of compositions. Future methods will consider methods such as wet mixing and loading. Microstructural and strength evaluations as well as density measurements, will be utilized to monitor homogeneity.

Consideration will also be given to particle size and shape effects on mixing and loading. It is possible that the use of even finer metal or metal carbide raw material than the -325 mesh being used will enhance both mixing and liquid phase

sintering. This, of course will be governed by practical limitations.

III. SUMMARY AND FUTURE WORK

Equipment modifications for improved hot press processing have been incorporated. These include introduction of a constant pressure device. An improved venting system has virtually eliminated error-inducing fumes in the optical pyrometry. Calibration of the hot pressing operation has shown that the sample temperature is closely indicated by the present arrangement of a sight tube inserted into the mold.

Attempts to hot press calcined petroleum coke at 3000°C with no metal additives have produced highly graphitic structures which exhibit poor bonding.

Investigations of heterogeneity in densities of niobium and hafnium graphite composites have shown that it is a result of carbide particle segregation. Examination of microstructures show that "denser" sections contain larger and more numerous carbide grains. It is probable that these sections contain amounts of metal in excess of the designed composition. Furthermore, flexural strength either shows an inverse relationship with density or is the same for different densities due to particle segregation. The usual direct relationship was not observed. Thus, higher density values alone are not always real indications of higher densification.

Future work will involve the following studies:

1. Effect of using different carbonaceous raw materials on the properties of hot pressed composites.
2. Effect of time of heating cycle and soak time at temperature on density and strength of composites.
3. Compositional studies to determine the optimum amounts of metal or metal carbide necessary for

desired properties. Two systems, Be-C and Th-C have been eliminated from additional study due to their pronounced sensitivity to atmospheric moisture.

IV. CONTRIBUTING PERSONNEL AND LOGBOOK RECORDS

Contributing personnel include S. L. Blum, S. A. Bortz, G. A. Rubin and G. Besbekis. All data are contained in Logbook Numbers C15688, C16001 and C16005.

Respectfully submitted,
IIT RESEARCH INSTITUTE

Y. Harada
Associate Chemist

APPROVED:

S. L. Blum
Director
Ceramics Research

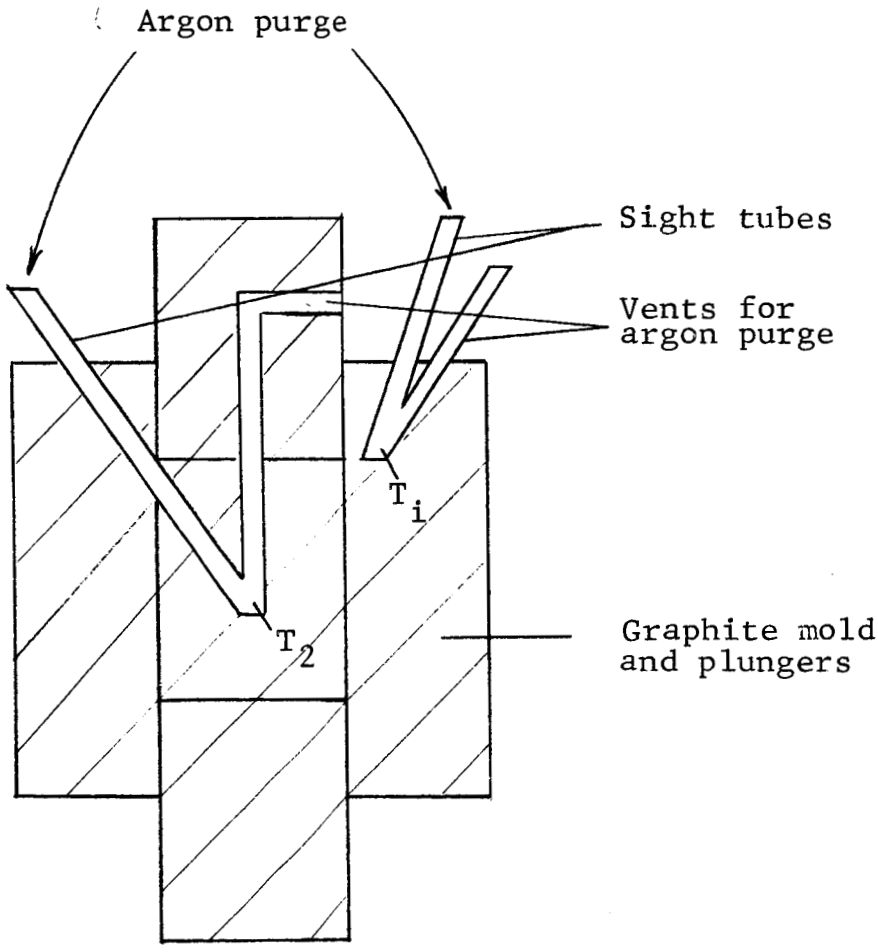

FIG. 1 - DIAGRAM OF MOLD ASSEMBLY FOR CALIBRATION BETWEEN SIGHT TUBE AND SAMPLE TEMPERATURE

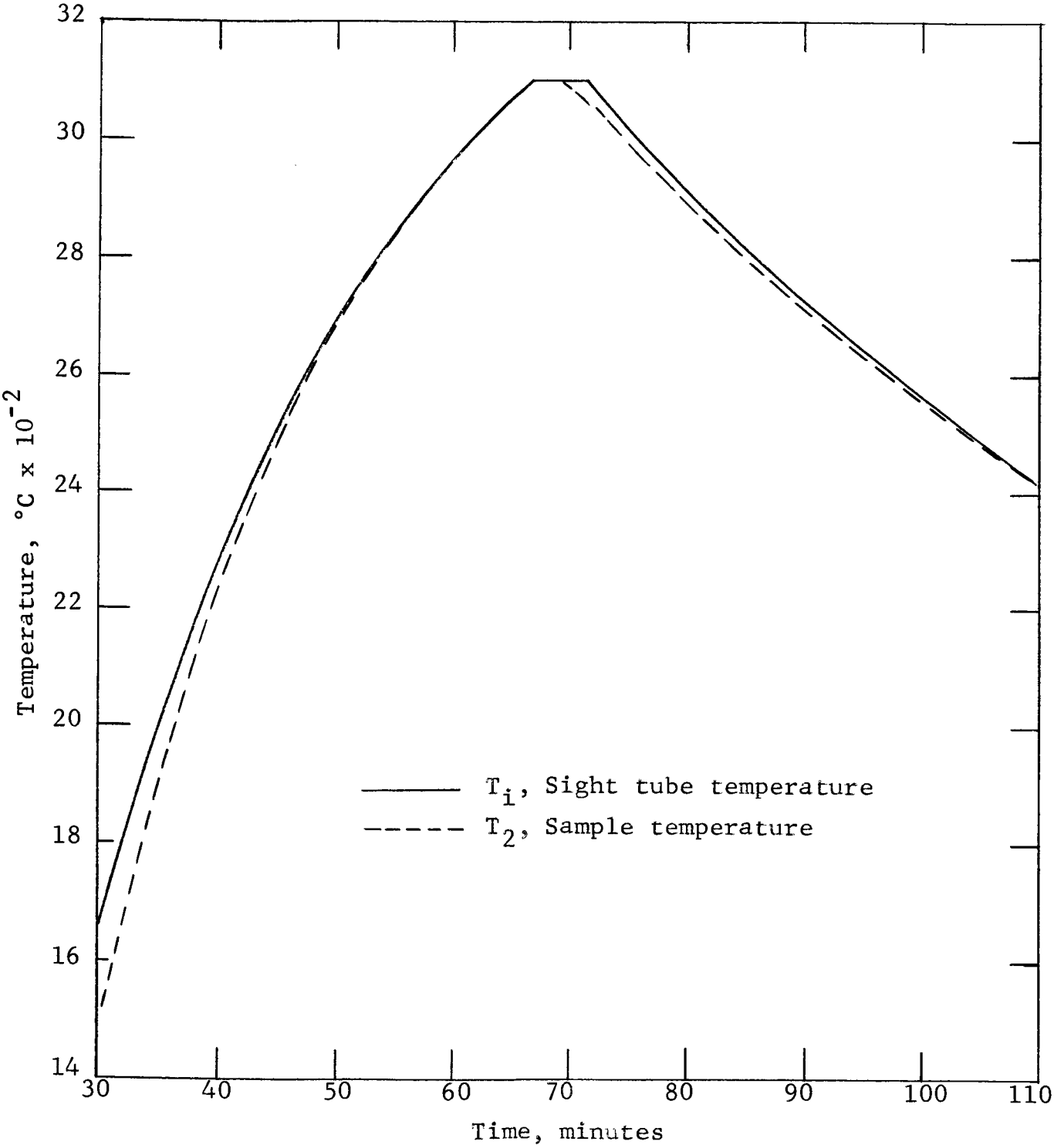

FIG. 2 - SIGHT TUBE TEMPERATURE VS. SAMPLE TEMPERATURE DURING SIMULATED HOT PRESSING EXPERIMENT

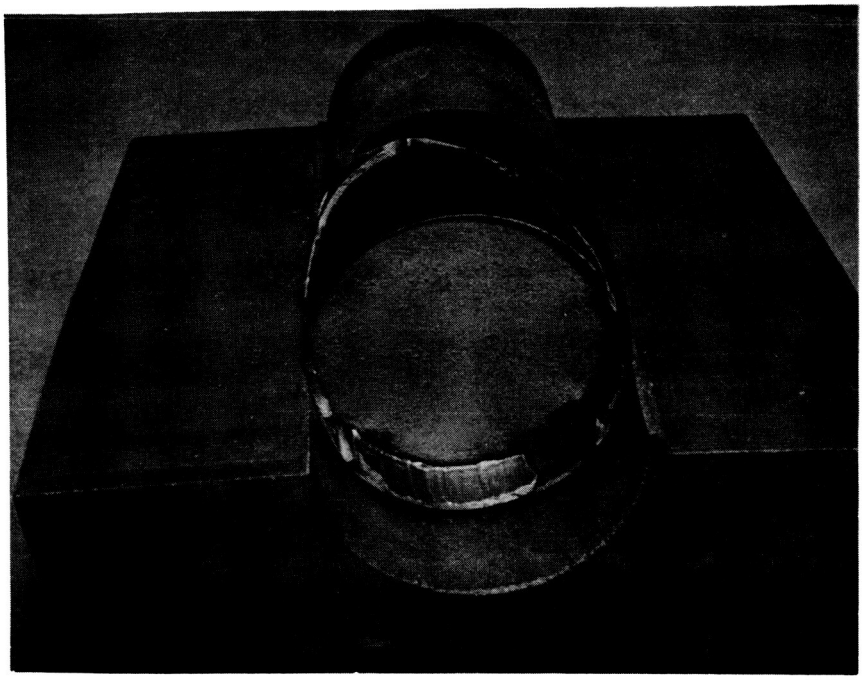

FIG. 3 - CUT-AWAY VIEW OF MOLD CONTAINING CALCINED PETROLEUM COKE SAMPLE PRESSED AT 3000°C, SHOWING SHEAR FRACTURE AND MATERIAL EXTRUSION AROUND PLUNGER

FIG. 4 - SAME VIEW WITH FRACTURED CONICAL SECTION REMOVED

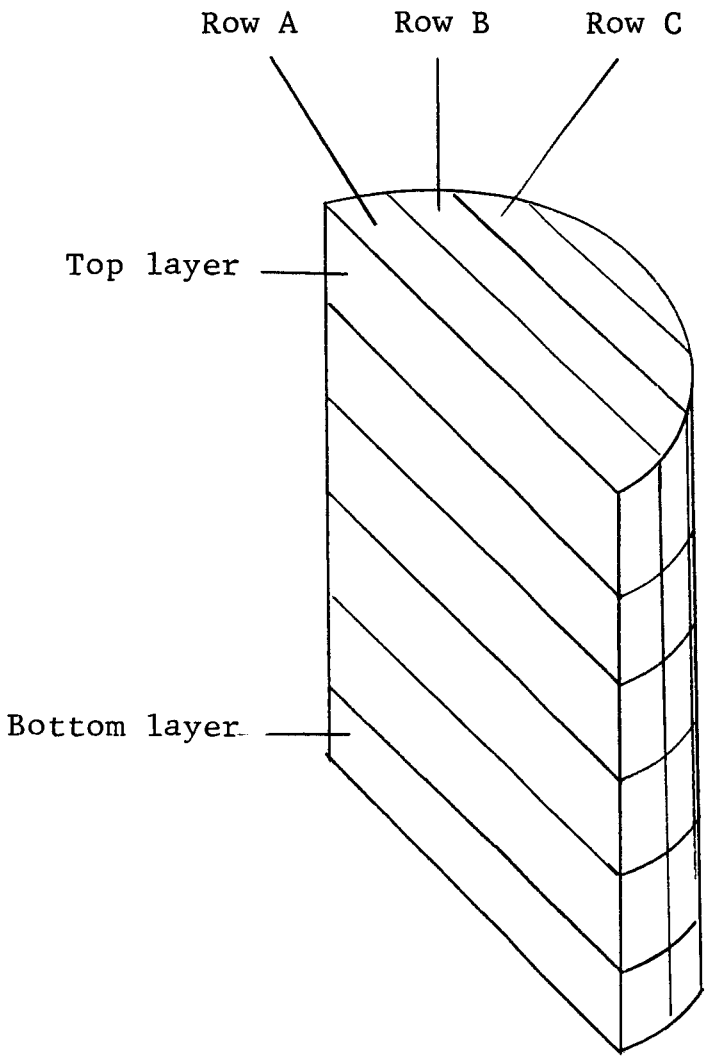

FIG. 5 - SECTIONING OF PRESSED BILLETS FOR DENSITY PROFILING

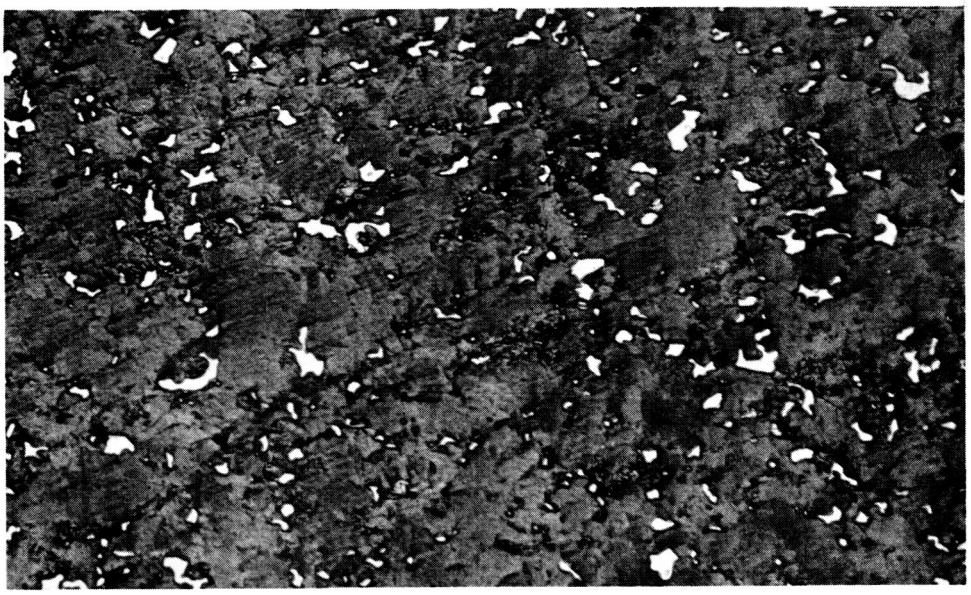

FIG. 6 - MICROSTRUCTURE OF 50 WT% Nb-GRAPHITE (Sample T1, density = 3.18 g/cc), PRESSED AT 3000°C (320X)

FIG. 7 - MICROSTRUCTURE OF 50 WT% Nb-GRAPHITE (Sample T6, density = 3.51 g/cc), PRESSED AT 3000°C (320X)

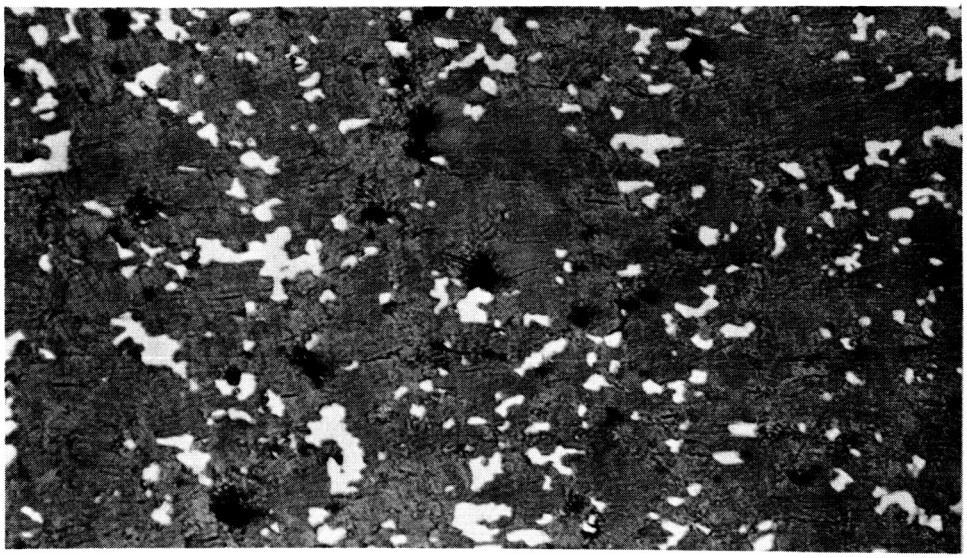

FIG. 8 - MICROSTRUCTURE OF 50 WT% Nb-GRAPHITE (Sample A-1, density = 2.75 g/cc), PRESSED AT 3000°C (320X)

FIG. 9 - MICROSTRUCTURE OF 50 WT% Nb-GRAPHITE (Sample A-4, density = 2.89 g/cc), PRESSED AT 3000°C (320X)

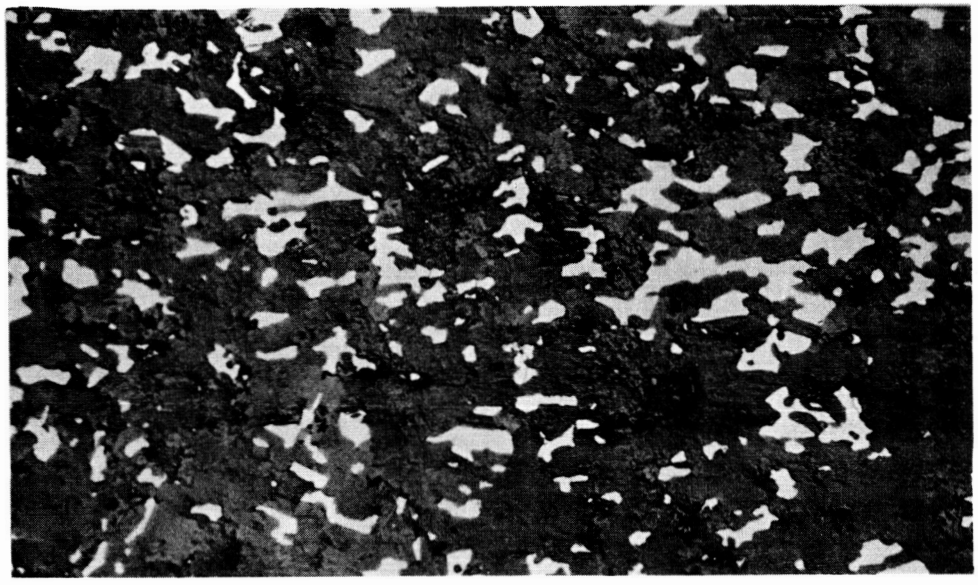

FIG. 10 - MICROSTRUCTURE OF 50 WT% Nb-GRAPHITE (Sample B-1, density = 3.05 g/cc), PRESSED AT 3000°C (320X)

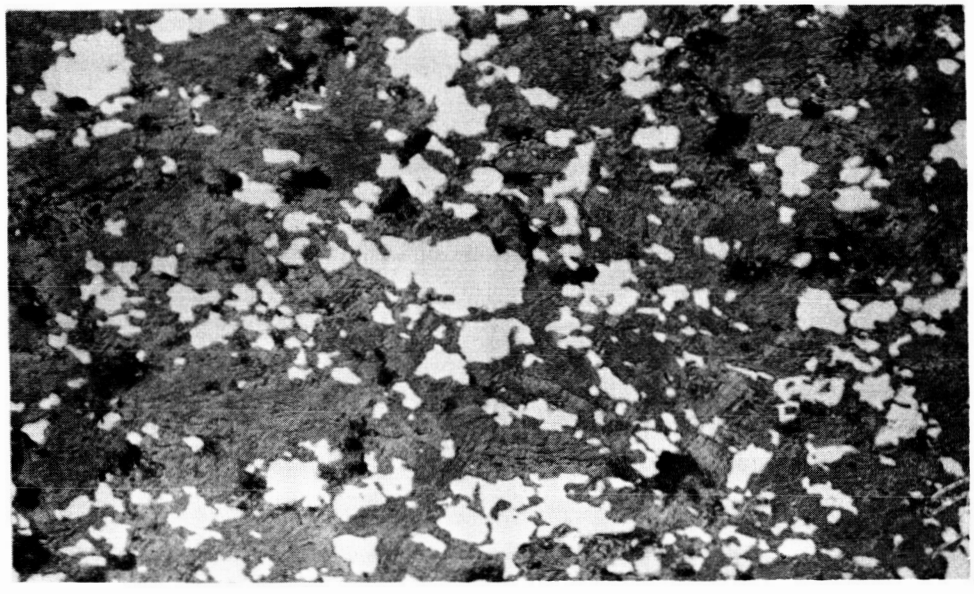

FIG. 11 - MICROSTRUCTURE OF 50 WT% Nb-GRAPHITE (Sample B-4, density = 3.37 g/cc), PRESSED AT 3000°C (320X)