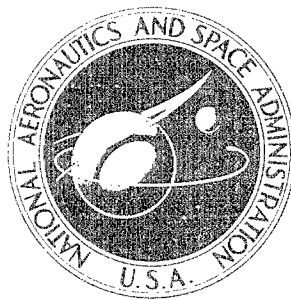


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GRAPHITE-METAL CARBIDE COMPOSITES

by Y. Harada

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(GRAPHITE-METAL CARBIDE COMPOSITES)

By Y. Harada

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Prepared under Contract No. NASr 65-(09)¹³ by
⑤ IIT RESEARCH INSTITUTE
⑥ Chicago, Ill.

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION ¹²

GRAPHITE-METAL CARBIDE COMPOSITES

ABSTRACT

Investigations ^{were} have been conducted to determine the feasibility of fabricating metal-graphite composites by hot pressing at 2800°-3000° C. Mixtures of calcined petroleum coke with varying amounts of different metals (or their carbides) were used as the raw materials, and no binders were involved in this simple, one-step process. Ten metal additions were studied in this program: niobium, hafnium, molybdenum, tantalum, zirconium, titanium, boron, beryllium, uranium, and thorium. Evaluation of the resulting bodies included measurements of physical properties and examination of microstructure. _{end}

The results show that strong, dense bodies can be realized by this method. Liquid phase sintering occurs through formation and diffusion of a carbide-carbon eutectic under the hot pressing conditions, and subsequent recrystallization of this phase yields strong bonding.

The strongest bodies to emerge from these studies are in the Nb-C, Hf-C, and Mo-C systems. Compositions containing 50 wt% metal (or 6 to 11 at%) have exhibited flexural strengths in excess of 10,000 psi, the highest being 16,000 psi for 50 wt% Nb-C processed at 3000° C. This system and a 50 wt% Hf-C also pressed at 3000° C have displayed increases in strength at 2000° C. Intermediate (~5000 psi) strengths were shown by most of the other systems incorporating other metal additives. _{end}

The graphite-metal carbide composites studied in this program were: niobium-graphite, hafnium-graphite, molybdenum-graphite, tantalum-graphite, zirconium-graphite, titanium-graphite, boron-graphite, beryllium-graphite, uranium-graphite and thorium-graphite.

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GRAPHITE-METAL CARBIDE COMPOSITES

I. INTRODUCTION

The purpose of this program was to investigate the feasibility of preparing graphite-metal composites of high density and strength by application of pressure at high temperatures (2800°-3000°C). This technique employs no binders and being a simple, one-step operation, does not require impregnation of the finished piece. The initial screening studies have yielded selected composites of high strengths through exploitation of two mechanisms:

1. Above 2200°C plastic deformation of carbon under pressure results in increased densification. Pressure also accelerates graphitization whereby randomly oriented graphite layers become ordered.
2. The formation of relatively low melting carbide-carbon eutectics promotes liquid phase sintering. Diffusion of the metal or carbide and subsequent recrystallization as a fine dispersion yields an improved bonding in the composite.

Metal additions to the graphite were selected to give a range of composites of different properties of varied applications. The guest metal phases which were investigated are titanium, zirconium, hafnium, niobium, tantalum, molybdenum, beryllium, boron, thorium and uranium.

During the course of the program, the following variables were studied for each metal carbide-graphite system.

1. Amount of metal addition - to determine the levels necessary for producing sound bodies.
2. Fabrication temperature - to assess the effect of increased temperature on the degree of densification and bonding.
3. Particle size of starting materials - to determine if finer, high surface area material of greater surface energy would enhance the process of liquid phase sintering.

The influence of these factors upon fabricability, density, flexural strength, and coefficient of thermal expansion was determined. Metallographic and electron microprobe techniques were also employed to characterize the various composites. The results of these experiments are herein presented.

II. EXPERIMENTAL PROCEDURE

A. Materials and Preparation

The raw materials used for preparing the various graphite-metal composites were obtained from various suppliers. The calcined petroleum coke used as the carbon source was Continental No. 90 coke flour obtained from Union Carbide. Metals and carbides were furnished by the different manufacturers as listed in Table I.

In the preparation of raw batches of metal-carbon or metal carbide-carbon mixtures, a dry blending technique of roller milling with rubber stoppers for 16 hours was used. After loading of the mold, a low pressure was applied and released several times to insure proper alignment of punches and also of the mold in relation to the press. Hot pressing of samples was conducted in graphite molds (CS mold stock) employing induction heating. A diagram of the apparatus appears in Figure 1.

The initial pressure applied was 500 psi; this level was maintained until a temperature of 1800°C was attained at which time it was increased to 3000 psi for the remainder of the processing. As indicated in Figure 1, temperature readings were taken with an optical pyrometer (L and N brightness type) sighting into the mold through an argon purged sight tube. The original power input with the 80-KW motor-generator was 20 KW. This was steadily increased to 60 KW over a half hour period and maintained at this level for the duration of the pressing. The temperature of the experiment (2800° or 3000°C) was attained in approximately one hour from room temperature at which time the processing was concluded.

Some difficulty was encountered in accurate measurement of temperature due to the presence in the optical path of volatiles from the mold. A complementary method of temperature determination was also employed which involves use of a calibrated time-temperature plot at a

TABLE I
METAL ADDITIVES AND SUPPLIERS

Material	Description	Supplier
Niobium	-200 mesh	Fansteel
Niobium carbide	-325 mesh	Shieldalloy
Hafnium carbide	-200 + 325 mesh	Hermann C. Starck
Hafnium carbide, reactor grade	-325 mesh	Wah Chang
Molybdenum	-200 mesh	Fansteel
Zirconium carbide, vacuum grade	-200 + 325 mesh	Hermann C. Starck
Zirconium carbide	-325 mesh	Wah Chang
Titanium carbide	-200 + 325 mesh	Hermann C. Starck
Tantalum carbide	-200 + 325 mesh	Hermann C. Starck
Beryllium		Beryllium Corporation
Boron carbide	-325 mesh	Norton
Thorium	-200 + 325 mesh	Lindsay (American Potash and Chemical)
Uranium carbide	(Prepared at IITRI)	

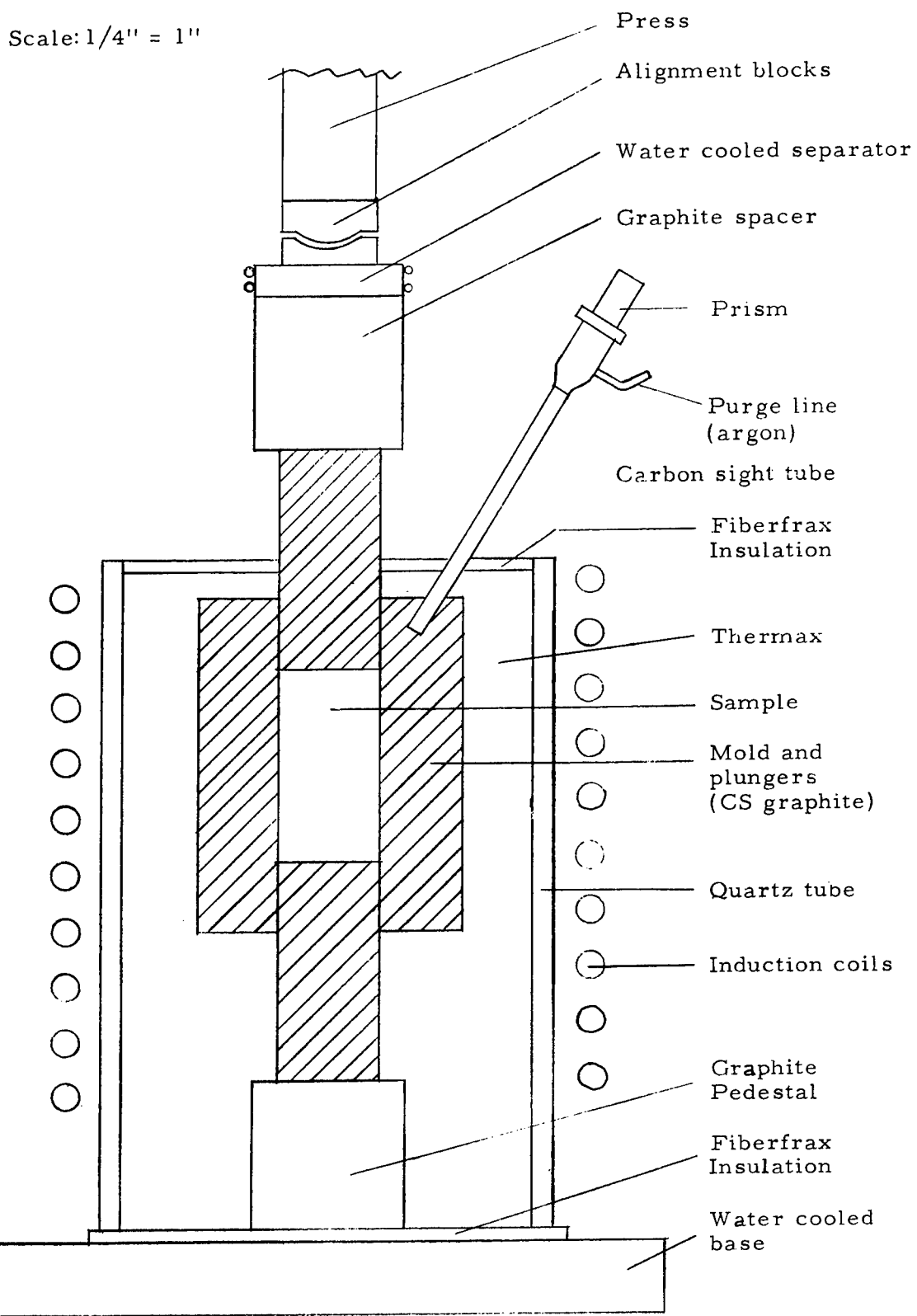


FIG. 1 - DIAGRAM OF HOT PRESS APPARATUS

constant 60 KW power. Thus, some of the anomalies in the data may be attributed to possible errors in pyrometry. Since the emitted radiation from the mold would be weaker due to the fumes, the actual temperatures during processing were probably somewhat higher than experimentally reported.

To obtain the processed billet, the mold was cut open. Deformation of the sample configuration (increased diameter) occurring during pressing precluded simple ejection. Samples of both orientations for physical testing were sectioned and machined from halves of the finished billet which had a diameter of 2 1/2 inches and a height of approximately the same dimensions (Figure 2). Test pieces measured 1/4 in. x 1/4 in. x 2 in.

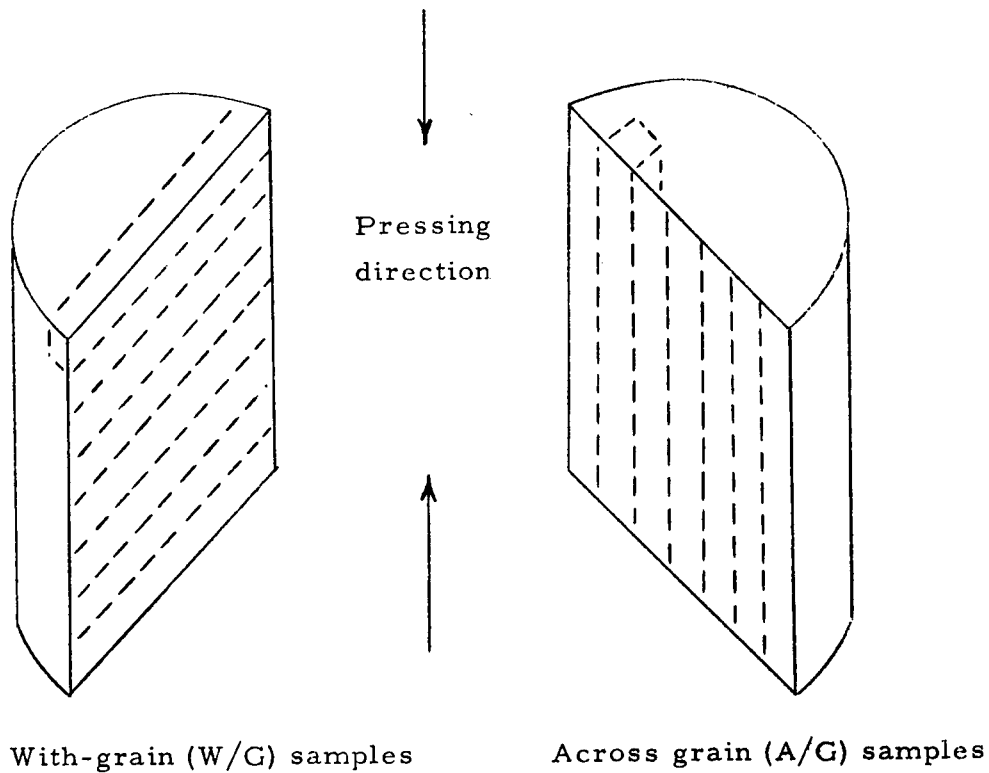


FIG. 2 - SECTIONING OF HOT PRESSED BILLETS FOR PHYSICAL PROPERTY MEASUREMENTS.

B. Measurement of Physical Properties

Flexural strengths were determined at room temperature and at 2000°C. A three point loading method in a universal testing machine was used for measurements at room temperature, and four point loading was employed for high temperature evaluation. The latter determinations were made under nitrogen in a carbon resistor tube furnace; the load is applied through a slot in the top of the tube and is monitored with a calibrated deflection ring.

Thermal expansion measurements were also made under N₂ in a carbon resistor furnace. Dimensional changes were followed using telemicroscopes sighting on the sample through a window in the side of the furnace.

C. Microstructural Examination

Samples for metallographic study were mounted in a cold setting epoxy type of plastic. These were then wet ground on a 400 grit silicon carbide paper and then rough polished on a hard napped nylon cloth charged with 9μ diamond abrasive. Final polishing was accomplished on a silk cloth using an aqueous slurry of ~0.05μ alumina (Linde "B"). No etchant was used.

The electron microprobe analyzer was employed to examine diffusion of metal carbide into the graphite matrix. This technique is based on the principle that when a metal is bombarded with high energy electrons, a portion of the kinetic energy is converted to x-radiation which contains components that are uniquely characteristic to the metal. The emitted radiation is analyzed by a spectrometer which can be tuned to a specific radiation, e.g., niobium. Paired electron and x-ray image photographs are presented in this report. The former shows microstructure since the differing composition of the two phases possess differing reflectivities for the incident electron. The x-ray image is the result of tuning to a specific radiation which in our case is the particular metal carbide phase being studied.

III. RESULTS AND DISCUSSION

During the course of the program, it has been demonstrated that densification and bonding of graphite-metal composites can be achieved by a simple hot pressing technique. The degree to which strengthening occurs varied, depending on the metal additive and on the parameters introduced for any given system. The variables which have been studied for the various systems are:

1. Metal levels up to 50 wt%.
2. Pressing temperatures of 2800° and 3000° C.
3. Two particle size ranges in raw materials of -200 + 325 mesh (74-44 microns) and -325 mesh (<44 microns).

The different systems will be discussed individually in the following sections. Some systems received more study than others; this was dictated by the varying degrees of promise and direction shown by the individual compositions.

Compositions which have been investigated are plotted in terms of atomic percent metal versus weight percent metal in Figure 3. The theoretical volume percent of carbide as a function of metal levels used is illustrated in Figure 4. These curves show more clearly the portion of the metal-carbon phase diagram in which we worked, and the volume level of the carbides in relation to the carbon.

Theoretical densities found in the Tables were calculated assuming the metal carbide phase and its x-ray density to be as follows for the various systems: NbC, 7.85 g/cc; HfC, 12.7 g/cc; Mo₂C, 8.8 g/cc; TaC, 14.5 g/cc; ZrC, 6.4 g/cc; TiC, 4.9 g/cc; B₄C, 2.51 g/cc; Be₂C, 1.9 g/cc; UC₂, 13.6 g/cc; and ThC₂, 9.6 g/cc. The range in stoichiometry which can exist for any carbide and also the other carbides which can be present in a single system (e.g. UC, U₂C₃) is known. The value used for the theoretical density of the graphite matrix was 2.26 g/cc. This is probably too high a figure; e.g., commercial hot pressed ZTA graphite usually exhibits a range of about 1.80 to 2.10 g/cc. However, for purposes of comparison in a single system or among different systems, these calculated theoretical densities form reasonable if not exact standards.

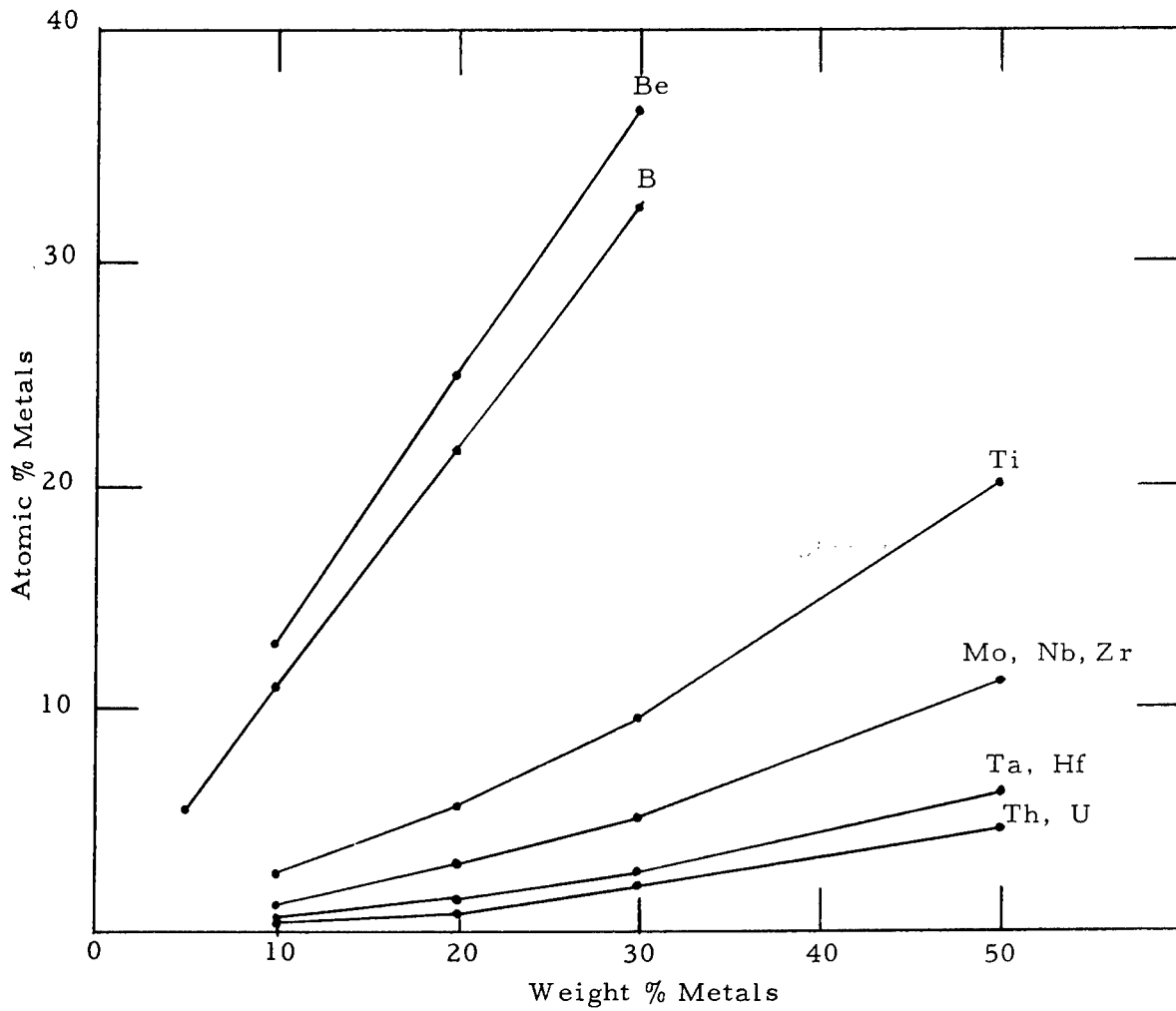


FIG. 3 - ATOMIC % METAL AS A FUNCTION OF WT% METAL ADDITION

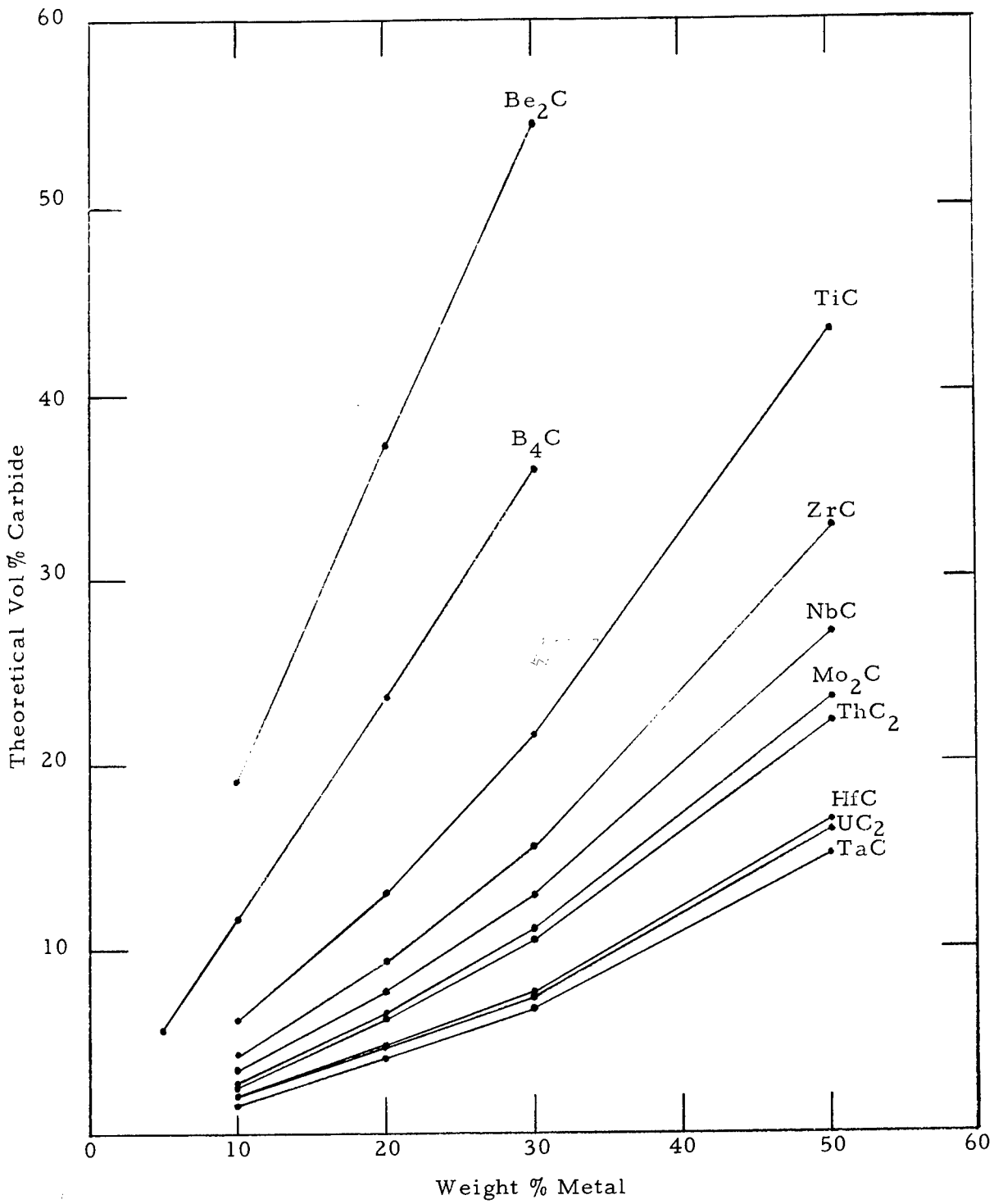


FIG. 4 - THEORETICAL VOL % CARBIDE AS A FUNCTION OF WT % METAL ADDITION

Porosity measurements were made using a water absorption technique to determine open porosity in some of the systems. Values of less than 1% was exhibited by compositions containing 50 wt% of hafnium, niobium, or molybdenum which were the strongest systems developed on this program. Slightly higher porosities of 3 to 6% were measured for zirconium and titanium incorporating samples. However, as the density values in the Tables later in the report show, the titanium and zirconium systems were of relatively low densities and strengths. Porosity measurements will also be made in future work to determine their significance in reported strength values.

Each value in the physical property data represents an average of three or more determinations or measurements. Although the population of values is limited, the trends indicated by the data were deemed of greater importance than absolute data in this initial study. Figure 5 contains a summary of flexural strengths as a function of wt% metal incorporated for all systems studied on this program.

A. Niobium-Graphite

The strongest composite produced on this program was a 50 w/o niobium-graphite system pressed at 3000°C which exhibited room temperature and 2000°C flexural strengths of 16,080 and 18,660 psi respectively in the W/G direction. Strengths of greater than 10,000 psi were also shown by a 30 w/o niobium body processed at 3000°C. These strengths are considerably higher than those reported for ZTA, a commercial hot pressed graphite, which has a strength of about 5000-9000 psi. (1)

The data summarizing the investigations of this system appear in Table II. At metal weight levels of 10 and 20% pressed at 2800°C, samples were difficult to machine and had essentially zero strength. At this same processing temperature increased metal contents of 30 and 50 w/o yielded bodies which, although stronger than those of lower metal level, were still relatively weak. Examination of the microstructure (Figure 6) reveals large carbide grains which appear essentially unaltered.

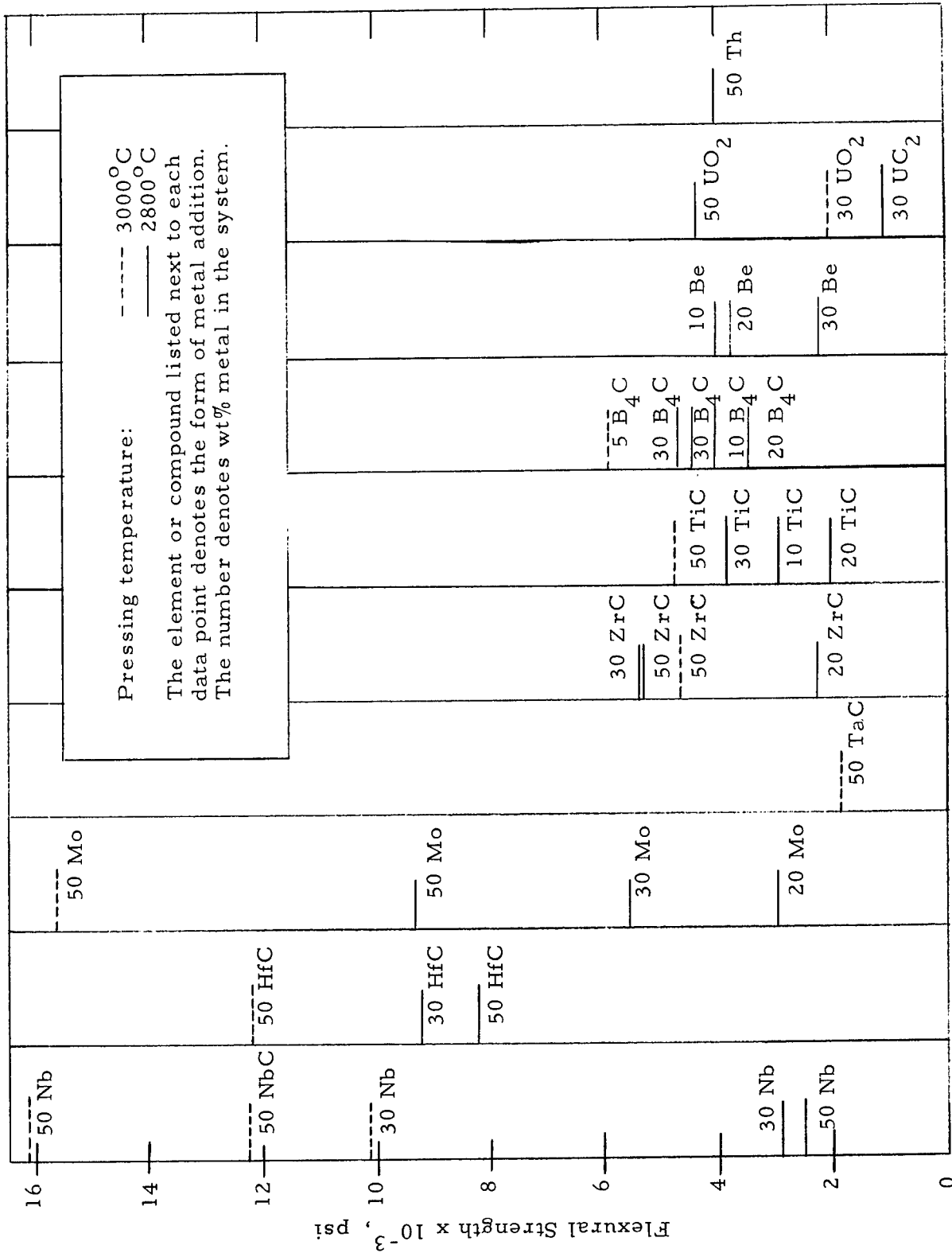


FIG. 5 - SUMMARY OF FLEXURAL STRENGTH AS A FUNCTION OF COMPOSITION

TABLE II
GENERAL SUMMARY OF Nb-C SYSTEM

Compositional Designation	METAL ADDITIVE		GRAIN SIZE (mesh)		Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide
	Form	Metal, Wt% Metal, At%	Metal Carbide	Carbon			
Nb-a	Nb	10 1.42	-200 + 325	-200	2800	2.46	3.5
Nb-b	Nb	20 3.13	-200 + 325	-200	2800	2.69	7.8
Nb-c	Nb	30 5.25	-200 + 325	-200	2800	2.98	12.8
Nb-d	Nb	30 5.25	-325	-325	3000	2.98	12.8
Nb-e	Nb	50 11.44	-200 + 325	-200	2800	3.78	27.1
Nb-f	Nb	50 11.44	-325	-325	3000	3.78	27.1
Nb-g	NbC	50 11.44	-325	-325	3000	3.78	27.1

NOTE: Property data are contained in Table II-a.

TABLE II-a

PROPERTIES:

Comp.	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi						Coeff. of Thermal Exp. x 10 ⁻⁶ in/in/°C (0-2000°C)					
			Room Temperature			2000°C			W/G	A/G	W/G	A/G	W/G	A/G
			W/G	A/G	Ratio W/G:A/G	W/G	A/G	Ratio W/G:A/G						
Nb-a			Low	Low										
Nb-b			120	Low										
Nb-c	2.26	75.8	2890	1260	2.29									
Nb-d	2.69	90.3	10,120	2850	3.55	10,470	2240	4.67	2.7	10.6	3.9			
Nb-e	3.25	86.0	2510	1790	1.40									
Nb-f	3.38	89.4	16,080	3550	4.53	18,660	6110	3.05	4.9	8.6	1.8			
Nb-g	3.61	95.5	12,210	4140	2.95	12,280	5190	2.37						

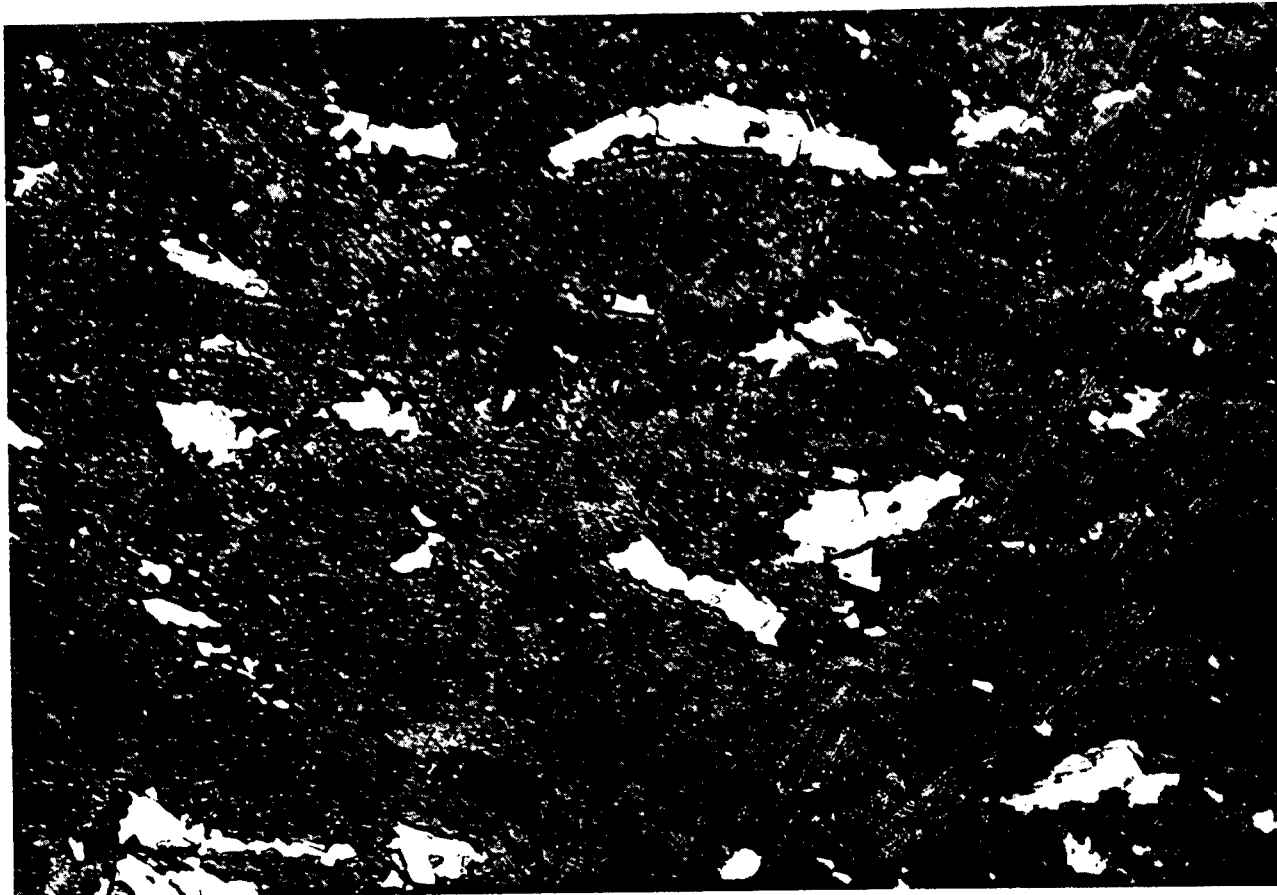


FIG. 6 - MICROSTRUCTURE OF 30 WT% NIOBIUM-GRAPHITE,
PRESSED AT 2800°C. (320X)

Raising the processing temperature to 3000°C and the use of finer particle size starting materials resulted in bodies which had excellent strengths (compositions "Nb-d," "Nb-f" and "Nb-g"). It is felt that the bonding mechanism leading to high strengths may be due to the presence of a metal carbide rich graphite phase surrounding the carbide grains. Such a condition can result from eutectic formation, diffusion, and precipitation upon cooling. When the level of carbide phase is high enough, and the carbide particles are fine enough so that a complete and uniform reaction occurs resulting in an overlap of eutectic phase, a strong bond can result.

The dramatic improvement realized by use of the higher temperature suggests that a liquid eutectic phase may have been attained, promoting carbide diffusion. The NbC-C eutectic temperature is reported to be $3250 \pm 50^\circ\text{C}$.⁽²⁾ Metallographic examination (Figure 7) shows a fairly uniform dispersion of fine carbide grains for composition "Nb-d."

Examination of samples pressed at 2800° and 3000°C employing the microprobe analyzer shows limited metal diffusion in both cases (Figure 8 and 9), with perhaps somewhat greater amounts of metal in the graphite matrix for the higher temperature sample.

Some thermal properties of these composites were examined. Only slight increases in strength at 2000°C were noted. It is reported that NbC of 95% theoretical density has a room temperature flexural strength of 35,600 psi, but a 2000°C strength of only 2800 psi and shows creep at 2190°C.⁽³⁾ This drastic loss in strength for NbC may account for the relatively small increase in strength for the composite.

Thermal expansion of the 30 w/o Nb composite showed a fairly strong degree of anisotropy, and the values were close to that of ZTA graphite (2.5 W/G and 11.5 A/G).⁽¹⁾ At the higher metal content the directional values were not as divergent, showing the influence of the isotropic metal carbide inclusion.

Another property which was studied was resistance to humidity. Weight and dimensional changes were essentially zero after 8 months in a room temperature-100% humidity condition. This dimensional stability to humidity was shown by all other systems except Th-C and U-C.

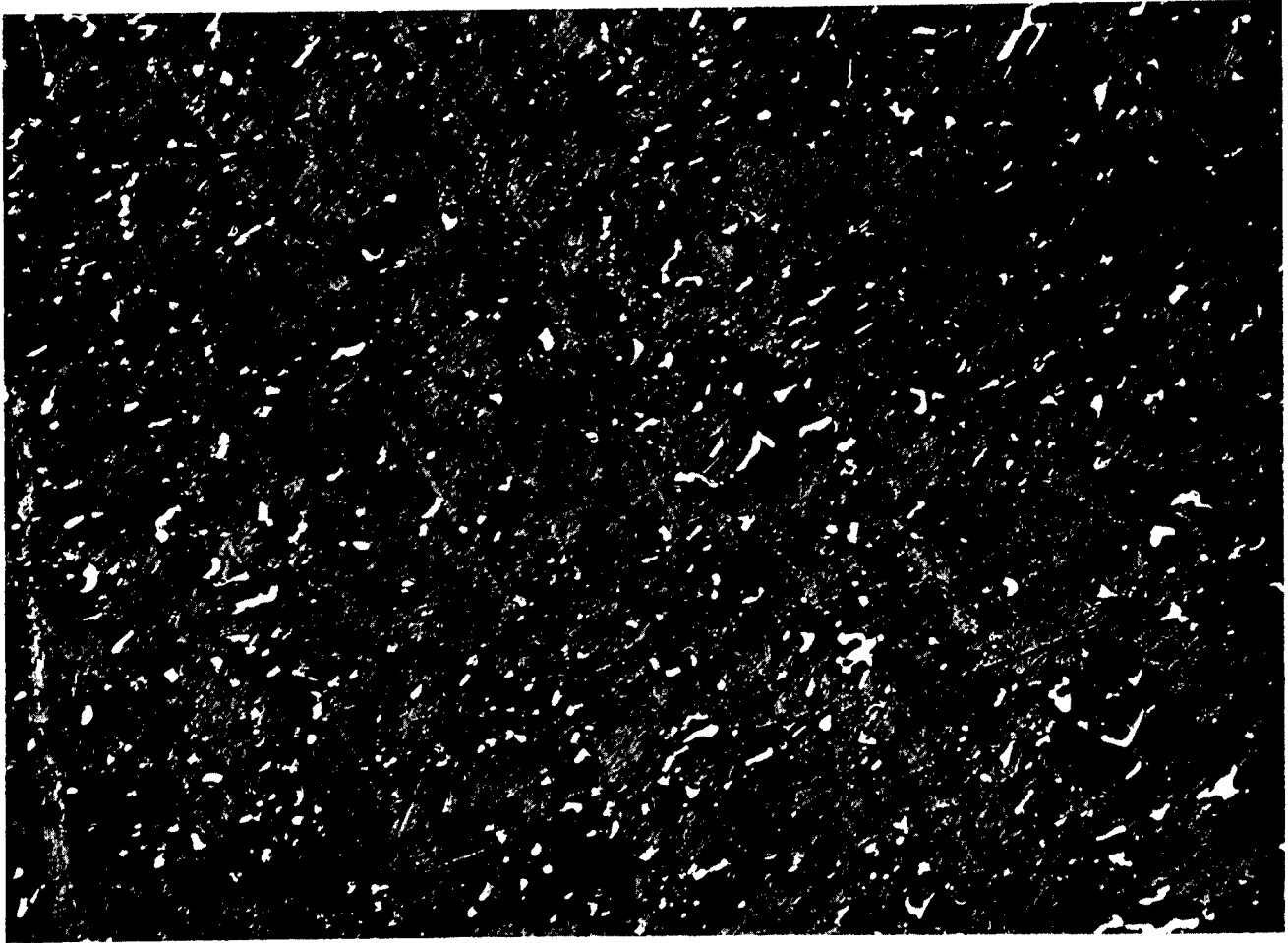
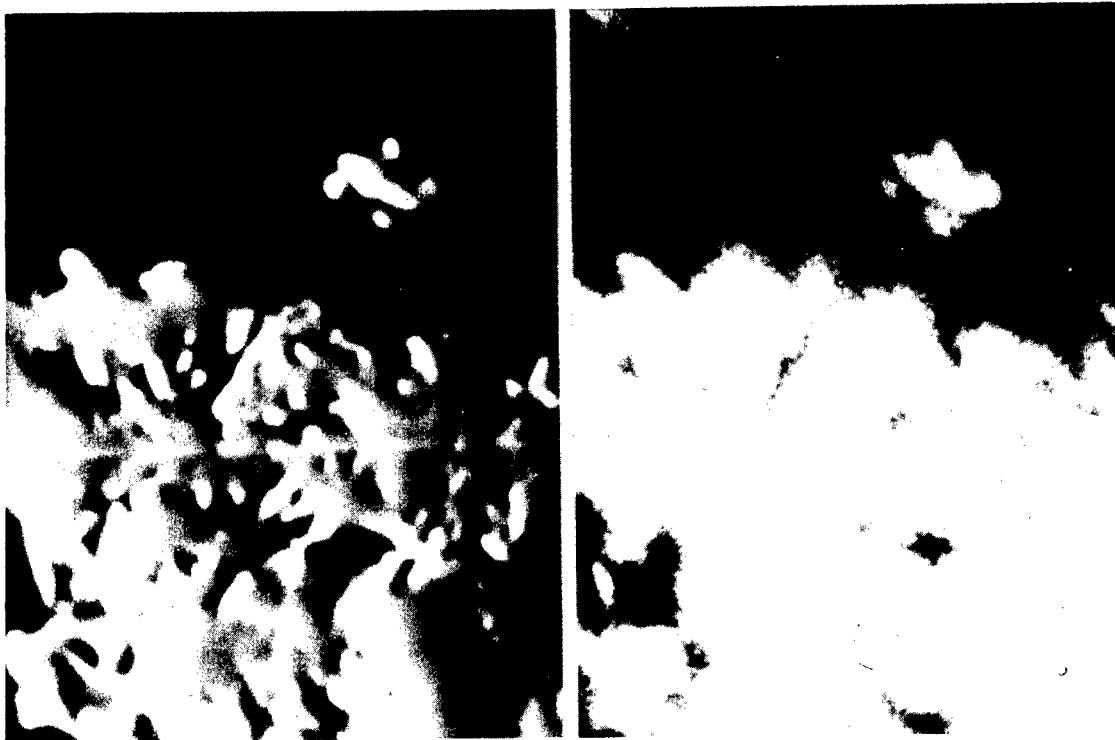


FIG. 7 - MICROSTRUCTURE OF 30 WT% NIOBIUM-GRAPHITE,
PRESSED AT 3000°C. (320X)



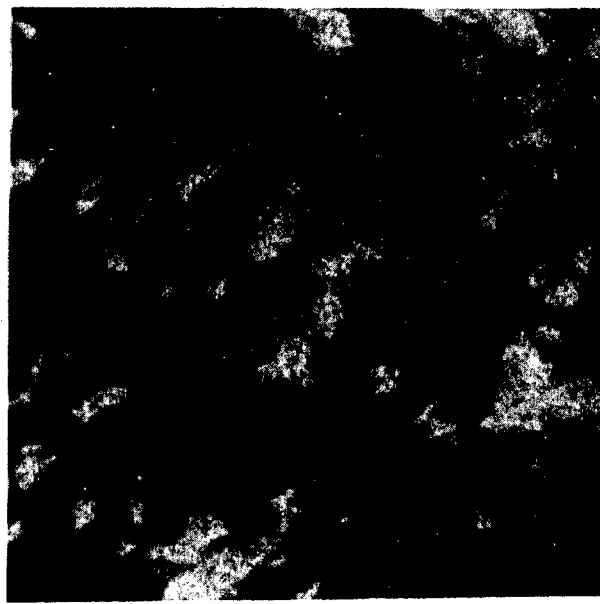
Electron Image

X-ray Image

FIG. 8 - CARBIDE DIFFUSION AREAS IN 30 WT% NIOBIUM-GRAPHITE, PRESSED AT 2800°C. (Electron Microprobe Analyzer, X680)



Electron Image



X-ray Image

FIG. 9 - CARBIDE DIFFUSION AREAS IN 50 WT% NIOBIUM-GRAPHITE, PRESSED AT 3000°C. (Electron Microprobe Analyzer, X680)

Form of Metal Addition - An experiment was conducted to investigate the influence of the form of metal addition, i. e., metal vs carbide. When hot pressed as a metal-graphite mixture, the metal grains could undergo limited liquid formation in the dynamic process of carbide formation. If a temperature of 2335°C is reached during processing prior to complete carburization of the metal, liquid eutectic formation in the range $NbC_{0.08}$ to $NbC_{0.39}$ can occur.⁽²⁾ On the other hand, the NbC-graphite system would not form a liquid until the processing temperature had been reached, thus limiting liquid diffusion.

In the hot pressing, four 1/2 in. discs of 50 w/o niobium were prepared simultaneously in the same mold as shown in Figure 10. As indicated, additions as the metal or carbide were alternated.

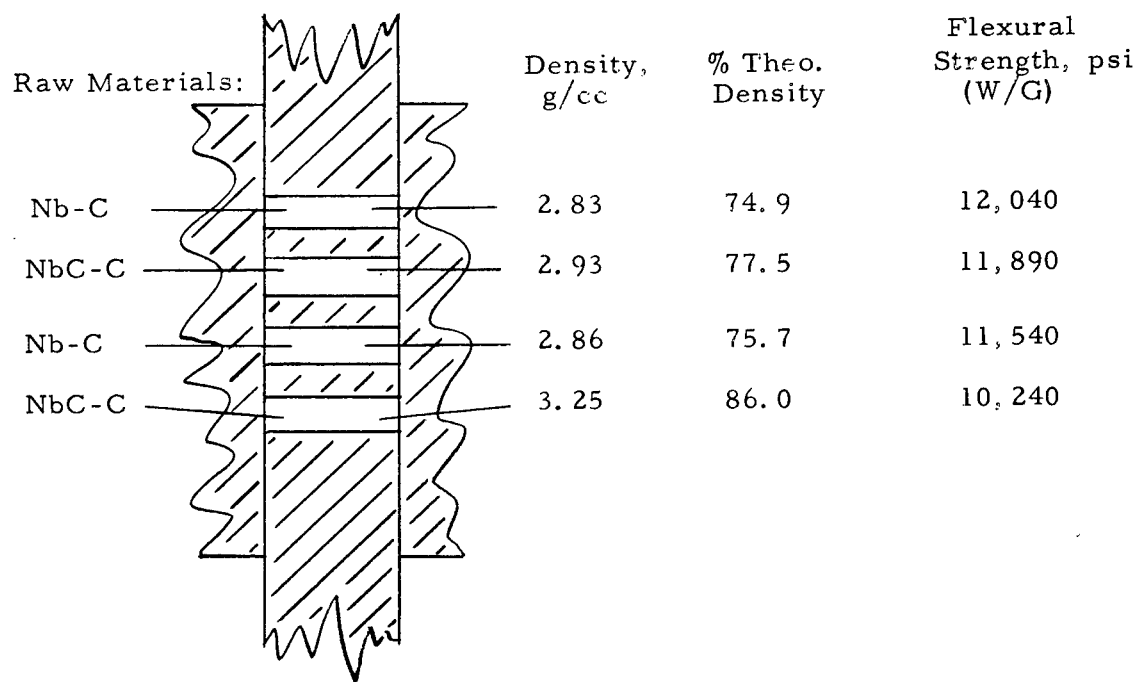


FIG. 10 - HOT PRESSING OF Nb-C AND NbC-C SAMPLES.

It would appear from the densities that the samples incorporating NbC in the starting mix sintered to a greater extent. However, the strengths showed no correlation with density, and were all quite similar. The influence of porosity on the strength of brittle ceramics is an inverse exponential relationship; thus the NbC-C samples of 3.25 g/cc were expected to be somewhat stronger. The same anomaly exists for the larger samples, "Nb-f" and "Nb-g", presented in Table II. Examination of the microstructure does not indicate any significant differences (Figures 11 and 12). The lower densities in general seen for the "sandwich" experiment in comparison to the larger billets is probably due to some decreased efficiency in pressure transfer imposed by the use of graphite dividers.

B. Hafnium-Graphite

Bodies of hafnium carbide-graphite have also shown good strengths. Unlike the niobium carbide-graphite system, a processing temperature of 2800°C and the use of the coarser carbide particles (-200 + 325 mesh) produced high strength samples at the 30 w/o metal level. Data concerning this system are tabulated in Table III.

At the lower metal contents of 10 and 20 wt%, bodies were extremely weak and showed little or no bonding. An abrupt emergence of a high strength body occurs at the 30 wt% metal level, as seen by the data for "Hf-c." It is interesting to note that at this level, the atomic percent Hf (2.80%) is still less than that for Nb at the 20 wt% level (3.13 at%), and the theoretical volume percent of carbide has the same relationship (see Figures 3 and 4). However, it must be remembered that niobium systems do not show appreciable strengths until the processing temperature is raised to 3000°C, and thus, a 20 wt% niobium-graphite composition pressed at 3000°C could conceivably show significant bonding.

Metallographic examination of composition "Hf-c" shows considerable diminution of the carbide particles (Figure 13) as compared to its niobium counterpart (Figure 5). An increase in metal content yielded bodies of somewhat lower strengths ("Hf-d"). The microstructure of this

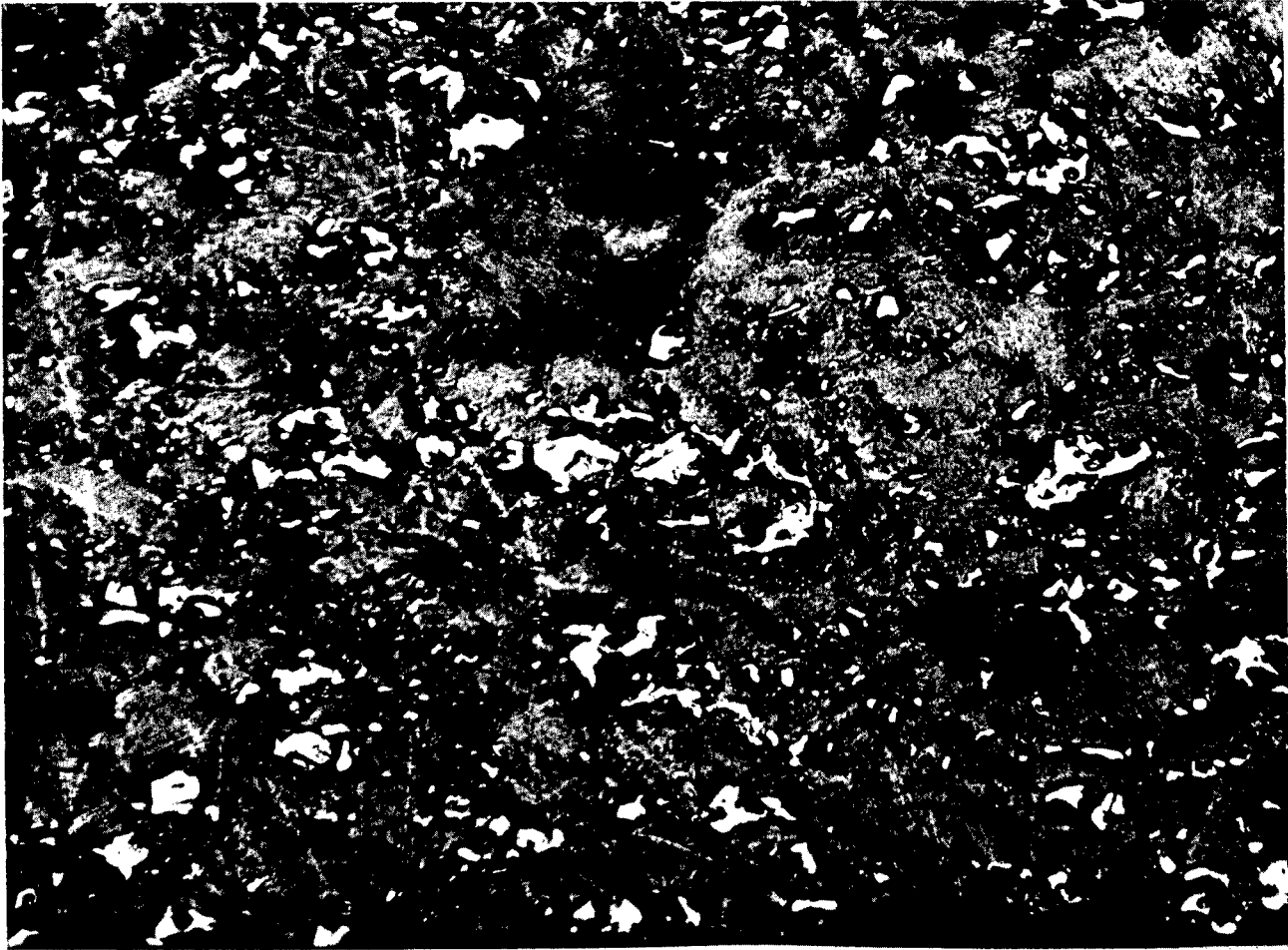


FIG. 11 - MICROSTRUCTURE OF 50 WT% NIOBIUM-GRAPHITE,
PRESSED AT 3000°C. (320X)

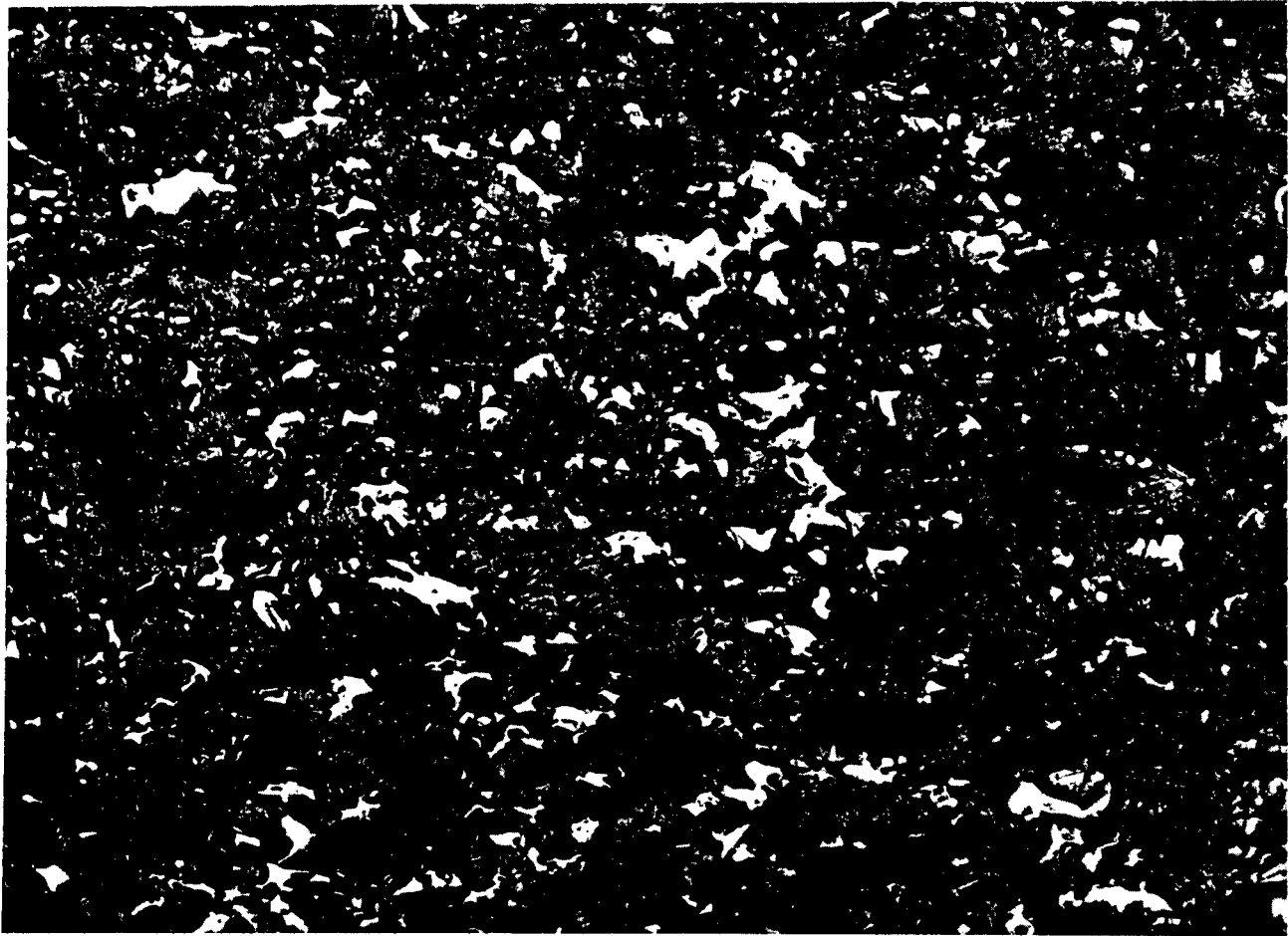


FIG. 12 - MICROSTRUCTURE OF 50 WT% NIOBIUM-GRAPHITE
(ADDED AS NbC) PRESSED AT 3000°C. (320X)

TABLE III
GENERAL SUMMARY OF Hf-C SYSTEM

Compositional Designation	METAL ADDITIVE		GRAIN SIZE (mesh)		Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide
	Form	Metal, Wt% Metal, At%	HfC	Carbon			
Hf-a	HfC	10 0.74	-200 + 325	-200	2800	2.48	2.1
Hf-b	HfC	20 1.65	-200 + 325	-200	2800	2.74	4.6
Hf-c	HfC	30 2.80	-200 + 325	-200	2800	3.07	7.7
Hf-d	HfC	50 6.30	-200 + 325	-200	2800	4.03	16.9
Hf-e	HfC	50 6.30	-325	-325	3000	4.03	16.9

NOTE: Property data are contained in Table III-a.

TABLE III-a

PROPERTIES:

Comp.	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi				Coeff. of Thermal Exp. $\times 10^{-7}$ in/in/ $^{\circ}$ C (0-2000 $^{\circ}$ C)					
			Room Temperature		2000 $^{\circ}$ C		Ratio		Ratio			
			W/G	A/G	W/G	A/G	W/G:A/G	Ratio	W/G	A/G	A/G:W/G	
Hf-a			Low	Low								
Hf-b	2.33	85.0	260	70	3.71							
Hf-c	2.79	90.9	9240	2270	4.07	12,630	5700	2.22	4.1	9.5	2.3	
Hf-d	3.37	83.6	8200	2500	3.28							
Hf-e	3.02	74.9	12,230	2190	5.58	14,710	3940	3.73	3.8	5.4	1.4	



FIG. 13 - MICROSTRUCTURE OF 30 WT% HAFNIUM-GRAPHITE,
PRESSED AT 2800°C. (320X)

composition reveals some larger carbide particles (Figure 14) and considerable heterogeneity in carbide distribution. In addition a fine carbide phase can be seen, also in a non-uniform distribution. The anomalous decrease in strength is probably not a real trend, and may be due to some processing variation.

The strongest bodies of this system were achieved at a 50 wt% metal level, pressing at 3000°C, and with the use of finer starting materials ("Hf-e"). A uniform dispersion of a fine carbide phase was seen for this system (Figure 15). A somewhat greater diffusion of metal carbide into the graphite matrix is seen for HfC-C (Figure 16) than for NbC-C (Figure 8).

Increased strengths occur for hafnium carbide-graphite composites at 2000°C as seen in Table III. A similar relationship in directional thermal expansion exists for HfC-C as for NbC-C, i. e., a higher carbide content yields less anisotropy.

The obtaining of strong bodies of Hf-C at 2800°C whereas a 3000°C processing temperature was necessary for NbC-C can be related to the respective eutectic temperatures. The values reported for HfC-C range from 2800° to 3250°C, ⁽²⁾ and are somewhat lower than those reported for NbC-C. Thus liquid eutectic formation occurs at a lower temperature for the HfC-C system, enhancing diffusion and subsequent bonding.

It is felt that the full potential of this system has not yet been attained. For example, the strongest bodies developed (composition "Hf-e") were of relatively low density; it is reasonable to assume that further densification would yield bodies of much higher strengths. Furthermore, in terms of atomic percent of metal and theoretical volume percent carbide, a relatively small amount of HfC is incorporated. Increase in atomic percent of HfC to the level used for NbC, 11.3 at%, may produce even stronger systems.

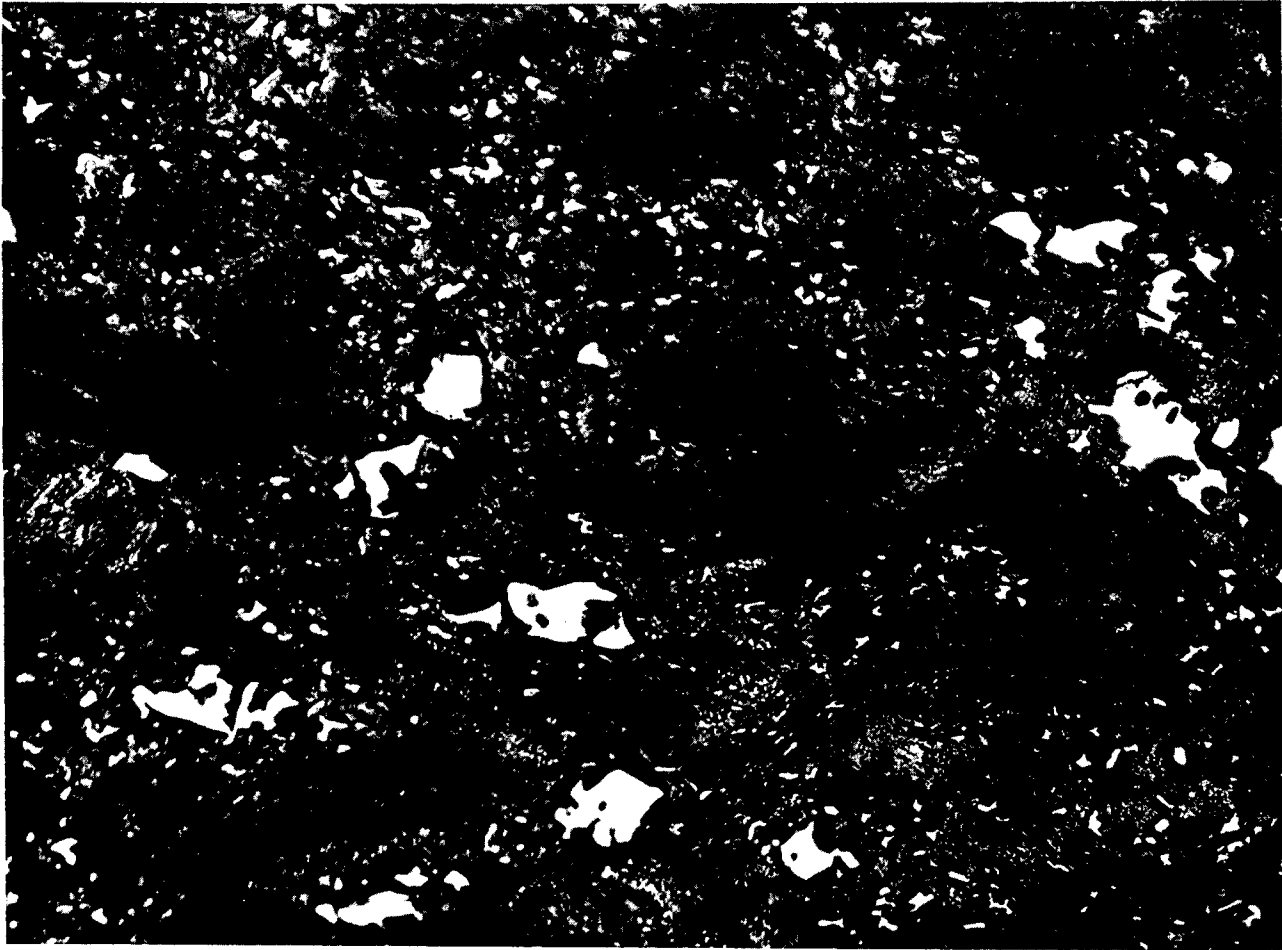


FIG. 14 - MICROSTRUCTURE OF 50 WT% HAFNIUM-GRAPHITE,
PRESSED AT 2800°C. (320X)

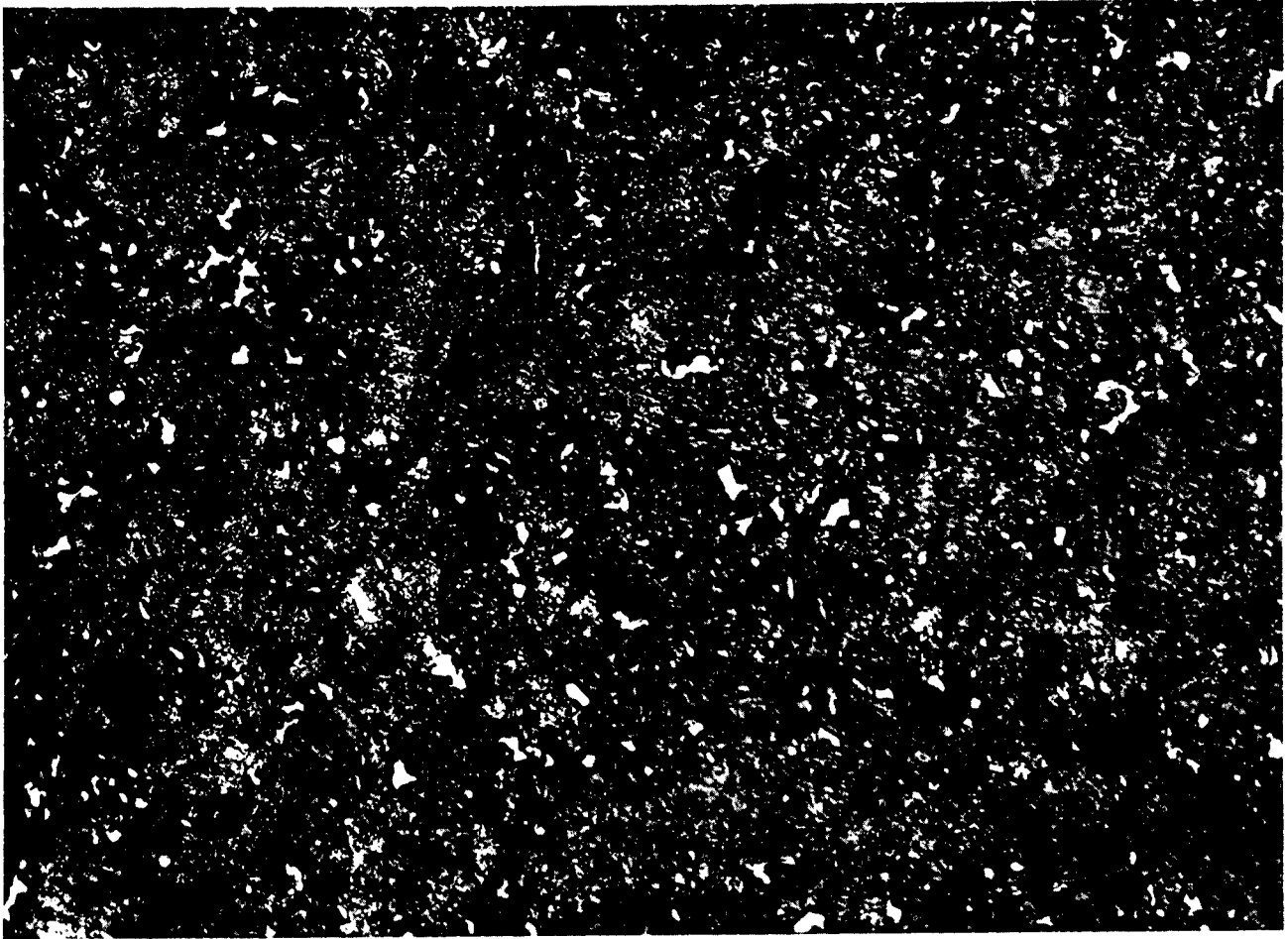
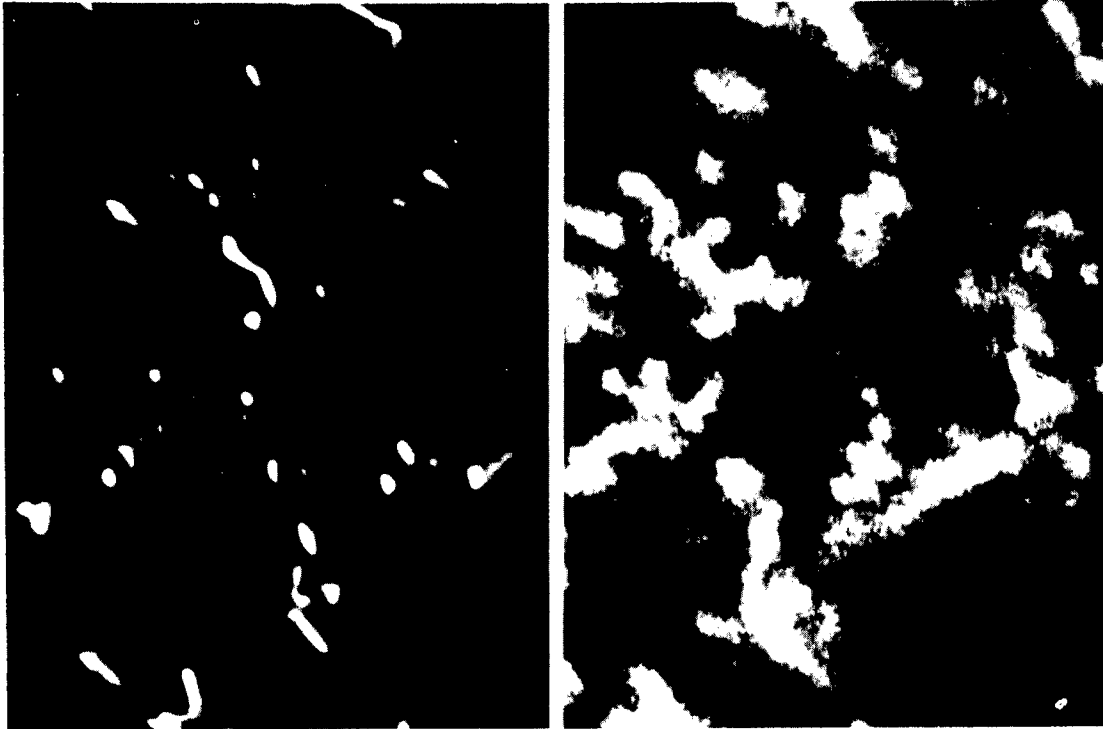


FIG. 15 - MICROSTRUCTURE OF 50 WT% HAFNIUM GRAPHITE,
PRESSED AT 3000°C. (320X)



Electron Image

X-ray Image

FIG. 16 - CARBIDE DIFFUSION AREAS IN 30 WT% HAFNIUM-GRAPHITE, PRESSED AT 2800°C. (Electron Microprobe Analyzer, X680)

C. Molybdenum-Graphite

The molybdenum-graphite system was the only one other than NbC-C and HfC-C in which flexured strengths of greater than 10,000 psi was achieved. At a metal wt% level of 20 and a 2800°C pressing temperature, bodies of appreciable strength were produced. A steady improvement in properties were realized, both with rising metal content as well as with increased processing temperature (3000°C). The data for molybdenum compositions appear in Table IV.

Formation of a liquid phase occurs at lower temperatures for molybdenum-graphite than for NbC-C or HfC-C. The eutectic temperature between Mo₂C and Mo is reported at 2200 ± 25°C.⁽²⁾ The melting points of Mo₂C and MoC are listed as 2410 ± 15°C and 2700°C respectively.⁽⁴⁾ Thus, liquid carbide diffusion should have occurred readily during the pressings at 2800° and 3000°C.

Examination of the microstructure of composition "Mo-c" shows diminution of the carbide grain size and a somewhat non-uniform distribution of these carbide particles (Figure 17). Microprobe analysis of this composition reveals the carbide diffusion into the graphite matrix (Figure 18).

A more uniform distribution of the carbide phase is apparent for compositions containing 50 wt% metal. Although finer starting materials and a higher processing temperature were used for composition "Mo-f" (Figure 19) as compared to "Mo-e" (Figure 20), the microstructures appear quite similar. However, from the differences in strength, it would appear that more extensive and uniform carbide diffusion had occurred for the composition pressed at 3000°C.

As in the HfC-C system, the strong 50 wt% metal compositions had densities of only 75% theoretical. Increases in strength can probably be expected with higher densities.

Samples containing 30 wt% metal showed a slight increase in flexural strength at 2000°C. Specimens containing greater amounts of carbide ("Mo-f") exhibited a loss in strength in the A/G direction and strong creep in the W/G direction (Figure 21). Apparently at the higher

TABLE IV
GENERAL SUMMARY OF Mo-C SYSTEM

Compositional Designation	METAL ADDITIVE		Metal, At%	GRAIN SIZE(mesh) Carbon		Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide
	Form	Metal, Wt%		Mo.	Carbon			
Mo-a	Mo	10	1.37	-200 + 325	-200	2800	2.47	3.0
Mo-b	Mo	20	3.03	-200 + 325	-200	2800	2.72	6.6
Mo-c	Mo	30	5.10	-200 + 325	-200	2800	3.03	11.0
Mo-d	Mo	30	5.10	-325	-325	3000	3.03	11.0
Mo-e	Mo	50	11.12	-200 + 325	-200	2800	3.92	23.7
Mo-f	Mo	50	11.12	-325	-325	3000	3.92	23.7

NOTE: Property data are contained in Table IV-a.

TABLE IV - a

PROPERTIES:

Comp.	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi				Coeff. of Thermal Exp. $\times 10^{-6}$ in/in/ $^{\circ}$ C (0-2000 $^{\circ}$ C)							
			Room Temperature		2000 $^{\circ}$ C		Ratio		Ratio					
			W/G	A/G	W/G	A/G	W/G:A/G	Ratio	W/G	A/G	W/G	A/G	A/G:W/G	
Mo-a			Low	Low										
Mo-b	2.32	85.3	2500	2000	1.25									
Mo-c	2.49	82.2	5540	2670	2.07									
Mo-d	2.60	85.8	8060	3510	2.30	9250	4310	2.15	1.9	8.7	4.6			
Mo-e	2.90	74.0	9350	3540	2.64									
Mo-f	2.96	75.5	14,320	4660	3.07	9370	Creep		5.2	8.7	1.7			

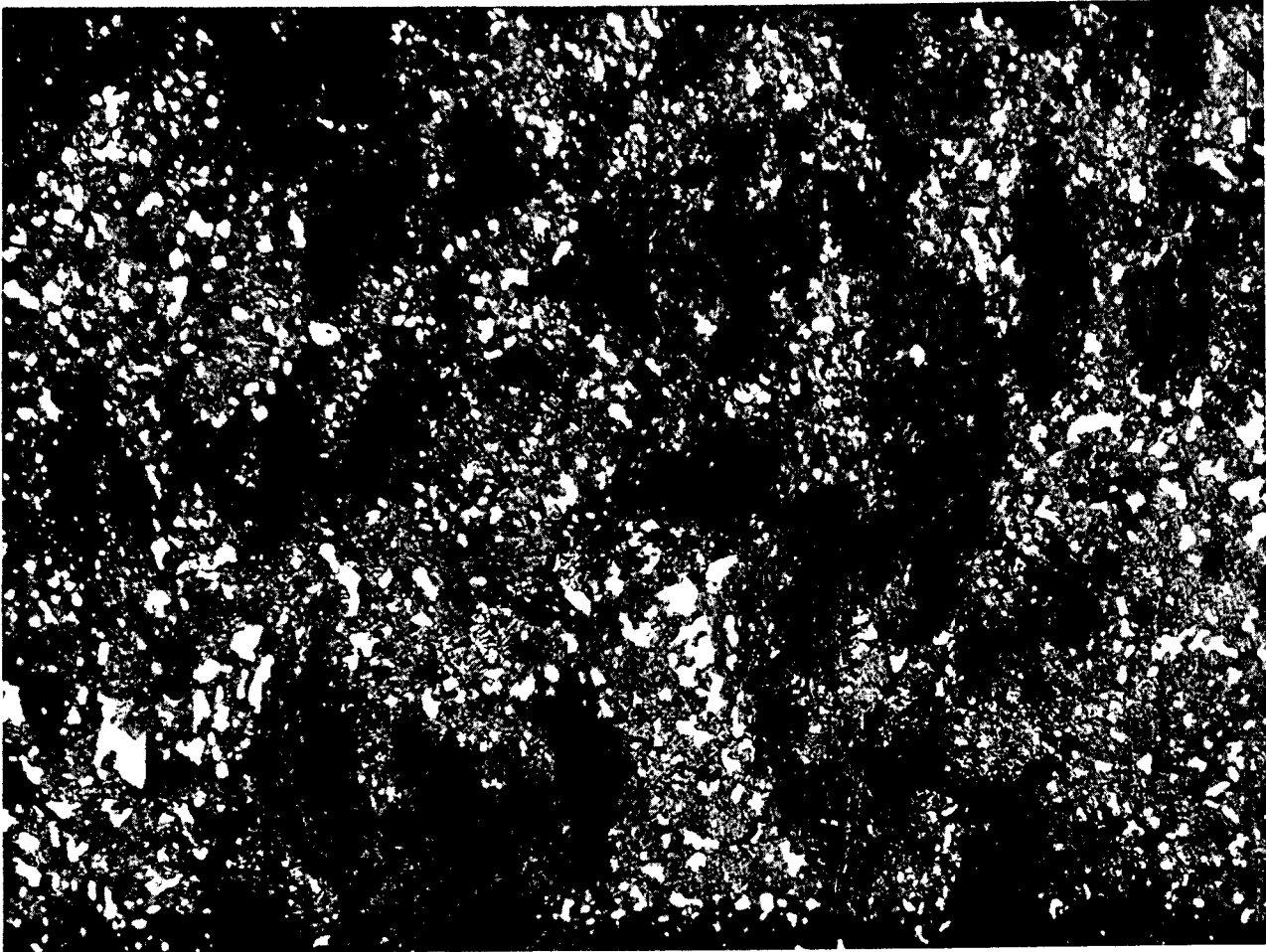
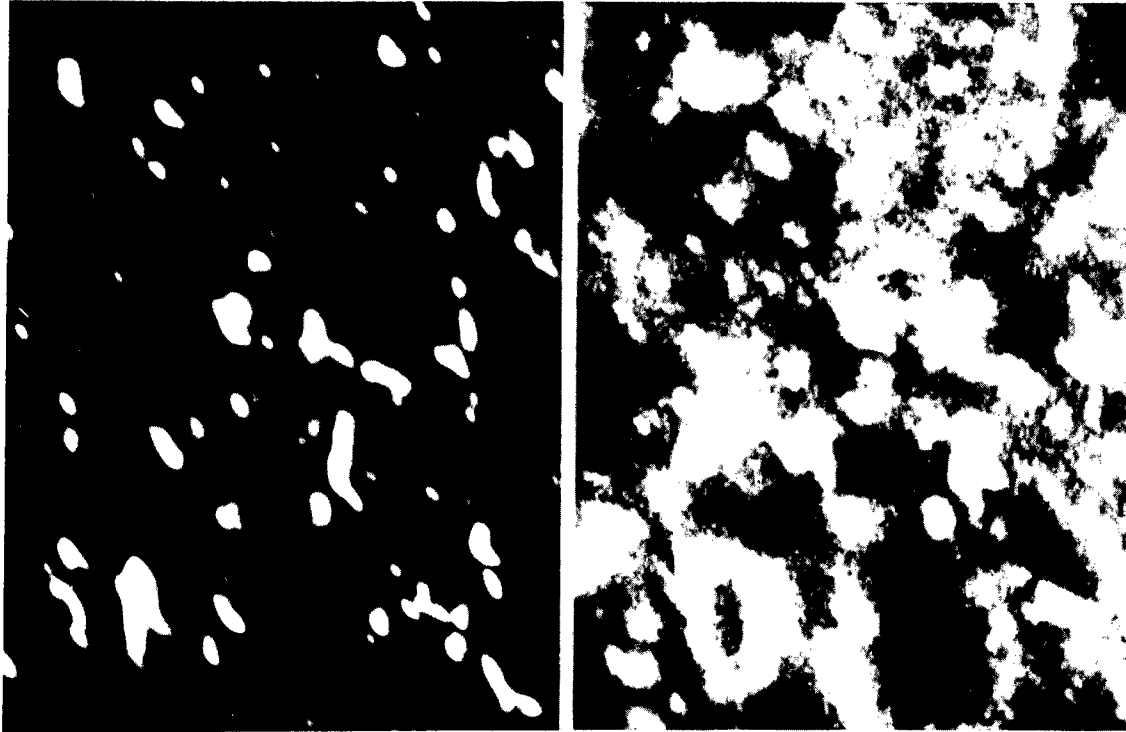


FIG. 17 - MICROSTRUCTURE OF 30 WT% MOLYBDENUM-GRAPHITE,
PRESSED AT 2800°C. (320X)



Electron Image

X-ray Image

FIG. 18 - CARBIDE DIFFUSION AREAS IN 30 WT% MOLYBDENUM-GRAPHITE, PRESSED AT 2800°C. (Electron Microprobe Analyzer, X680)

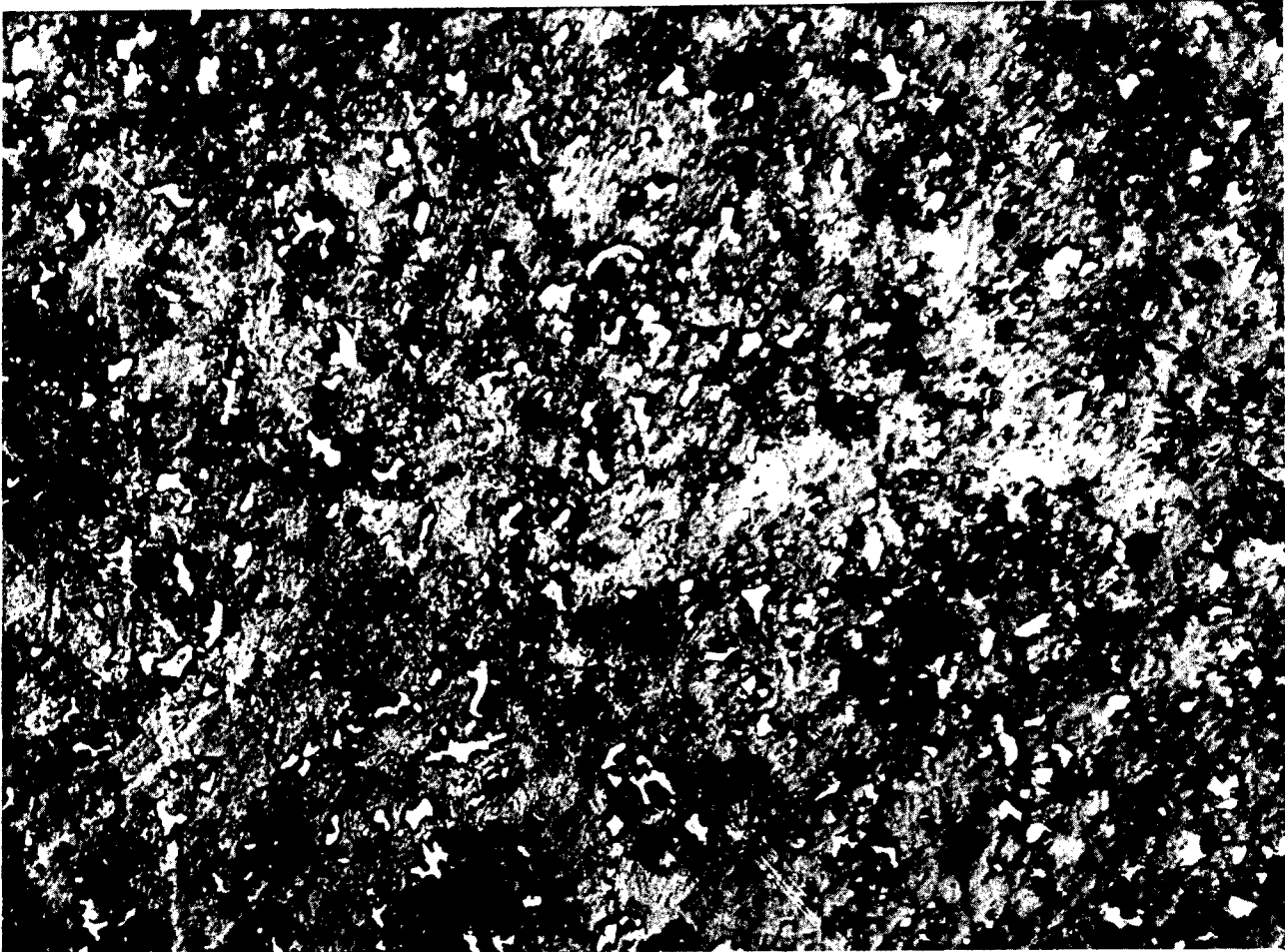


FIG. 19 - MICROSTRUCTURE OF 50 WT% MOLYBDENUM-GRAPHITE,
PRESSED AT 3000°C. (320X)

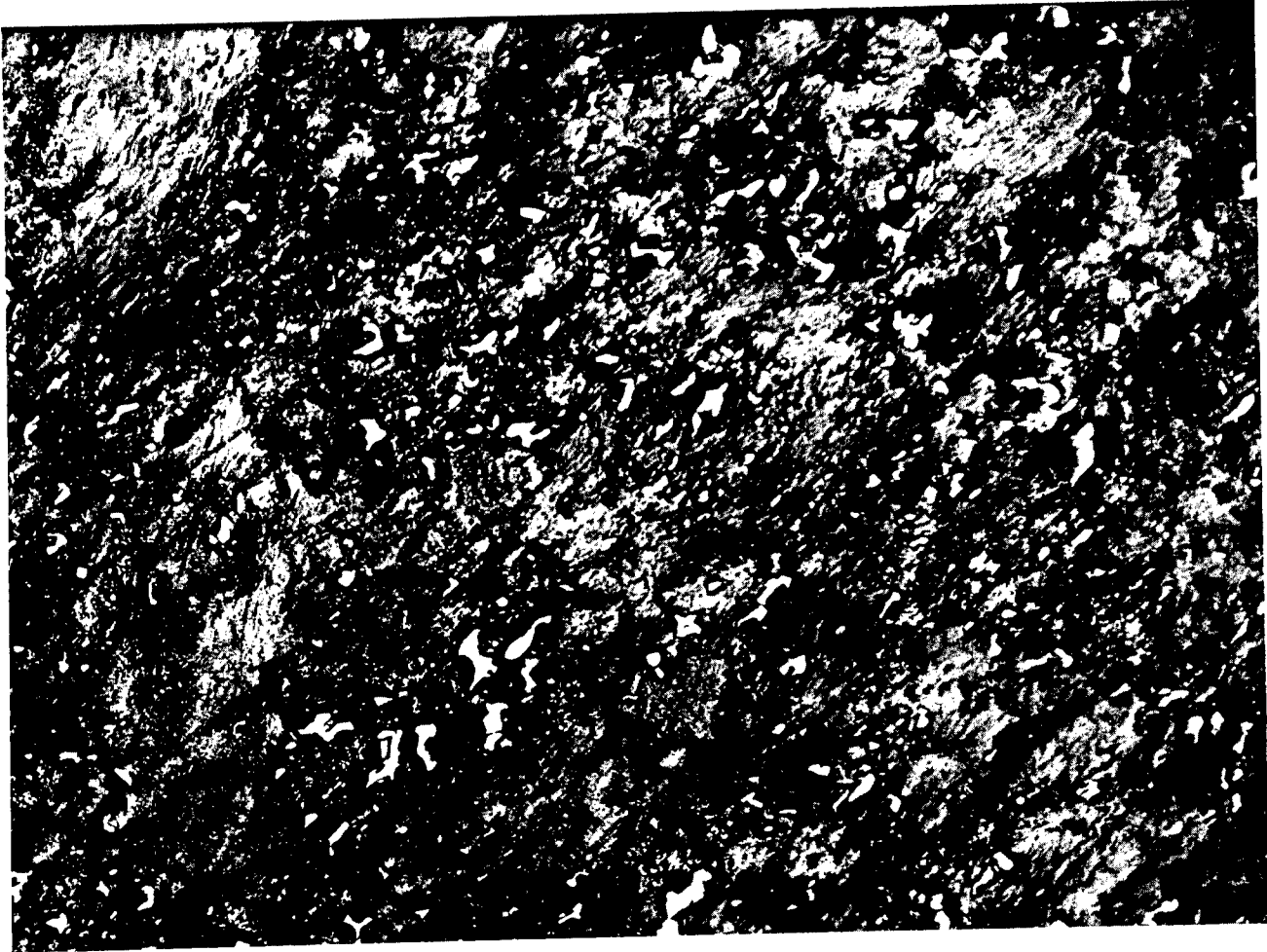


FIG. 20 - MICROSTRUCTURE OF 50 WT% MOLYBDENUM GRAPHITE,
PRESSED AT 2800°C. (320X)



SENCOR RULER

FIG. 21 - CREEP IN A/G DIRECTION DURING
FLEXURE TEST AT 2000°C
(50 WT% MOLYBDENUM-GRAPHITE)

metal concentration, the influence of creep exhibited by molybdenum carbide at 2000°C, ⁽³⁾ becomes dominant.

The tendency toward non-directionality in thermal expansion with added metal content is evident for the MoC-C as it was for the niobium and hafnium containing systems.

D. Tantalum-Graphite

Of the various systems examined on this program, the highest eutectic temperature between any metal carbide and carbon exists for the TaC-C system (3710°C). ⁽²⁾ The processing temperatures are considerably lower than this temperature, and it is doubtful that any liquid was formed during fabrication of tantalum carbide containing composites. The data presented in Table V reflect the lack of bonding in this system.

Composites of measureable strength emerged only when the metal content was raised to 50 wt%. Microstructural examination shows the body to be fairly dense although the carbide particles are large and apparently unaltered (Figure 22). Measurements of density reveal that this system is 90% dense. However, the strength values clearly show very limited bonding. High temperature tests showed that a substantial increase in strength occurs for the TaC-C system.

In order to achieve liquid formation which will enhance diffusion and bonding, several methods can be used. Increasing the processing temperature is perhaps the most obvious, but may not be the most practical. The incorporation of a carbide such as W₂C to lower the melting point of TaC and the use of finer starting materials will probably produce bodies of improved strengths in the tantalum system.

E. Zirconium-Graphite

In view of the promising properties achieved by one of the group - 4A metals, both zirconium and titanium systems were rather disappointing. The highest flexural strengths exhibited by zirconium carbide-graphite compositions were in the 5000 psi range as shown in Table VI. An increase in strength can be expected at 2000°C for this system as shown by the results for composition "Zr-e." A plateau in

TABLE V
GENERAL SUMMARY OF Ta-C SYSTEM

Compositional Designation	METAL ADDITIVE			GRAIN SIZE (mesh)	Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide
	Form	Metal, Wt%	Metal, At%				
Ta-a	TaC	10	0.73	-200 + 325 -200	2800	2.49	1.8
Ta-b	TaC	20	1.64	-200 + 325 -200	2800	2.76	4.1
Ta-c	TaC	30	2.77	-200 + 325 -200	2800	3.10	6.8
Ta-d	TaC	30	2.77	-200 + 325 -200	3000	3.10	6.8
Ta-e	TaC	50	6.22	-200 + 325 -325	3000	4.14	15.2

NOTE: Property data are contained in Table V-a.

TABLE V-a

PROPERTIES:

Composition	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi						
			Room Temperature			2000°C			
			W/G	A/G	Ratio W/G:A/G	W/G	A/G	Ratio W/G:A/G	
Ta-a			Low	Low					
Ta-b			Low	Low					
Ta-c	2.68	86.5	270	70	3.86				
Ta-d			Low	Low					
Ta-e	3.71	89.6	1870	450	4.16	3040	1090		2.79



FIG. 22 - MICROSTRUCTURE OF 50 WT% TANTALUM-GRAPHITE,
PRESSED AT 3000°C. (320X)

TABLE VI
GENERAL SUMMARY OF Zr-C SYSTEM

Compositional Designation	METAL ADDITIVE		GRAIN SIZE (mesh)	Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide		
	Form	Metal, Wt%					Metal At%	ZrC
Zr-a	ZrC	10	1.45	-200 + 325	-200	2800	2.44	4.3
Zr-b	ZrC	20	3.18	-200 + 325	-200	2800	2.65	9.4
Zr-c	ZrC	30	5.34	-200 + 325	-200	2800	2.95	15.6
Zr-d	ZrC	50	11.63	-200 + 325	-200	2800	3.70	32.7
Zr-e	ZrC	50	11.63	-325	-325	3000	3.70	32.7

NOTE: Property data are contained in Table VI-a.

TABLE VI-a

PROPERTIES:

Composition	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi							
			Room Temperature			2000°C				
			W/G	A/G	Ratio W/G:A/G	W/G	A/G	Ratio W/G:A/G		
Zr-a			Low	Low						
Zr-b	2.19	82.6	2280	1260	1.81					
Zr-c	2.14	72.5	5380	1790	3.01					
Zr-d	3.03	81.9	5320	2540	2.09					
Zr-e	2.10	56.8	4620	1410	3.28	7670	2610			2.94

strengths appeared to have been reached at the 30 wt% metal level. Increasing the metal content to 50 wt% with the use of finer starting material and higher processing temperature did not result in improved physical properties.

Metallographic examination of a 30 wt% (by metal) ZrC-C specimen prepared at 2800°C reveals a fairly uniform dispersion of a fine carbide phase (Figure 23). The particle size of the carbide indicates that eutectic formation occurred with subsequent recrystallization. The eutectic temperature between the carbide and carbon is listed as $2850 \pm 50^\circ\text{C}$.⁽²⁾ Microprobe analysis of this composition shows diffusion of the carbide into the graphite matrix (Figure 24).

The bulk densities with the exception of composition "Zr-d" remain constant with increasing metal content, and hence, the percent theoretical density values show a decrease. The microstructure of the exception (3.03 g/cc density) reveals large carbide grains (Figure 25) whereas its equivalent composition pressed at 3000°C (Figure 26) shows a carbide dispersion similar to that of the 30 wt% metal composite pressed at 2800°C (Figure 23). It would appear from these photographs that an amount of carbide in excess of 50 wt% metal was present for composition "Zr-d," accounting for the high density.

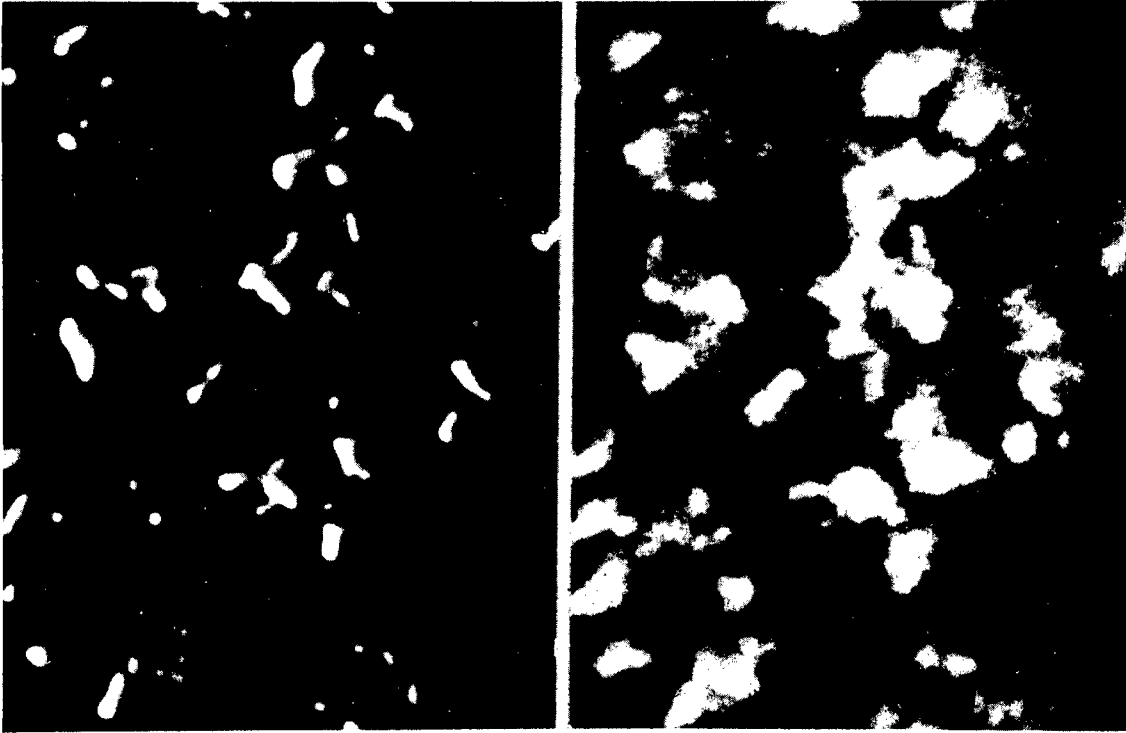
This lack of densification with increasing metal content is probably responsible for the plateau in strengths. That liquid formation and diffusion has occurred is apparent from the photomicrographs. It is not known at this time why this system does not show the bonding and densification achieved by some of the other systems.

F. Titanium-Graphite

Investigations of the titanium carbide-graphite system yielded results similar to those for the ZrC-C compositions. Appreciable strengths were realized at a 10 wt% metal content; in terms of atomic percent metal and theoretical volume percent carbide (see Figures 3 and 4) it can be seen that a substantial metal level exists at this wt% addition. Again, a constancy in bulk densities was shown, seemingly unaffected by increased metal contents (Table VII). However, increases in flexural



FIG. 23 - MICROSTRUCTURE OF 30 WT% ZIRCONIUM-GRAPHITE,
PRESSED AT 2800°C. (320X)



Electron Image

X-ray Image

FIG. 24 - CARBIDE DIFFUSION AREAS IN 30 WT% ZIRCONIUM-GRAPHITE, PRESSED AT 2800°C. (Electron Microprobe Analyzer, X680)

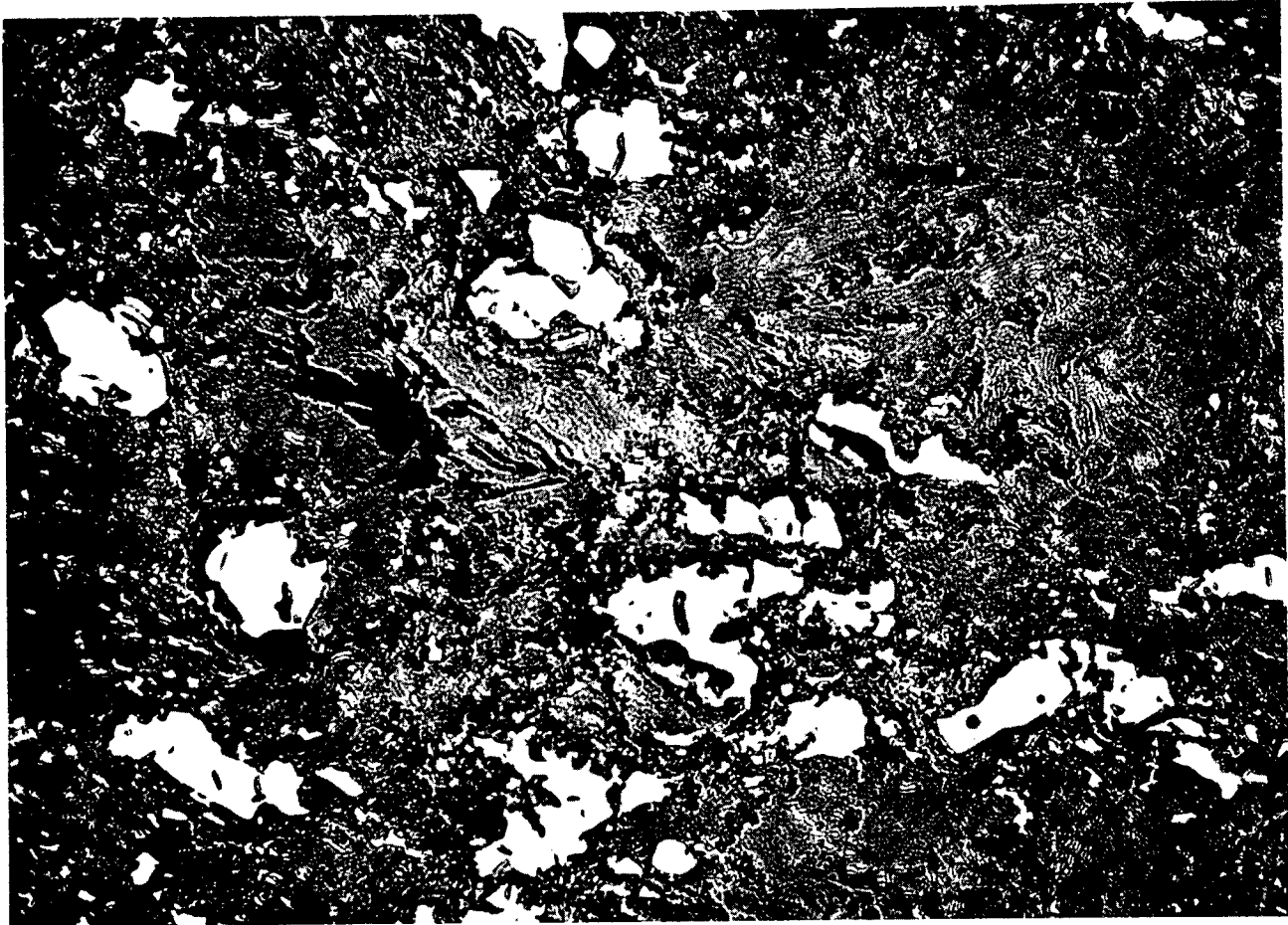


FIG. 25 - MICROSTRUCTURE OF 50 WT% ZIRCONIUM-GRAPHITE,
PRESSED AT 2800°C. (320X)

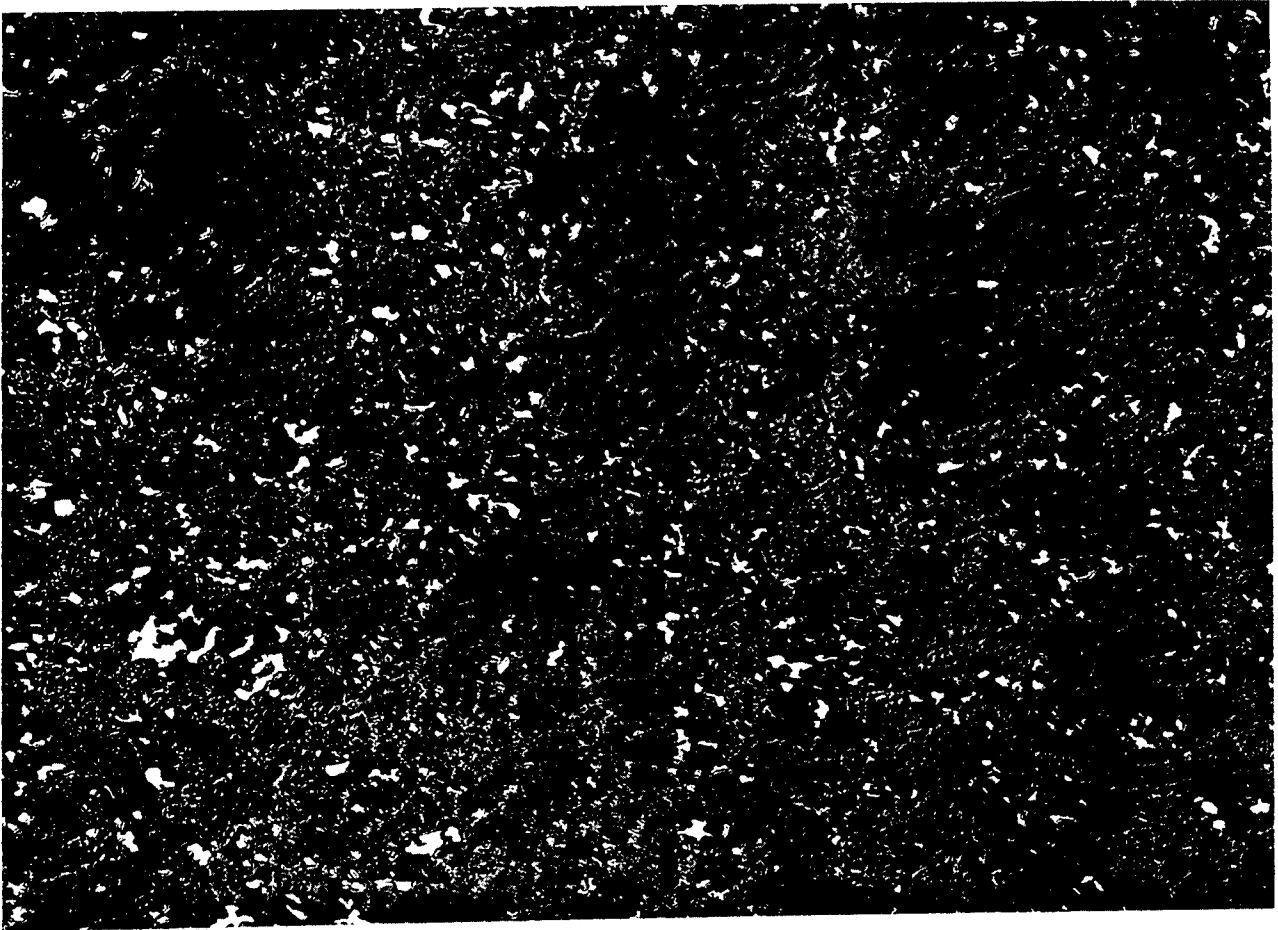


FIG. 26 - MICROSTRUCTURE OF 50 WT% ZIRCONIUM-GRAPHITE,
PRESSED AT 3000°C. (320X)

TABLE VII
GENERAL SUMMARY OF Ti-C SYSTEM

Compositional Designation	METAL ADDITIVE		GRAIN SIZE(mesh)		Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide
	Form	Metal Wt%	Metal At%	TiC			
Ti-a	TiC	10	2.71	-200 + 325	2800	2.42	6.2
Ti-b	TiC	20	5.89	-200 + 325	2800	2.61	13.3
Ti-c	TiC	30	9.70	-200 + 325	2800	2.83	21.7
Ti-d	TiC	50	20.04	-325	3000	3.41	43.5

PROPERTIES:

Composition	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi				
			Room Temperature		2000 °C		
			W/G	A/G	W/G	A/G	
Ti-a	2.08	86.0	2920	1270	2.30		
Ti-b	2.07	79.3	2050	1480	1.39		
Ti-c	1.96	69.3	3830	1570	2.44		
Ti-d	2.02	59.2	4710	1140	4.13	6580	
						2100	3.13

strength were realized with rising metal levels. The 2000°C strength was substantially higher than the room temperature value.

A fairly homogeneous dispersion of a fine carbide phase attests to liquid eutectic formation during hot pressing for composition Ti-C (Figure 27). Considerable diffusion of carbide is illustrated in Figure 28. Eutectic melting between TiC and C occurs at $2780 \pm 25^\circ\text{C}$.⁽²⁾

The inability to obtain strong dense bodies with either the ZrC-C or TiC-C compositions has been somewhat puzzling. The eutectic temperatures of these binary systems would appear ideal for enhanced liquid phase sintering to occur at the processing temperatures used. Microstructural examination suggests that this mechanism, i. e. eutectic liquid formation, does occur. The lack of strong bonding and the limited densification with increasing metal content indicates that bonding offered by TiC-C or ZrC-C eutectic phases is inferior to that offered by HfC-C or NbC-C.

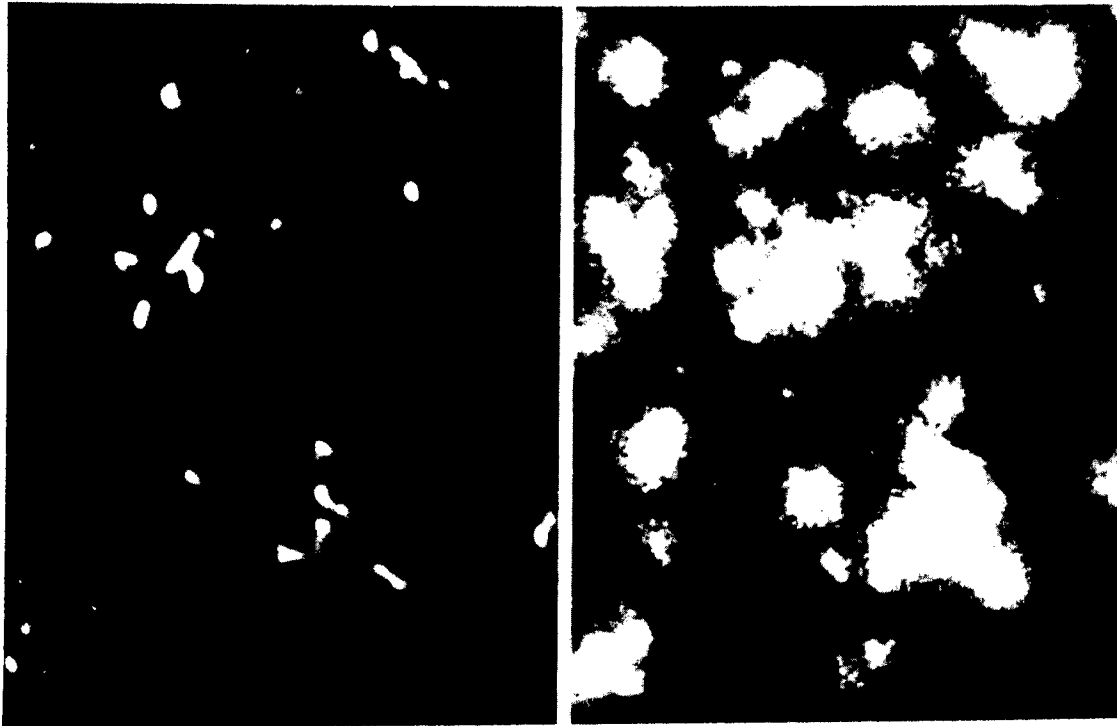
G. Boron-Graphite

The boron carbide-graphite system was characterized by large amounts of liquid phase. This was evidenced by extrusion of sample material around the punches in processing, and in one case, by reaction zones through the mold wall. The melting point of B_4C is listed as 2350°C ,⁽⁵⁾ and the B_4C -C eutectic is reported as about 70°C lower than the melting point.⁽⁶⁾ Studies in this system were limited to 30 wt% metal; as seen in Figures 3 and 4, these additions were relatively high in terms of atomic percent boron and volume percent of carbide due to the low atomic weight of boron.

At a processing temperature of 2800°C , metal wt% additions of 10, 20 and 30 had little influence on strength, but increased the anisotropy (Table VIII). Lowering the pressing temperature to 2300°C had negligible effect on strength; raising the temperature to 3000°C and lowering the metal content to 5 wt% yielded the densest and strongest bodies in this system. The boron bodies showed the least anisotropy of any system studied in this program.



FIG. 27 - MICROSTRUCTURE OF 30 WT% TITANIUM-GRAPHITE,
PRESSED AT 2800°C. (320X)



Electron Image

X-ray Image

FIG. 28 - CARBIDE DIFFUSION AREAS IN 30 WT% TITANIUM-GRAPHITE, PRESSED AT 2800°C. (Electron Microprobe Analyzer, X680)

TABLE VIII
GENERAL SUMMARY OF B₄C SYSTEM

Compositional Designation	METAL ADDITIVE		GRAIN SIZE (mesh)		Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide
	Form	Metal Wt% Metal At%	B ₄ C	Carbon			
B-a	B ₄ C	5 5.52	-325	-325	3000	2.27	5.8
B-b	B ₄ C	10 10.98	-325	-200	2800	2.29	11.7
B-c	B ₄ C	20 21.71	-325	-200	2800	2.32	23.6
B-d	B ₄ C	30 32.24	-325	-200	2800	2.35	35.9
B-e	B ₄ C	30 32.24	-325	-200	2300	2.35	35.9

PROPERTIES:

Comp.	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi				Coeff. of Thermal Exp. x 10 ⁻⁶ in/in/°C (0-2000°C)					
			Room Temperature		2000°C		W/G		A/G			
			W/G	A/G	W/G	A/G	W/G:A/G	Ratio	W/G	A/G	W/G	A/G
B-a	1.96	86.3	5890	4880	9830	8420	1.21	0.98	1.17	3.4	4.6	1.4
B-b	1.83	79.9	4070	4160								
B-c	1.81	78.0	3450	2940			1.17					
B-d	1.83	77.9	4460	2100			2.12					
B-e	1.84	78.3	4680	2590			1.81					

The uniformity in bulk densities and strengths may be due in part to the extrusion and loss of some of the boron carbide rich phase. The microstructure of the 30 wt% metal composition (Figure 29) shows very small amounts of free carbide; possibly the bulk of the B_4C is too fine to be seen at this magnification. Photomicrograph of the 5 wt% metal sample shows a similar amount, or possibly slightly more of the free carbide phase (Figure 30).

Excellent high temperature strengths were exhibited by composition "B-a." Of the various systems studied the most substantial increase in strength at 2000°C was exhibited by the B_4C -C composite. Measurement of thermal expansion reflects the isotropy revealed in flexural strength tests.

H. Beryllium-Graphite

The lowest melting carbide examined on this program was Be_2C which is reported to decompose at 2100°C. ⁽³⁾ In the range of metal wt% additions studied, beryllium systems represented the largest volume content of carbide incorporated (Figure 4).

Three compositions were prepared at 2800°C. The results presented in Table IX, show that increased bulk densities and a closer approach to theoretical density are realized with increasing metal content. However, this densification is accompanied by a loss in strength, indicating that the optimum metal amount for good bonding lies in wt% additions of less than 10%.

I. Uranium-Graphite

Uranium-graphite systems were prepared using either the carbide or oxide of uranium as the starting material. Due to the relatively low melting points (<2500°C) of the uranium carbides, it was felt that ample liquid phase would be available for diffusion and subsequent recrystallization as a strong bonding phase. The results of these studies are presented in Table X.



FIG. 29 - MICROSTRUCTURE OF 30 WT% BORON-GRAPHITE,
PRESSED AT 2300°C. (320X)

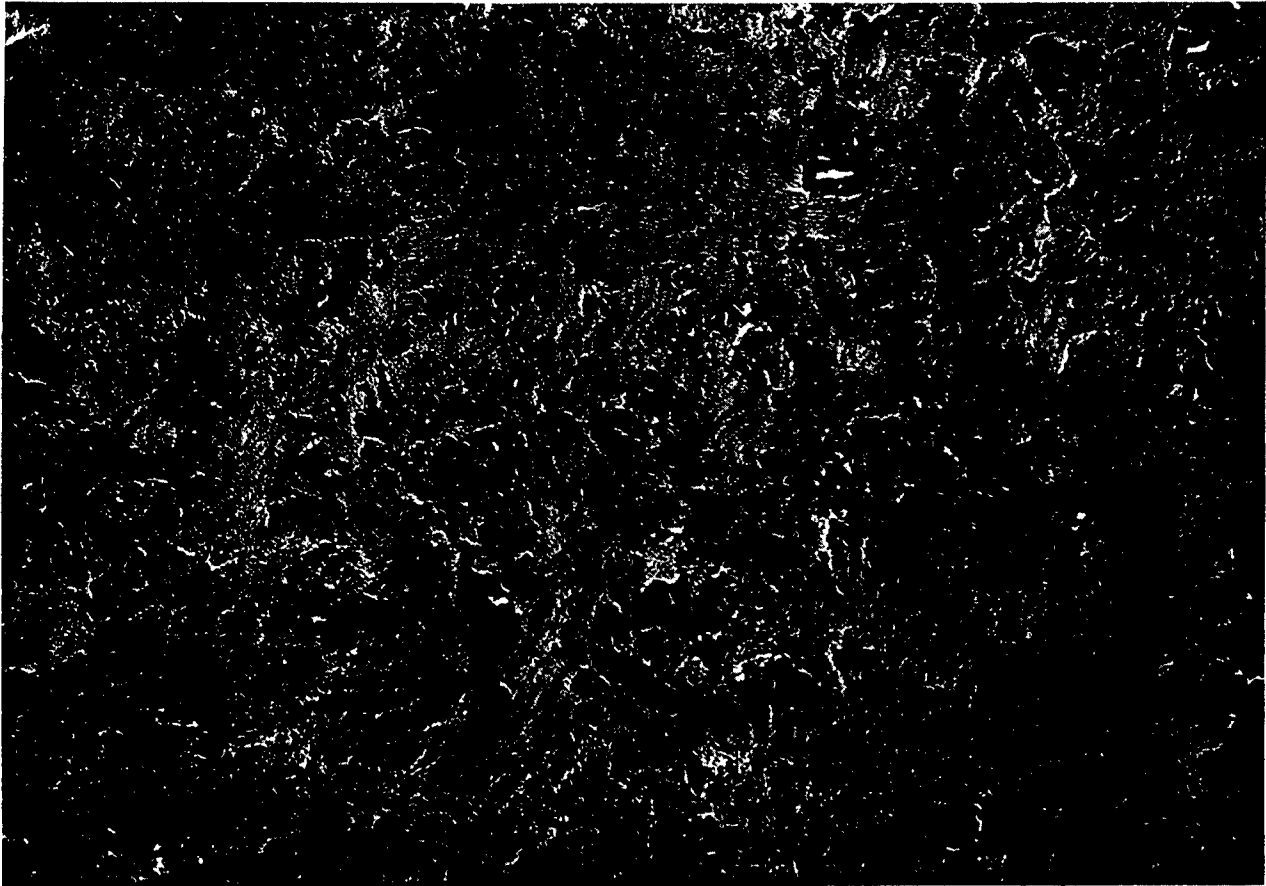


FIG. 30 - MICROSTRUCTURE OF 5 WT% BORON-GRAPHITE,
PRESSED AT 3000°C. (320X)

TABLE IX
GENERAL SUMMARY OF Be-C SYSTEM

Compositional Designation	METAL ADDITIVE			GRAIN SIZE (mesh)		Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide
	Form	Metal Wt%	Metal At%	Be-C	Carbon			
Be-a	Be	10	12.90	-200	-200	2800	2.19	19.2
Be-b	Be	20	25.00	-200	-200	2800	2.13	37.3
Be-c	Be	30	36.36	-200	-200	2800	2.06	54.3

PROPERTIES:

Composition	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi		
			W/G	A/G	Ratio W/G:A/G
Be-a	1.76	80.4	4000	1400	2.86
Be-b	1.84	86.4	3780	1210	3.12
Be-c	1.94	94.2	2210	1230	1.80

TABLE X
GENERAL SUMMARY OF U-C SYSTEM

Compositional Designation	METAL ADDITIVE		GRAIN SIZE (mesh) Carbide/Oxide Carbon	Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide
	Form	Metal Wt% Metal At%				
U-a	UC ₂	10 0.56	-200 + 325	2800	2.49	2.0
U-b	UC ₂	20 1.25	-200 + 325	2800	2.77	4.5
U-c	UC ₂	30 2.12	-200 + 325	2800	3.12	7.6
U-d	UO ₂	30 2.12	-200 + 325	3000	3.12	7.6
U-e	UO ₂	50 4.80	-200 + 325	2800	4.10	16.6

PROPERTIES:

Composition	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi		
			Room Temperature		
			W/G	A/G	Ratio W/G:A/G
U-a			Low	Low	
U-b			Low	Low	
U-c	2.24	71.8	1050	530	1.98
U-d	2.48	79.5	2020	690	2.93
U-e	3.53	86.1	4370	2970	1.47

At the 10 and 20 wt% metal levels, bodies were too weak to machine and can be considered to have zero strength. In this respect, a similarity to hafnium and tantalum systems is seen, and Figure 4 shows that the volume percent carbide at these levels is quite low. At the 30 wt% level, a low strength level is achieved. Substitution of UO_2 for UC_2 at this metal content and processing at 3000°C yielded somewhat denser, stronger bodies. A still further increase in strength is realized at 50 wt% metal pressed at 2800°C .

From these results indications are that further increases in uranium content would result in bodies of even higher strengths. However, humidity resistance of this system was poor; after exposure to 100% humidity conditions for one week, dimensional changes and zones of reaction were observed (Figure 31). Thus the usefulness of this system would be limited to dry conditions at room temperature.

J. Thorium-Graphite

Hot pressed bodies of the thorium-graphite system were extremely susceptible to sample failure during fabrication. At all metal contents, gross internal cracking occurred probably during cooling. The strengths listed for compositions "Th-c" and "Th-e" represent samples obtained from selected portions of the billets which had not cracked. This fissuring can be attributed to changes in thermal expansion attending the crystal transformation of ThC_2 from monoclinic to cubic at about 1400°C .

Included in Table XI are the various compositions which were studied. A second deterrent to the usefulness of this system is the gross susceptibility to atmospheric moisture. Extensive bloating and distortion is readily seen in a sample which had been exposed for one week at room temperature in a 100% relative humidity atmosphere (Figure 31).



FIG. 31 - EFFECT OF HUMIDITY ON ThC-C AND UC-C

TABLE XI
GENERAL SUMMARY OF Th-C SYSTEM

Compositional Designation	METAL ADDITIVE			GRAIN SIZE (mesh)	Pressing Temp. °C	Theo. Density, g/cc	Theo. Vol% Carbide
	Form	Metal Wt% At%	Th Carbon				
Th-a	Th	10	0.58	-200 + 325	2800	2.47	2.8
Th-b	Th	20	1.27	-200 + 325	2800	2.72	6.3
Th-c	Th	30	2.17	-200 + 325	2800	3.03	10.4
Th-d	Th	30	2.17	-200 + 325	3000	3.03	10.4
Th-e	Th	50	4.91	-200 + 325	2800	3.91	22.5

PROPERTIES:

Composition	Density, g/cc	% Theo. Density	FLEXURAL STRENGTH, psi		
			W/G	A/G	Ratio W/G:A/G
Th-a			Low	Low	
Th-b			Low	Low	
Th-c	2.36	77.9	1200	100	
Th-d			Low	Low	
Th-e	2.36	60.4	3990	1380	2.89

IV. SUMMARY AND FUTURE WORK

The initial program to assess the feasibility of fabricating metal-graphite composites by hot pressing has been concluded. Examination of fabricability and some physical properties has led to the following observations:

1. Preparation of dense, strong metal-graphite composites by hot pressing has been shown to be feasible, with notable success in selected systems. This simple, one step method involves no binders and eliminates the need for reimpregnation. In addition, the finished bodies are easily machinable, adding further versatility to this method.
2. The formation of a liquid phase in a metal carbide-graphite system enhances sintering and leads to bodies of high strength. The mechanism is thought to be diffusion of the carbide-carbon eutectic liquid at high temperatures under pressure, and subsequent recrystallization of this phase which yields strong bonding.
3. Among the systems studied, additions of niobium, hafnium and molybdenum carbides to the graphite produces the strongest bodies with strengths in excess of 10,000 psi in the with-grain direction. Intermediate strengths were exhibited by compositions containing the carbides of zirconium, titanium, boron, beryllium, and uranium. Composites incorporating tantalum carbide or thorium carbide had low strengths. The former system did not form any liquid at the processing temperatures used, and the latter system was subject to failure on cooling due to dimensional changes accompanying a phase transformation for ThC_2 .
4. A higher processing temperature (3000° vs 2800°C) and the use of finer starting materials (< 44 microns vs. $44\text{-}74$ microns) results in improved densification and bonding for the systems NbC-C , $\text{Mo}_2\text{C-C}$, and HfC-C .

5. Hot pressed bodies in the Nb-C and Hf-C systems offer good physical properties at 2000°C and exhibit high strength to weight ratios. They show excellent potential for high temperature applications.
6. A minimum amount of metal carbide appears necessary for densification and strength in any system. In terms of theoretical volume% carbide, the amount is ~6%.

The results obtained from these preliminary investigations have been of great interest not only in themselves, but also as indications of areas of study which show great potential. From the number of different compositions studied in the ten systems, certain trends are seen, giving direction to full optimization of a given system. For example, in the HfC-C system, additional experimentation should include:

1. Incorporation of more metal--present data shows that the optimum amount for best properties has not yet been reached.
2. Fuller densification--since strengths of 12,000 psi are shown by a 75% dense body, a level of 20,000 psi may be realized by composites more closely approaching theoretical density.

Future work will be characterized by more rigid control in the basic preparation of various systems. Simple operations such as mixing of raw materials and loading of the hot press mold can yield heterogeneous bodies if not properly conducted. Temperature control and monitoring during processing is greatly improved by the use of a two-color pyrometer. This instrument measures the ratio of radiation intensity at two wavelengths and thus obviates the factor of error inducing fumes. The effect of soaking at the pressing temperature for varying times should be explored; it is anticipated that denser, stronger bodies will result.

As the number of candidate systems and compositions narrows, characterization to a fuller and more sophisticated degree is warranted. The completeness of such characterization should be of great help in establishing bases on which the behavior of other compositions and systems can be closely predicted and controlled.

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