UNPUBLISHED PRELIMINARY DATA

IIT Research Institute
10 West 35 Street, Chicago, Illinois 60616
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Quarterly Report No. 2
GRAPHITE-METAL COMPOSITES
Contract No. NASr-65(09)

I. INTRODUCTION

This project was conceived as a means of fabricating high-strength bulk graphite-metal structures by taking advantage of the transient liquid phase which is formed in the carbide-carbon eutectic region to act as a bonding agent. This technique employs no binder materials, and is quite straightforward in operation. Carbon and metal powders (or carbides) are simply dry-mixed, poured into a graphite mold, and hot-pressed.

Ten metal elements were selected as "alloying" agents; these were:

1. Hafnium
2. Tantalum
3. Molybdenum
4. Columbium
5. Zirconium
6. Boron
7. Titanium
8. Beryllium
9. Uranium
10. Thorium

As will become evident later in the report, some metals are more amenable to the technique than others. Some of the results appear to be anomalous, and we hope we will be able to resolve these discrepancies during the next quarterly period.

II. RESULTS AND DISCUSSION

The results that we have generated to date are somewhat varied, and it is quite difficult to generalize at this stage of development. Table I presents a general summary of the composites made, and some of their physical properties. The rationale underlying each system is discussed in detail below.

A. Hafnium-Carbon Composites

This system has excellent potential for developing a high-strength material of exceptional refractoriness. As can be seen in Figure 1, metal additions of 10 and 20 wt%, pressed at 2800°C, have low strengths. With a 30 wt% addition, however, the flexural strength increases abruptly to 9200 psi. Figures 2 and 3 show the microstructure of the 30 wt% (2.8 at.%) composite. There are a considerable number of comparatively large pores, the original large carbide grains have all but disappeared, and instead there is a fine dispersion of carbide particles that precipitated out on cooling. The carbon grains show shadings of gray; the lighter areas indicating higher metal solution than the dark grains. It is evident that the carbide has reached the eutectic region with the formation of sufficient liquid phase to become self-bonding. It is also evident that this system has not yet reached its highest potential. The elimination of the pores, the use of finer starting materials, an increase in metal level, and higher process temperature (3000°C) should result in significantly higher strength. A test sample incorporating these changes has been made, but has not yet been evaluated. Test results on this sample will be included in the next report.

B. Tantalum-Carbon Composites

The tantalum-carbon system has resisted all efforts to date to make a composite of acceptable strength. Samples with 10, 20, and 30 wt% tantalum, pressed at 2800°C, all had flexural strengths below 300 psi. Increasing the pressing temperature to 3000°C at the 30 wt% metal level

TABLE I

GENERAL SUMMARY OF COMPOSITION, PROCESS TEMPERATURES, AND STRENGTH DATA

Series w/o Metal	Pressing Temp., °C	Flexural Strength, psi W/G	Flexural Strength, psi A/G	Form of Metal Addition	Density, g/cc	Remarks
30Hf	2800	9240	2270	Carbide	2.79	
20Hf	2800	264	71	Carbide	2.33	
10Hf	2800	Low	--	Carbide	--	
30Ta	3000	Low	--	Carbide	2.68	Very friable,
30Ta	2800	267	73	Carbide	--	and almost
20Ta	2800	Low	--	Carbide	--	impossible to
10Ta	2800	Low	--	Carbide	--	machine.
50Mo	2800	9347	3533	Metal	--	
30Mo	2800	5540	2670	Metal	2.49	
20Mo	2800	2500	2000	Metal	2.32	
10Mo	2800	Low	--	Metal	--	
50Cb	2800	2514	1793	Metal	--	
30Cb	2800	2890	1260	Metal	2.69	
20Cb	2800	119	--	Metal	2.26	
10Cb	2800	Low	--	Metal	--	
30Zr	2800	5380	2260	Carbide	2.14	
20Zr	2800	2281	934	Carbide	2.19	
10Zr	2800	Low	--	Carbide	--	
30B	2300	4680	2590	Carbide	1.84	
30B	2800	4460	2100	Carbide	1.83	
20B	2800	3450	2940	Carbide	1.81	
10B	2800	4070	4160	Carbide	1.83	
30Ti	2800	3830	1570	Carbide	1.96	
20Ti	2800	2050	1480	Carbide	2.07	
10Ti	2800	2915	1274	Carbide	2.08	
30Be	2800	2210	1400	Metal	1.94	
20Be	2800	3780	1210	Metal	1.84	
10Be	2800	4000	1230	Metal	1.76	
50U	2800	4370	2970	Oxide	--	
30U	3000	2016	691	Oxide	--	
30U	2800	1050	526	Carbide	--	
20U	2800	Low	--	Carbide	--	
10U	2800	Low	--	Carbide	--	
50Th	2800	3993	1376	Metal	--	Samples show
30Th	3000	--	--	Metal	--	severe inter-
30Th	2800	1200	100	Metal	2.36	nal cracking.
20Th	2800	--	--	Metal	--	
10Th	2800	--	--	Metal	--	

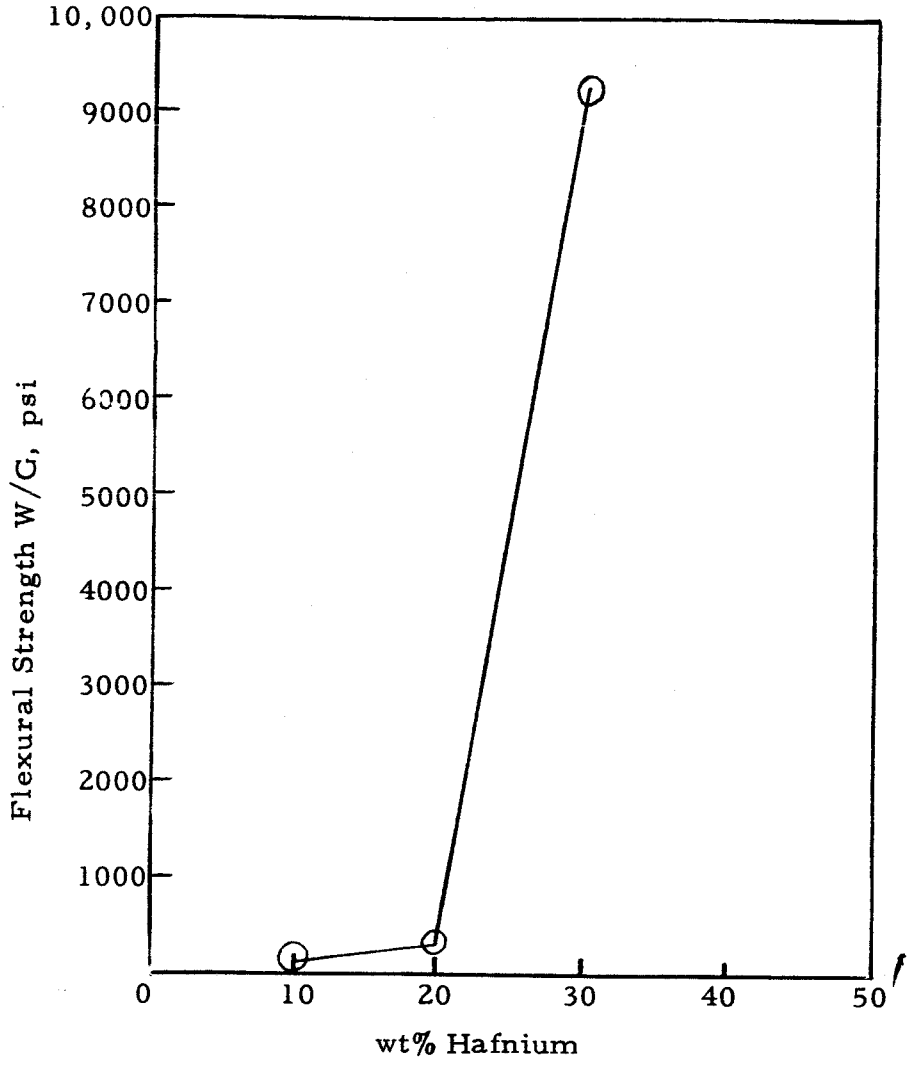

FIG. 1. FLEXURAL STRENGTH VS. METAL LEVEL FOR HAFNIUM-CARBON COMPOSITES. 2800°C PRESSING TEMPERATURE.

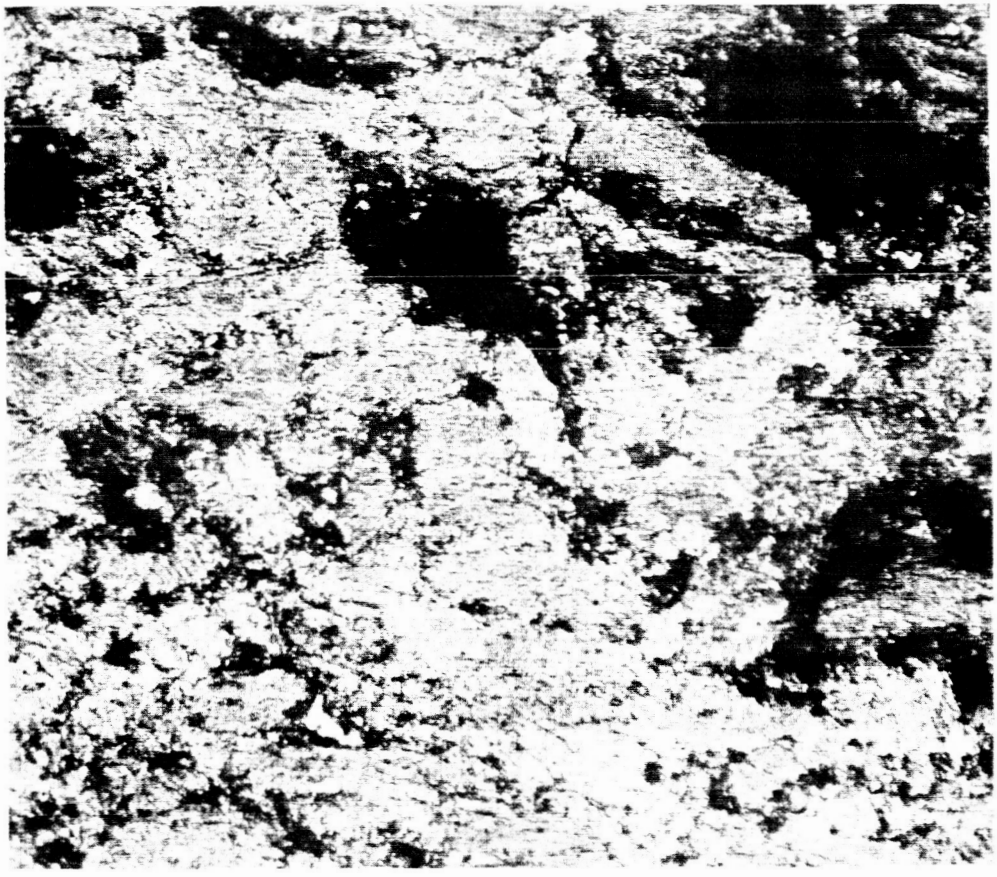

FIG. 2. MICROSTRUCTURE OF 30 WT% HAFNIUM-CARBON COMPOSITE, PRESSED AT 2800°C. (BLACK AREAS ARE VOIDS.)

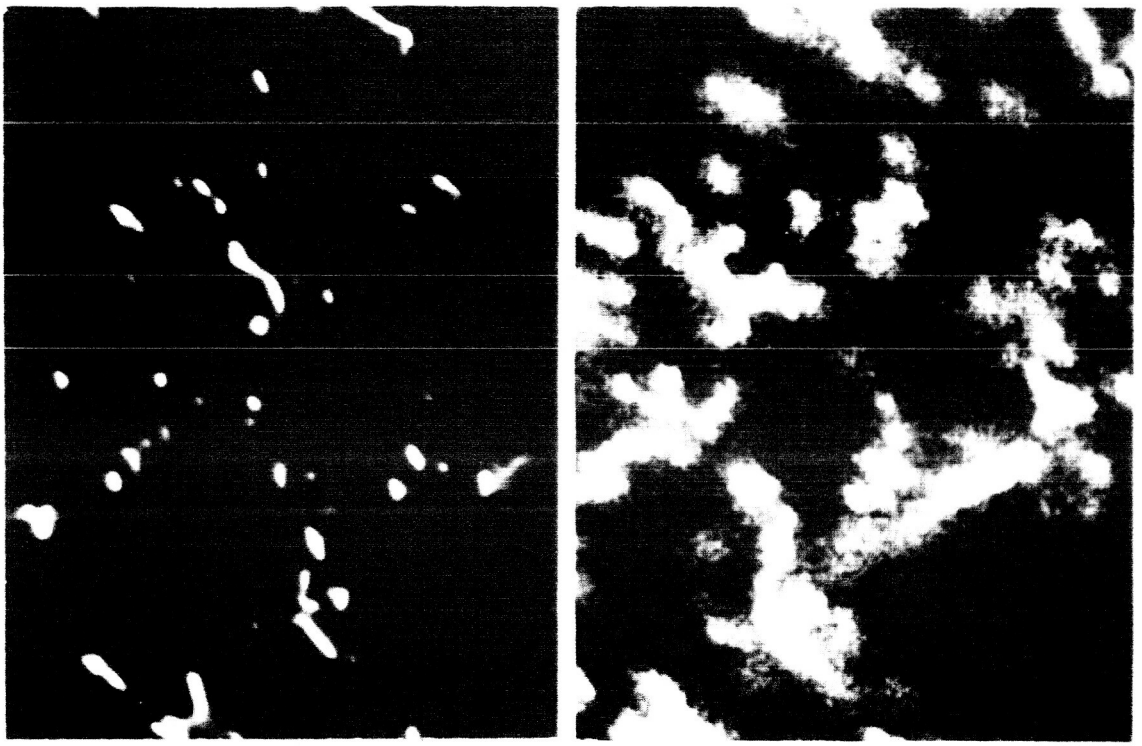

FIG. 3 - ELECTRON IMAGE (LEFT) OF SMALL FREE-CARBIDE GRAINS, AND X-RAY IMAGE (RIGHT) SHOWING HAFNIUM-RICH DIFFUSION AREAS. (Electron Microprobe Analyzer, X680).

showed no improvement in strength. Figure 4 shows the microstructure of the 30 wt% tantalum sample pressed at 2800°C. The carbide grains are essentially unaltered, except possibly for some rounding and flattening of the grains. Very little metal solution, if any, has occured, and is no doubt the reason for the low strengths.

It is reasonable to assume, therefore, that the metal-strengthening mechanism does not readily occur in the solid state, and that the liquid carbide-carbon eutectic region must be reached to derive the benefit of adding metals. With the tantalum carbide-carbon eutectic reported to be approximately 3450°C, it is not surprising that this series had low strength levels. It would also seem that the processing temperatures necessary to make high-strength composites with tantalum metal alone are impractical.

C. Molybdenum-Carbon Composites

The molybdenum-carbon system has been found to be a very interesting one. Pressed at 2800°C, composites at 10, 20, 30, and 50 wt% metal levels rose from too-low-to-test to increasing flexural strengths of 119 psi at 20%, 5540 psi at 30%, and 9350 psi at the 50% metal level (Figure 5). In Figure 6 (the 30% metal addition) it can be clearly seen that there are areas rich in dissolved molybdenum from which excess metal carbide has precipitated on cooling. The precipitation of the carbide might well be due to an inherent intoleration of molybdenum in the graphite lattice above some given level. We intend to try to determine the limits of solubility in this system by processing at higher temperatures for increased solubility, and then analyzing, at least semi-quantitatively, by microprobe X-ray analysis. Note also in Figure 5 that there are dark areas adjacent to the lighter colored molybdenum-rich areas. These dark areas are completely devoid, or nearly so, of metal, as evidenced by a line sweep on the electron microprobe. It can be surmised that the metal-free areas are of comparatively low strength and reduce the strength of the composite as a whole. Obviously, what is desired is a completely dense structure of uniform metal solution, with perhaps a slight excess of metal which will precipitate as a fine dispersion of free carbide.

Figure 7 shows a very small area of carbide precipitation and attendant metal solution. The system shows considerable promise, and

FIG. 4. MICROSTRUCTURE OF 30 WT% TANTALUM-CARBON COMPOSITE, PRESSED AT 2800° C.

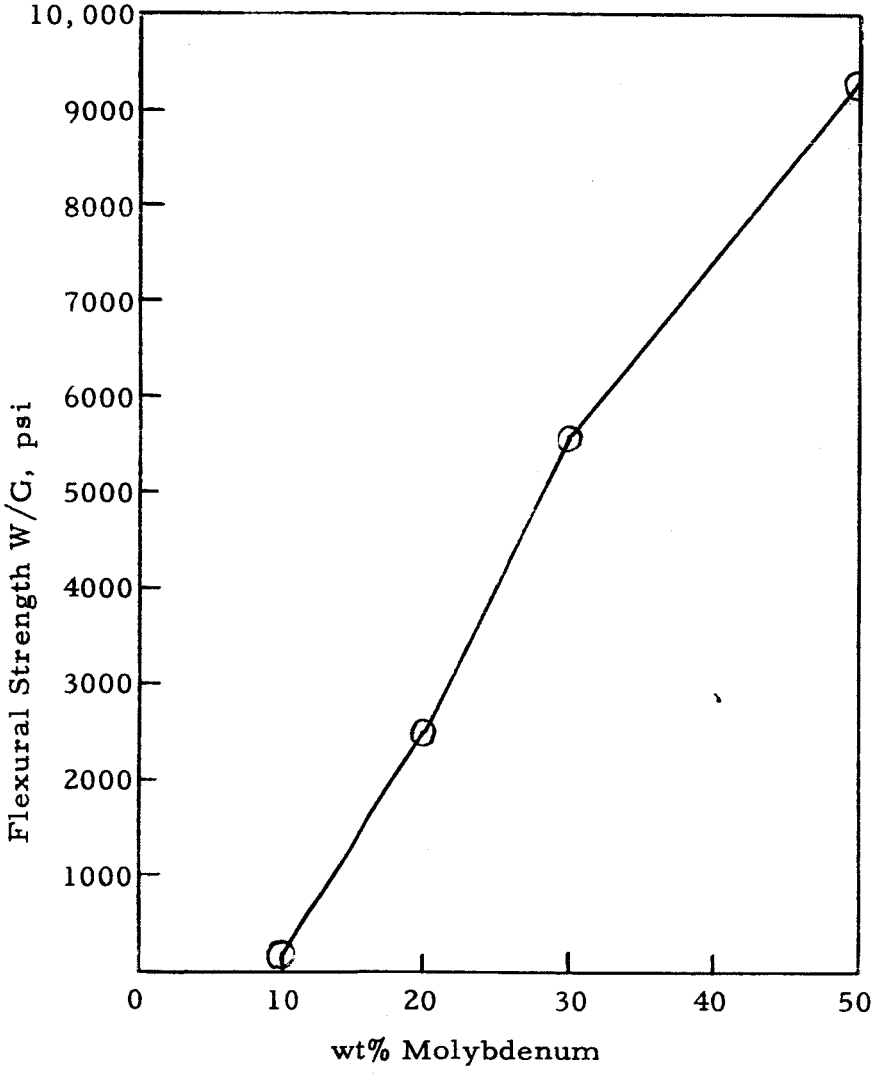

FIG. 5. FLEXURAL STRENGTH VS. METAL LEVEL FOR MOLYBDENUM-CARBON COMPOSITES. 2800°C PRESSING TEMPERATURE.

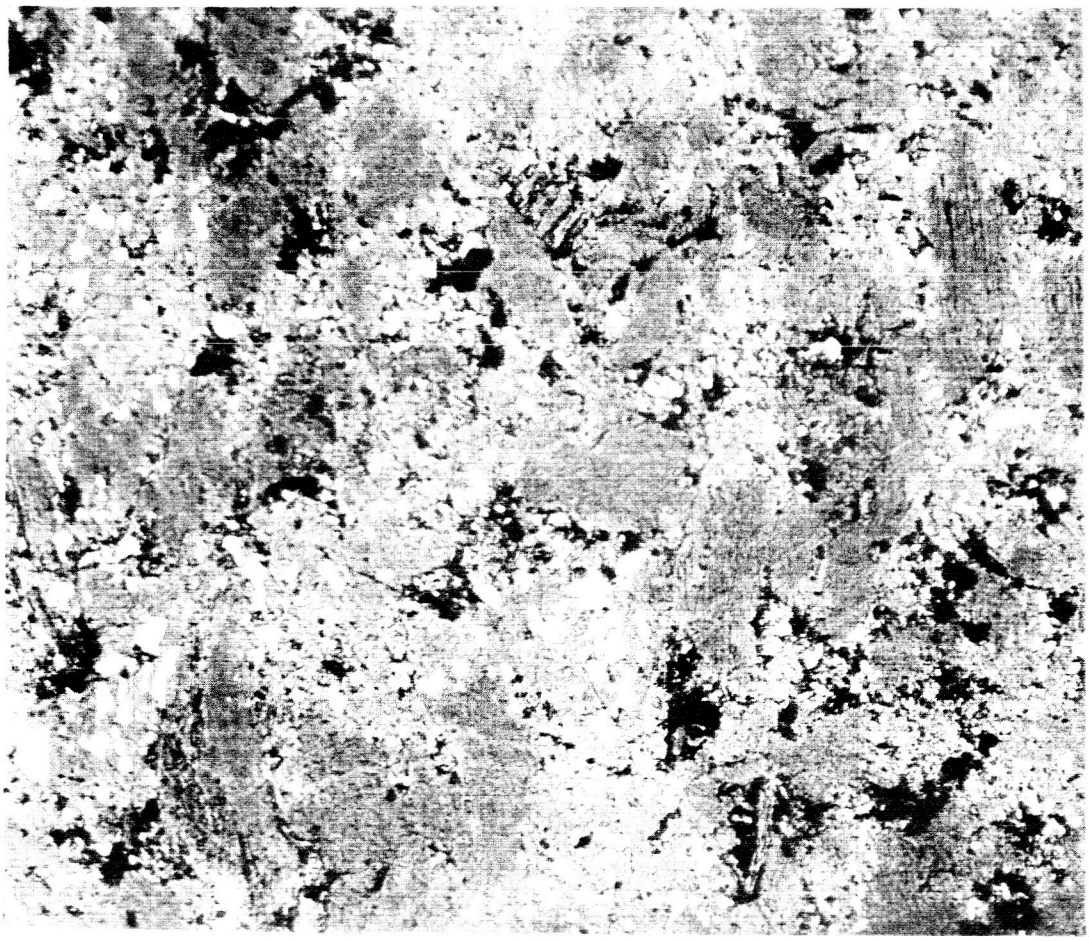

FIG. 6 - MICROSTRUCTURE OF 30 WT% MOLYBDENUM-CARBON COMPOSITE, PRESSED AT 2800°C.

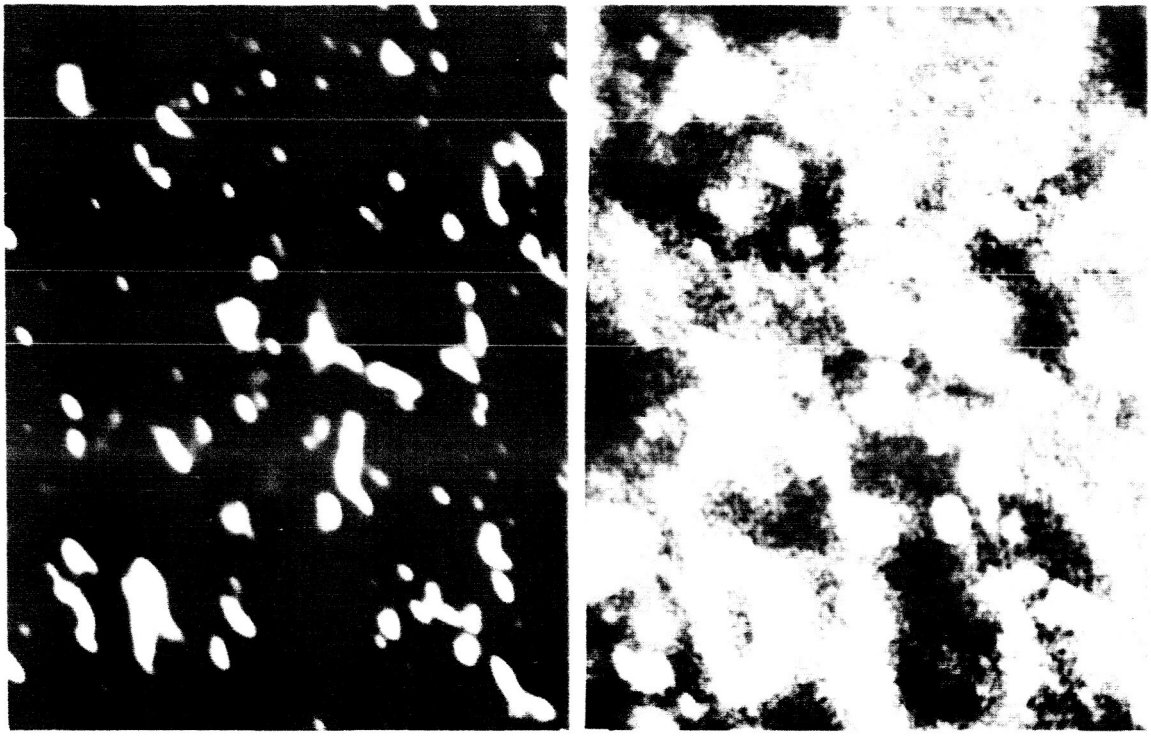

FIG. 7. ELECTRON IMAGE (LEFT) OF SMALL FREE-CARBIDE GRAINS, AND X-RAY IMAGE (RIGHT) SHOWING MOLYBDENUM-RICH DIFFUSION AREAS. (Electron Microprobe Analyzer, X680)

we will attempt to make a molybdenum composite of optimum properties during the current contract period.

D. Columbium-Carbon Composites

The columbium system appears to offer little potential without the use of higher temperatures. Pressed at 2800°C, samples with 10 and 20 wt% additions were extremely difficult to machine, and essentially had zero strength. However, at the 30% metal level, flexural strength values rose to 3800 psi. Examination of the microstructure (Figure 8) showed that most of the metal addition (added as metal) had converted to carbide, but that there was only limited solution of the carbide into the graphite lattice (Figure 9).

At the temperatures we are dealing with here, it is considered that the reactions involved in this type of system occur practically instantaneously. It follows, therefore, that at 2800°C, only limited amounts of solution occur. To make this system workable requires that process temperatures of at least 3000°C must be used to make composites with strength levels equivalent to the hafnium and molybdenum systems.

E. Zirconium-Carbon Composites

The zirconium-carbon system also shows considerable promise. Samples with 10% metal additions (as carbide) and pressed at 2800°C showed zero strength. At 20 and 30 wt%, strengths went to 2300 psi and 5400 psi, respectively. In looking at the microstructure of the 30% zirconium sample (Figure 10), it is apparent that a high degree of densification has occurred, and that for this degree of densification a considerable amount of liquid phase must have been present (Figure 11).

Our concern now is that the zirconium may not be distributed (in solution) evenly, thereby showing a lower strength value than may ultimately be attained. Our current intention is to remake a zirconium sample with excess metal (50%) at 3000°C. This should be capable of demonstrating the intrinsic value of zirconium as an alloying agent.

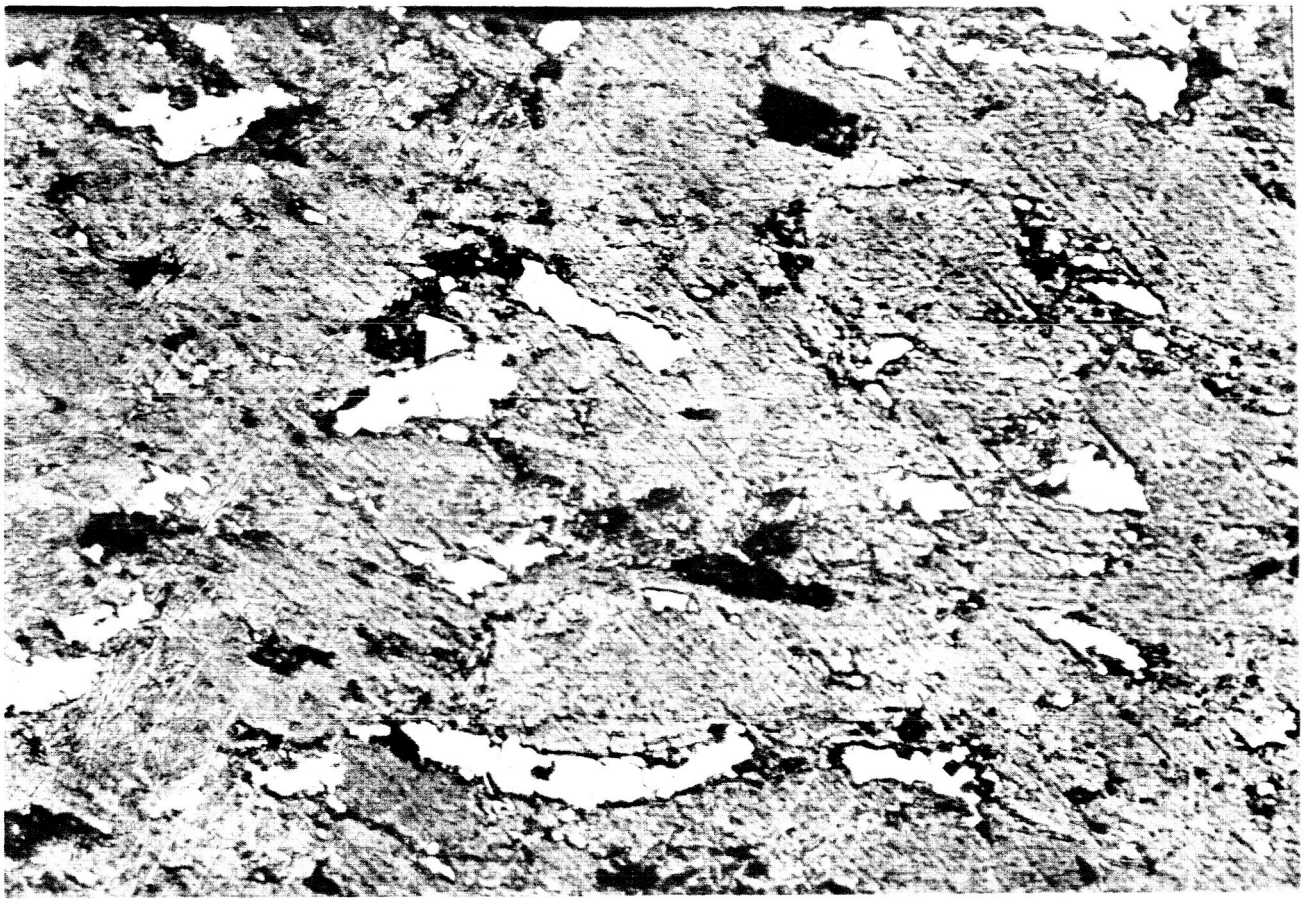

FIG. 8 - MICROSTRUCTURE OF 30 WT% COLUMBIUM-CARBON COMPOSITED, PRESSED AT 2800°C.

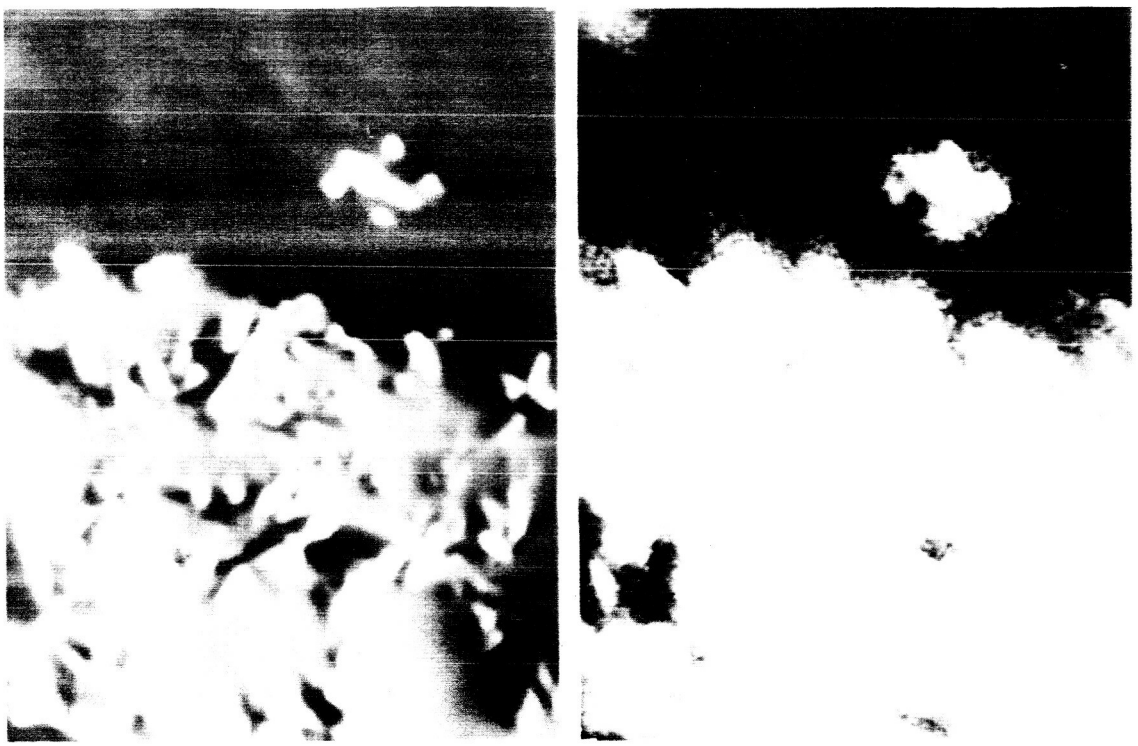

FIG. 9. ELECTRON IMAGE (LEFT) OF LARGE FREE-CARBIDE GRAINS, AND X-RAY IMAGE (RIGHT) SHOWING SMALL AMOUNT OF COLUMBIUM DIFFUSION AREAS. (Electron Microprobe Analyzer, X680)

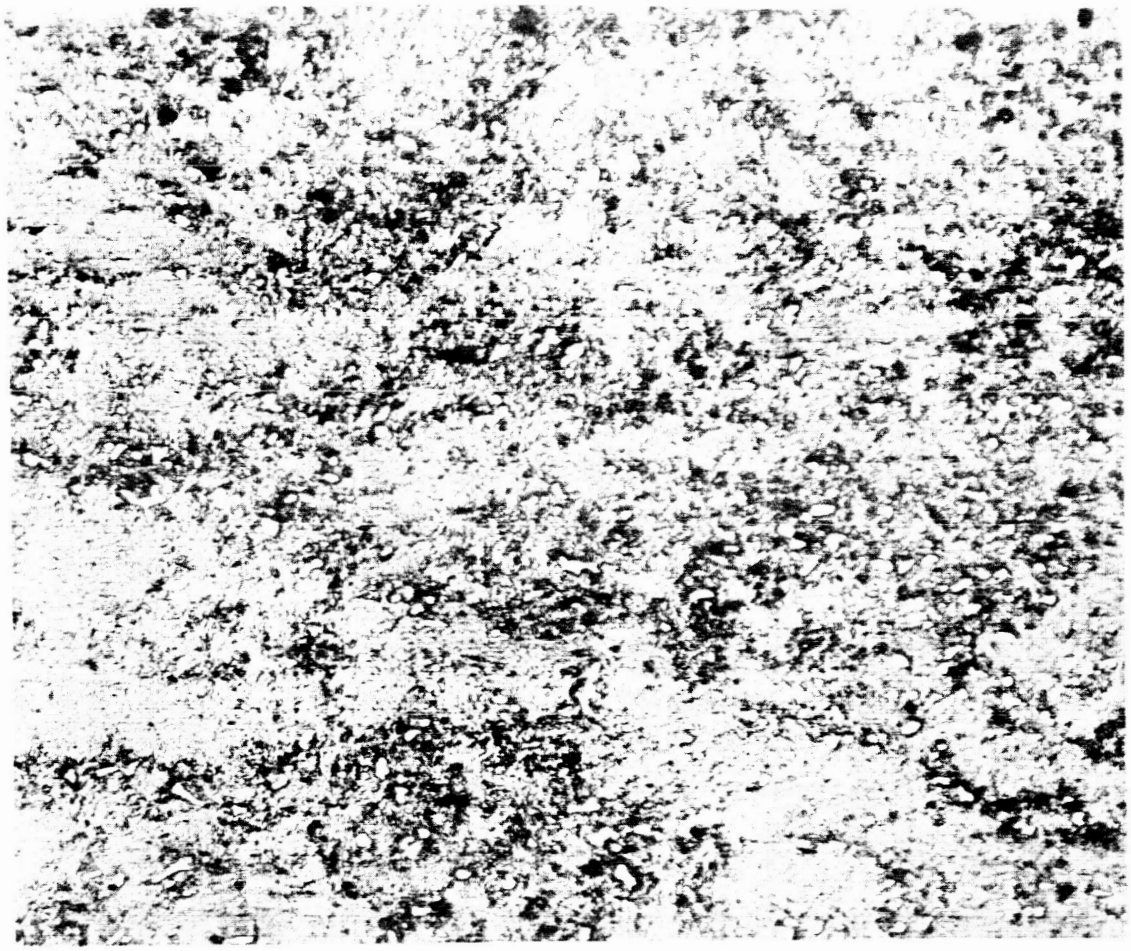

FIG. 10 - MICROSTRUCTURE OF 30 WT% ZIRCONIUM-CARBIDE COMPOSITE, PRESSED AT 2800°C.

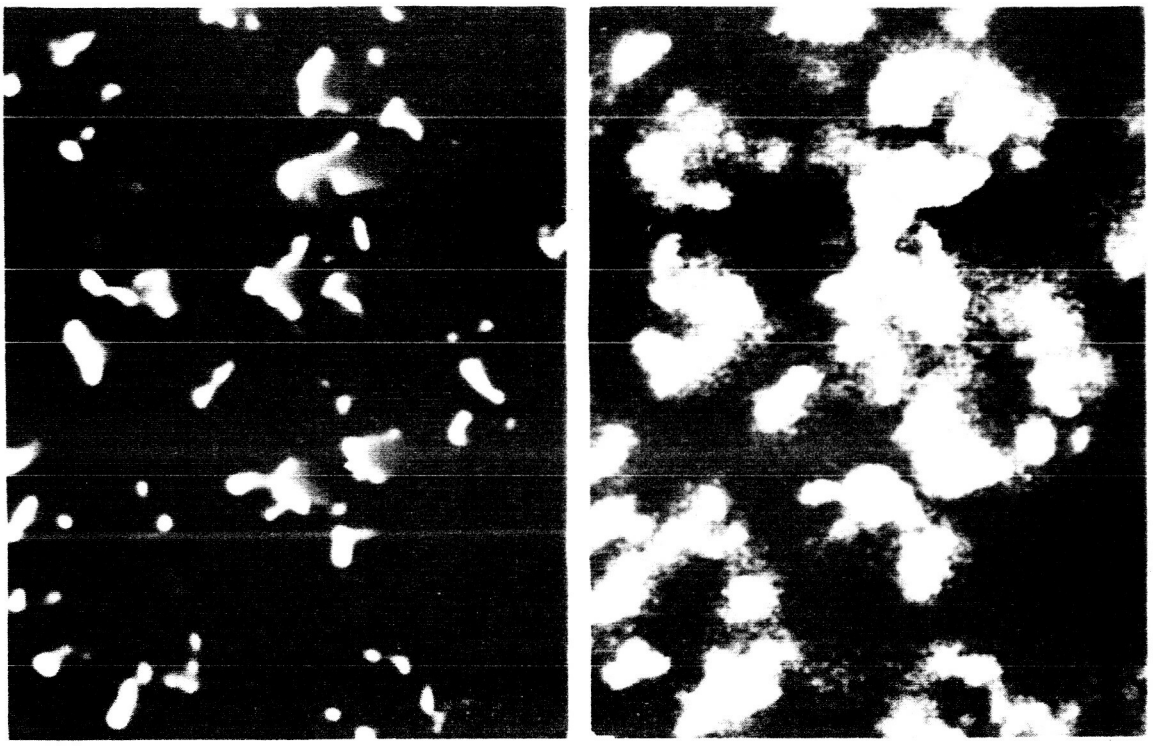

FIG. 11. ELECTRON IMAGE (LEFT) OF FREE-CARBIDE GRAINS, AND X-RAY IMAGE (RIGHT) SHOWING ZIRCONIUM-RICH DIFFUSION AREAS. (Electron Microprobe Analyzer, X680.)

F. Boron-Carbon Composites

The boron system has been of particular interest, largely because of anomalous results. Pressed at 2800°C, samples developed large amounts of liquid at all metal levels. At the 10% level, the with-grain flexural strength of 4100 psi is slightly lower than the across-grain strength of 4200 psi. As the metal percentage is increased to 20%, strengths drop off to about 3200 psi. The dropoff is unreasonable when compared to the 30% level sample which rises to 4500 psi in flexure with the grain, but is only 2100 psi across the grain. The qualitative observation that approximately 5% of the compact was lost through extrusion of liquid around the punches, and in one case ate 1/8 in. worm-holes through 2 1/2 in. of mold stock, is evidence of an abundant liquid phase.

These results led us to conclude that our processing temperature had been too high. A subsequent sample, 30% boron, pressed at 2300°C proved to have the highest strength of the series (4700 psi). Looking at the microstructure of this sample (Figure 12), there is very little evidence of any free boron carbide. We actually had to hunt for an area that showed even this small amount.

From this photomicrograph it would seem that the graphite matrix can accommodate 30% boron, one way or another, with little free carbide present.

It would be interesting to pursue this system to the point where boron was the major elemental phase, and the matrix was homogeneous but still retained the graphite ring structure.

G. Titanium-Carbon Composites

The titanium-carbon system seems to have little potential for developing into a strong, refractory bulk material. The highest strength attained in the series (10, 20, and 30%, pressed at 2800°C) was only 3800 psi in flexure. From the microstructure (Figure 13), one can see that a high degree of densification was achieved, but the mottled dark and light areas indicate that the titanium in solution is not distributed evenly. It is felt that another test piece with 50% titanium, and pressed at 3000°C,

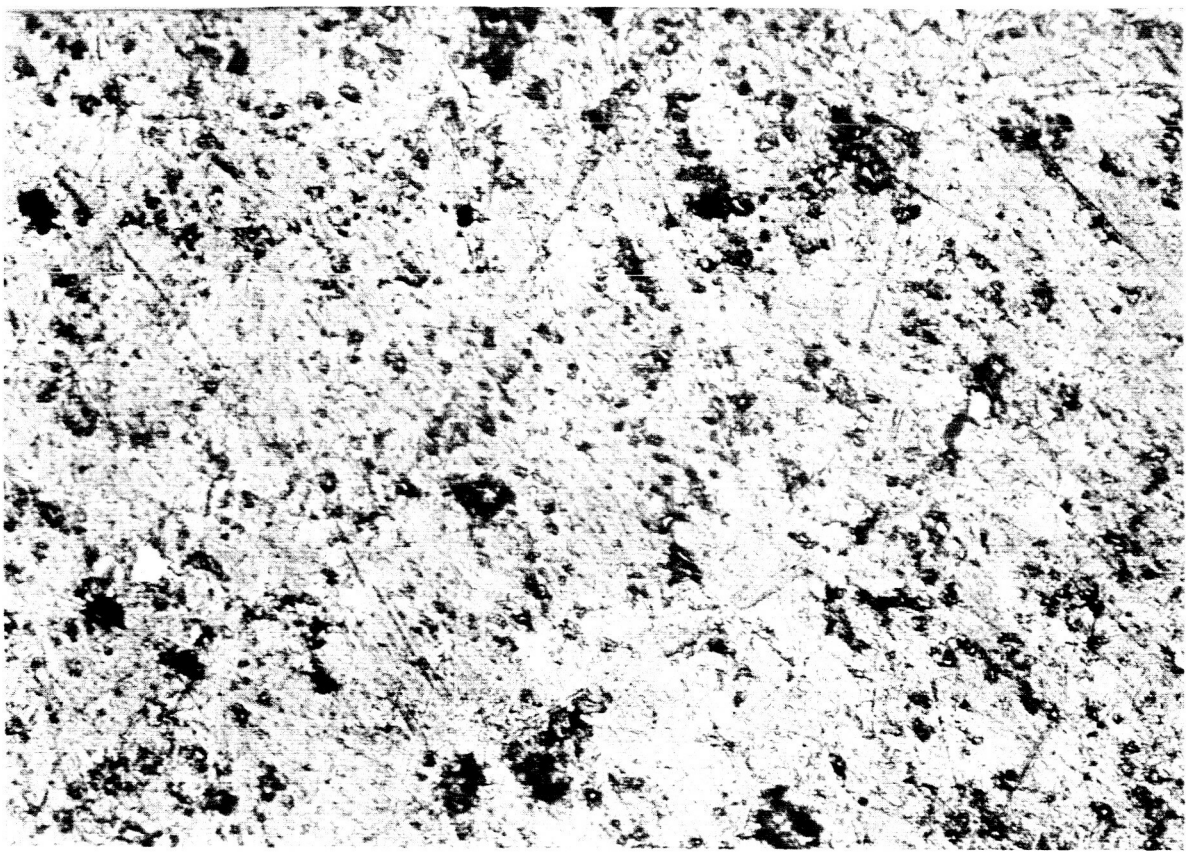

FIG. 12. MICROSTRUCTURE OF 30 WT% BORON-CARBON COMPOSITE PRESSED AT 2300°C. (As Opposed To All Previous Composites, Pressed at 2800°C.)

FIG. 13. MICROSTRUCTURE OF 30 WT% TITANIUM-CARBON COMPOSITE, PRESSED AT 2800° C.

should be made. This metal level and temperature should be sufficient to saturate the structure and indicate its true potential (Figure 14).

H. Beryllium-Carbon Composites

This important system has been disappointing, so far. The strength vs. metal content (Figure 15) appears to be anomalous in that the lower metal levels have the highest strength. We do not yet have a metallographic specimen for visual inspection, and thus can draw no conclusions on microstructural evidence.

Based on the low atomic weight of beryllium, these composites have a comparatively high atomic percentage present (34 at. % Be vs. 2.8 at. % Hf, at the 30 wt% level). This high atomic percentage, coupled with mandatory low process temperatures (about 2300° C) to prevent loss by vaporization, may indicate that 4000-5000 psi flexural strength is the upper limit that can be expected. This strength level is approximately the same as some of the better graphites, and would not appear to offer significant advantages.

The fact that these samples were all pressed at 2800° C, may mean that we suffered gross amounts of beryllium loss through vaporization. One additional sample will be made at the 30% level and pressed at the Be_2C dissociation temperature (2100° C).

I. Uranium-Carbon Composites

Uranium dicarbide (UC_2) melts at about 2400° C. Since this series was pressed at 2800° C, the melted carbide and the liquid eutectic should have offered sufficient liquid phase for realizing high strength. At the 10 and 20 wt% levles, the samples were too weak to machine, and therefore are considered to have zero strength. At 30 wt%, the strength was only 1050 psi in flexure. Increasing the pressing temperature to 3000° C (30 wt%), doubled the strength. Increasing the metal level to 50% and pressing at 2800° C, again doubled the strength to a level of 4400 psi in flexure. From these results, it would seem that we have not yet fully satisfied the lattice demand of dissolved metal to achieve maximum strength. The high molecular weight (238) of uranium, and therefore low

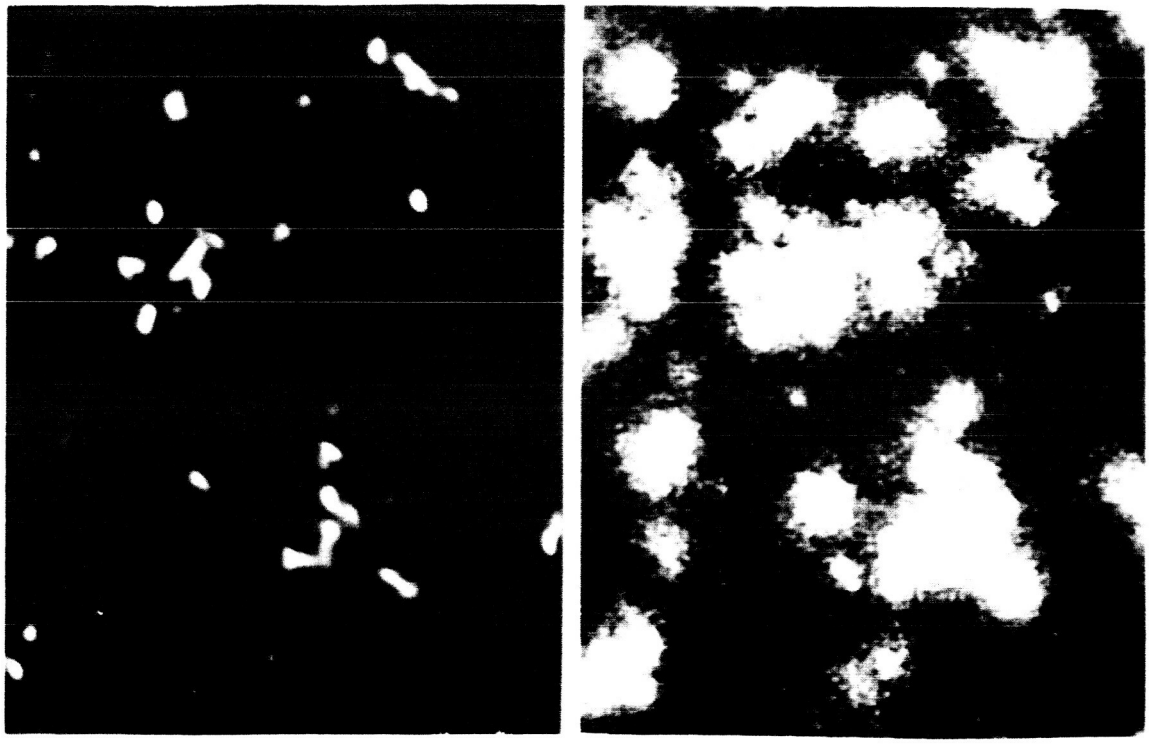

FIG. 14. ELECTRON IMAGE (LEFT) OF SMALL FREE-CARBIDE GRAINS, AND X-RAY IMAGE (RIGHT) SHOWING TITANIUM METAL DIFFUSION. (Electron Microprobe Analyzer, X680)

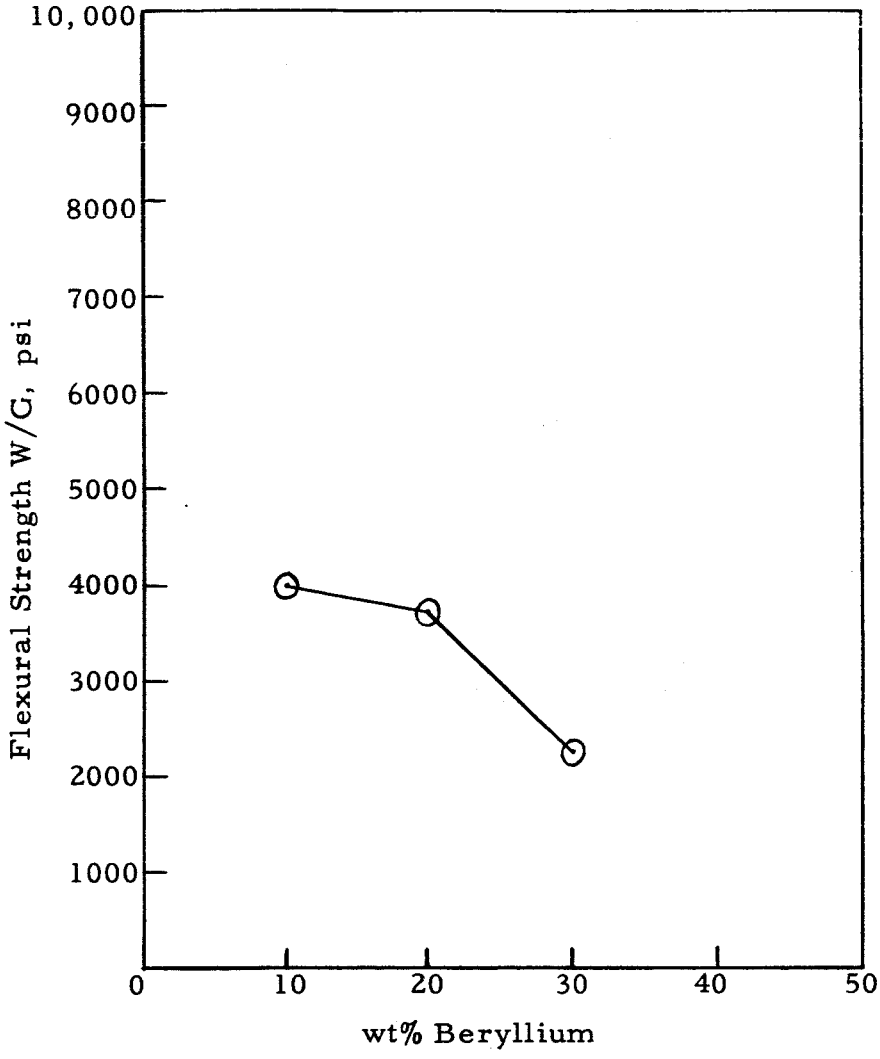

FIG. 15. FLEXURAL STRENGTH VS. METAL LEVEL FOR BERYLLIUM-CARBON COMPOSITES. 2800°C PRESSING TEMPERATURE.

atomic percentage present (2.1 at. % at 30 wt% level), indicates that still higher metal levels should be processed at a minimum of 3000° C.

At first glance, this might seem to be an impractical system, but the high refractoriness of oxidation product (UO_2) make it worthwhile to pursue this system further. It is felt that a composite can be made to reach a minimum of 10,000 psi, and might also have a protective mechanism for oxidation resistance at high temperature.

J. Thorium-Carbon Composites

The thorium compacts have many properties in common with the uranium samples. At the 10 and 20 wt% levels (2800° C), the compacts were again too weak to machine into test specimens. At 30 and 50% metal levels, samples could be cut, if the areas of gross internal cracking and fissuring were avoided. The internal cracking seems to be a characteristic of this system, and was experienced at all thorium levels. This was the only system that showed this phenomenon, and an explanation cannot be offered at this time. It does not seem worthwhile to pursue this system when so much more promise is exhibited by the other metals.

III. GENERAL SUMMARY

From the results to date, one can speculate, to a degree, on the role of metals in graphite strengthening. Based on these findings, it is not unreasonable to conclude that the individual metals have an intrinsic ability to strengthen the graphite lattice, and that this ability varies from metal to metal even at similar weight or atomic percentages.

We feel that we have just scratched the surface in this important materials field, and much remains to be done. Those systems showing high strengths at first try obviously deserve additional work to realize their full potential.

We, of course, are pleased that the concept of bonding bulk graphite structures by taking advantage of the transient liquid eutectic region has been demonstrated. Within the limits of time and budget, we intend to explore the compositional and temperature regions that appear to be most fruitful.

One further observation is probably in order. All of the above composites were pressed from room temperature to 2800°C, or above, within the short period of 1 1/4 hr or less. Some attempt should be made to evaluate the time factor; longer pressing times (slower temperature rise) might be one way to achieve more uniform metal distribution, and thereby increase strength levels.

IV. LOGBOOKS AND CONTRIBUTING PERSONNEL

All data pertaining to this project are recorded in IITRI Logbook Nos. C-14960, C-14969, and C-15136. Contributing personnel include Oswald Sanders and George Besbekis.

Respectfully submitted,

C. W. Boquist

C. W. Boquist,
Research Scientist

APPROVED:

S. L. Blum (S.L.B)

S. L. Blum,
Assistant Director
Metals and Ceramics Research