FABRICATION AND CHARACTERIZATION OF METAL CARBIDE-GRAPHITE COMPOSITES

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ABSTRACT

Refractory metal carbide-graphite composites have been prepared by hot pressing and the effect of variation of composition and processing conditions on phase equilibration and physical properties such as flexural strength, hardness, thermal shock resistance, thermal expansion, and electrical resistivity has been studied. The systems investigated include TiC-C, ZrC-C, HfC-C, VC-C, NbC-C, TaC-C, MoC-C and WC-C. It has been found that the strength of all the composite materials investigated increased with increasing carbide content reaching a peak for the metal-carbide-graphite eutectic composition. An essentially linear relationship between electrical resistivity and flexural strength was found to be useful to calculate the strength level of the material and to understand the strengthening mechanism with increasing carbide content.

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I. INTRODUCTION

The number of materials which can offer satisfactory performance diminishes rapidly as temperature requirements increase. Carbides and graphite have received increasing attention since they are the most refractory materials known. Composites of these two materials appear attractive in that the carbide offers high strength, and incorporation of graphite results in good thermal shock resistance and in easier machinability.

Investigations were conducted at IITRI to determine the feasibility of preparing metal carbide-graphite composites of high density and strength by hot pressing at temperatures of 2600° - 3100°C. This technique employs no binders and exploits 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 carbide or eutectic 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 for varied applications. The guest metal phases which were investigated include the Groups IV-A, V-A and VI-A metals with the exception of chromium.

II. EXPERIMENTAL PROCEDURE

The various composites were each prepared by hot pressing of binary mixtures of carbon and metal or metal carbide. Calcined petroleum coke was generally used as the source of graphite. With the Group IV-A metals (Ti, Zr and Hf) the carbide was used. Either the metal or the carbide was used in compositions incorporation the Group V-A or VI-A materials.

After dry blending for 16 hours, the metal-carbon mixture was hot pressed, using induction heating in a 2 1/2 in. ID CS graphite mold insulated with Thermax (Fig 1). Initial pressure applied was 500 psi; this level was maintained until a temperature of 2000°C was attained at which time it was increased to 3000 psi for the remainder of the processing. Temperature readings were taken with an optical pyrometer (L & N brightness type) sighting into the mold through an argon purged sight tube. Using an 80 KW motor generator power source, the processing temperature was reached in approximately one hour at which time the operation was concluded for most of the pressings.

To obtain the finished billet, the mold was cut open. Diametric deformation of the sample occurring during processing precluded simple ejection. Samples of both orientations were sectioned and machined for physical properties evaluation. Sample configurations were bars of 1/4 in. cross section ranging in length up to 2 1/2 in. The major portion of the evaluation has been concerned with density, microstructure and flexural strength.

III. DISCUSSION

A. Effect of Carbon Source

Experiments were conducted in which various carbon materials were hot pressed at 3000°C with no binder. These include calcined petroleum coke, Gilsonite coke, resin coke and synthetic graphite, all of less than 44μ particle size.

The data in Table I show that bonding was quite poor for all of the materials. Although a relatively high density was achieved with petroleum coke, flexural tests revealed this material to have very limited strengths.

X-ray analysis revealed a high degree of graphitization for the petroleum coke billet but only a limited ordering for the Gilsonite and resin coke bodies. This is to be expected since resin coke is a "glassy" carbon with a high degree of crosslinking which prevents easy graphitization.

The addition of 50 wt% molybdenum metal to each of the carbons and processing at 3000°C resulted in composites of high strength. X-ray diffraction studies showed that all of the systems were highly graphitized and ordered. At this processing temperature which is well above the MoC-C eutectic of 2580°C and the MoC melting point of 2600°C, liquid phases were formed which recrystallized on cooling. The microstructure of the petroleum coke-molybdenum system is shown in Fig 2.

The high degree of bonding may be attributed to the fine dispersion of a strong eutectic phase in the composite. Furthermore, the formation of the carbide-carbon liquid phase in processing would permit greater densification and ordering.

These experiments also showed that flat, plate-like carbon particles are preferable for obtaining good densification and bonding. The use of spherical or irregularly shaped particle materials such as Gilsonite coke and resin coke did not produce as good bonding as did petroleum coke or synthetic graphite.

B. Comparison of Systems

A number of carbide-graphite systems were prepared with metal contents from 10 to 50 wt% (and up to the eutectic composition for Nb and Zr) at temperatures of 2600° - 3100°C.

This work has revealed some general trends for all of the systems examined:

a. The use of finer particle size raw materials (-325 mesh vs 200-325 mesh) produce denser, more strongly bonded composites.

b. A close approach to the carbide-carbon eutectic temperature in processing results in good sintering and high flexural strengths. However, exceeding the eutectic temperature, especially in high metal content compositions can result in gross loss of material by extrusion around the plungers and reaction with the mold. Also, segregation of the carbide or carbide-carbon eutectic can occur. Both of these mechanisms can be detrimental to obtaining high strength bodies.

c. A minimum amount of metal carbide appears necessary for densification and strength in any system. In terms of volume % carbide, the amount is about 6%.

1. Microstructural Studies

Metallographic examination of the microstructure of these composites revealed a dispersion of carbide in a graphite matrix for the lower metal content composites. A 50 wt% tungsten composition processed at 3000°C is shown in Fig 3. The flexural strength of this body was 15,000 psi at room temperature. The lack of orientation for the carbide particles indicate that melting occurred with subsequent recrystallization upon cooling. The WC-C eutectic is reported as 2785°C. This is a similar structure to that for the MoC-C system shown in Fig 2.

With materials having higher eutectic temperatures such as TaC-C shown in Fig 4, a strong orientation is evident for the carbide particles. This 50 wt% Ta body was processed

at 3100°C which is well below the 3450°C reported for the TaC-C eutectic. A flexural strength of 8000 psi was exhibited by this composite. In comparison, fabrication of the same composition using coarser carbide particles and a lower temperature (3000°C) yielded a porous body of only 3000 psi flexural strength (Fig 5).

Similarly, a 50 wt% Nb composite hot pressed at 3100°C revealed orientation of the carbide phase. Eutectic melting for NbC-C occurs at 3250°C. At the higher metal content of 80 wt% Nb, the eutectic being 81.3 wt%, the matrix is now the carbide with a dispersion of graphite (Fig 6). When the eutectic temperature is exceeded at this hypereutectic composition, a eutectic structure is obtained with long platelets of graphite which have come out of solution (Fig 7). In this particular composition, extensive segregation of the carbide and eutectic phases occurred, resulting in strong heterogeneity in properties.

2. Electrical Resistivity

Microstructural examination has given us some clues as to the mechanism of strengthening, e.g., amount and particle size and shape of the carbide dispersion. Electrical resistivity measurements were conducted on test bars to determine if any trend could be detected.

In the various systems examined, there appeared to be a direct relationship between flexural strength and conductivity. Fig 8 illustrates this relationship for the Mo-C system; the relationship appears to hold regardless of density, processing temperature, wt% metal, grain direction, or carbon source. This linearity indicates that strength is directly proportional to particle-to-particle contact of the carbide or eutectic which is the strength providing phase. This may give us the capability of predicting strength up to the eutectic composition from the slope of the conductivity-strength curve.

3. Mechanical Properties

It is in the area of high temperature performance that the carbide-graphite composites are of importance. Naturally, the first limitation would be the melting point of the particular system. Among the combinations under study, the lowest carbide-carbon eutectic is the MoC-C which is 2580°C and the highest is the TaC-C reported at 3450°C.

A series of flexural measurements have been conducted at temperatures up to 2800°C. These were made in a graphite tube furnace under an argon atmosphere. The four point loading technique was used with graphite fixtures.

On Fig 9 we have plotted a series of strength vs temperature curves. The zirconium composites both displayed a higher strength at 2000°C but a fairly rapid dropoff at 2500°C. As can be seen, the higher metal content sample was weaker than the 50 wt% composite at 2500°C, reversing the relationship at room temperature and 2000°C. It is felt that the higher strength at 2000°C is due to a mechanism which exists for pure graphite, i.e., a relaxation at higher temperatures of residual stresses which exist at room temperature.

The vanadium sample had a 2000°C strength which was about the same as at room temperature, and at 2500°C, the strength was considerably lower and strong plastic deformation was observed. Tungsten carbide-graphite composites exhibited similar behavior.

The tantalum and hafnium composites have higher strengths at 2000°C. Good retention of strength is also exhibited at 2500°C; however, a distinct difference in behavior was noted in that the Hf sample displayed strong plastic deformation whereas little, if any was observed for the tantalum sample. Although

it is not plotted, this Ta composition was tested at 2800°C. A strength of about 7000 psi was measured. Plastic deformation was observed at this temperature.

Excellent room temperature strengths have been observed for niobium composites. Fig 10 illustrates strengths exhibited by composites incorporating varying amounts of niobium. As was the case for zirconium bodies, a stronger dropoff in strength at 2500°C was observed for the higher metal content composition. Tests at 2800°C of the 50 wt% composite processed at 3100°C revealed a strength of 14,000 psi and considerable plastic deformation.

A series of molybdenum containing composites were processed at 2800°C and 3000°C. The actual metal content of the finished billets (Fig 11) was considerably lower than the actual 50 wt% in the raw mixture, reflecting the loss of metal in processing at temperatures well above the 2580°C eutectic temperature. High room temperature strengths are exhibited by these compositions. Lower strengths are displayed by these bodies at 2000°C, and at 2500°C only the lower metal content samples could be stressed to failure. The others showed considerable plastic deformation.

In the testing of MoC-C composites at 2500°C, it was observed that small beads of material had exuded to the surfaces of the test specimen. The compositions listed in Fig 11 were heat treated at 2600°C for 30 minutes. This "sweating" phenomenon was exhibited by the higher metal content samples but not by the 27.5 wt% composite.

The microstructure of the area around one of these beads is shown in Fig 12. A depletion of carbide plus coalescing into larger particles is seen, but no strong porosity exists.

X-rays show that the exuded material is rich in alpha Mo_2C, which melts at 2470°C, with some MoC. This sweating leaves behind a graphite structure which is highly oriented as shown under polarized light in Fig 13.

IV. SUMMARY

In summary, our work has shown that dense metal carbide-graphite composites of high strengths can be fabricated by hot pressing, employing no binders. Our tests have shown that the niobium and tantalum systems exhibit the highest strengths and resistance to plastic deformation at temperature of 2500°C or higher.

Our future work will be involved in expanding physical properties measurements to include tensile and compressive strengths, elastic moduli, thermal conductivity and thermal expansion, all at temperatures up to 3000°C.

V. ACKNOWLEDGEMENTS

This work has been performed for the Los Alamos Scientific Laboratory, sponsored by the National Aeronautics and Space Administration through the Space Nuclear Propulsion Office. The valuable contributions of Dr. R. J. Dietz of LASL are gratefully acknowledged.

Table I

EFFECT OF GRAPHITE SOURCE MATERIAL ON DENSIFICATION AND BONDING

Carbon	No Additives A	No Additives B	50 w/o Mo Addition A	50 w/o Mo Addition B
Petroleum Coke	1.95	1420	2.88	13130
Gilsonite Coke	1.74	560	2.73	7660
Resin Coke	1.41	1000	2.79	7570
Synthetic Graphite	1.78	1140	2.69	9550

A - Density, g/cc

B - Flexural Strength, psi

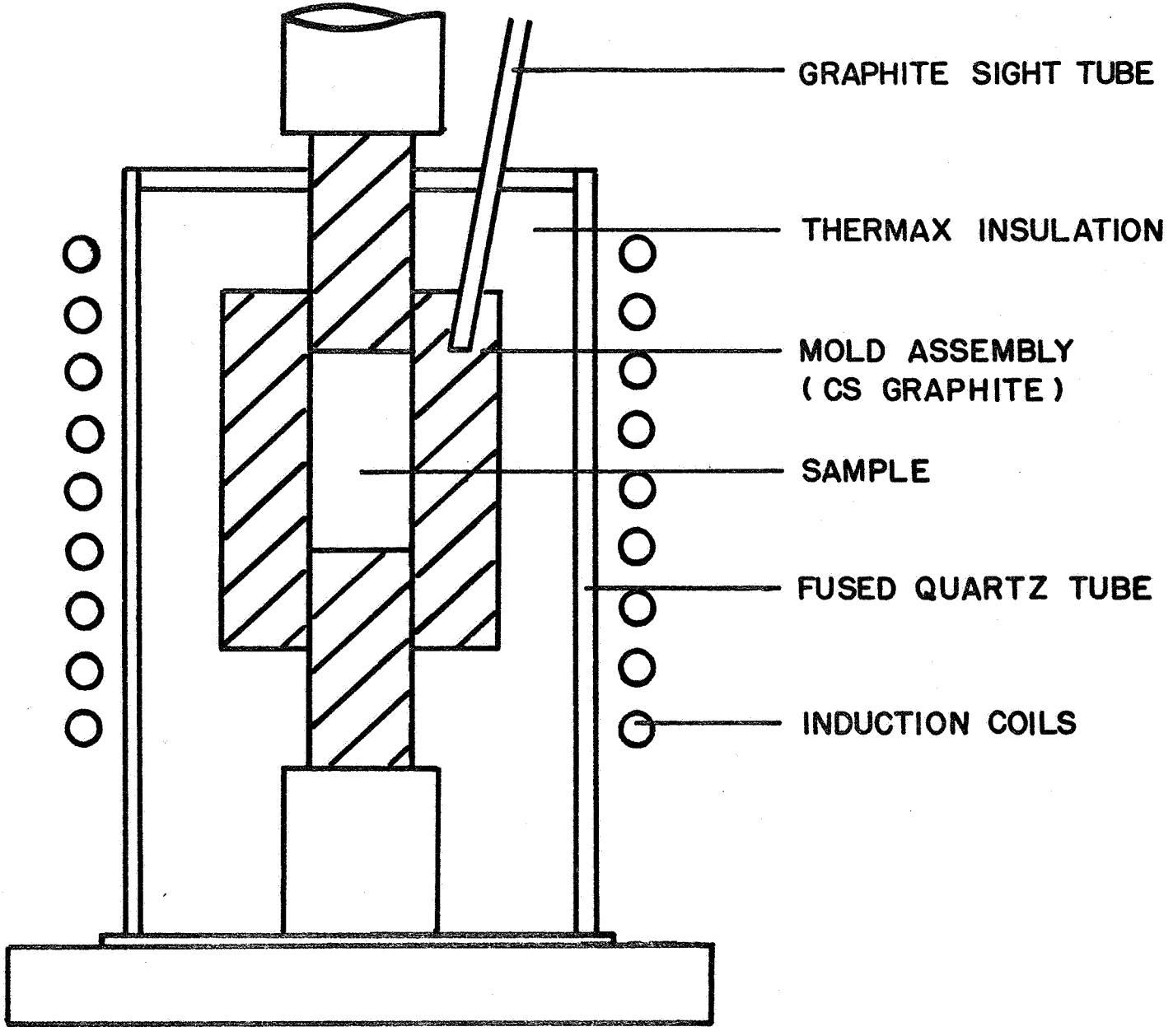

FIG 1 - HOT PRESSING APPARATUS

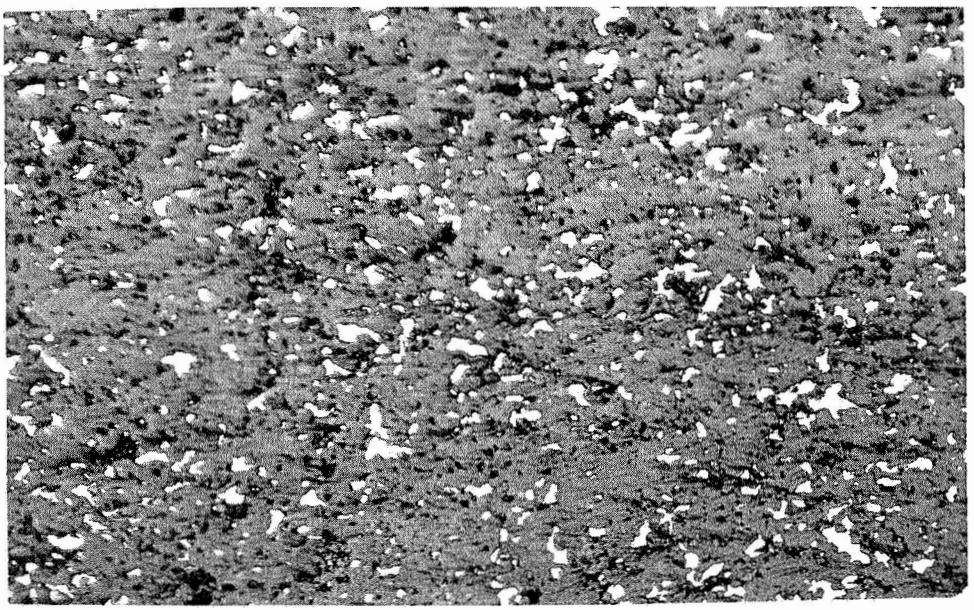

FIG 2 - MICROSTRUCTURE OF 50 WT% Mo-GRAPHITE PRESSED AT 3000°C (320x)

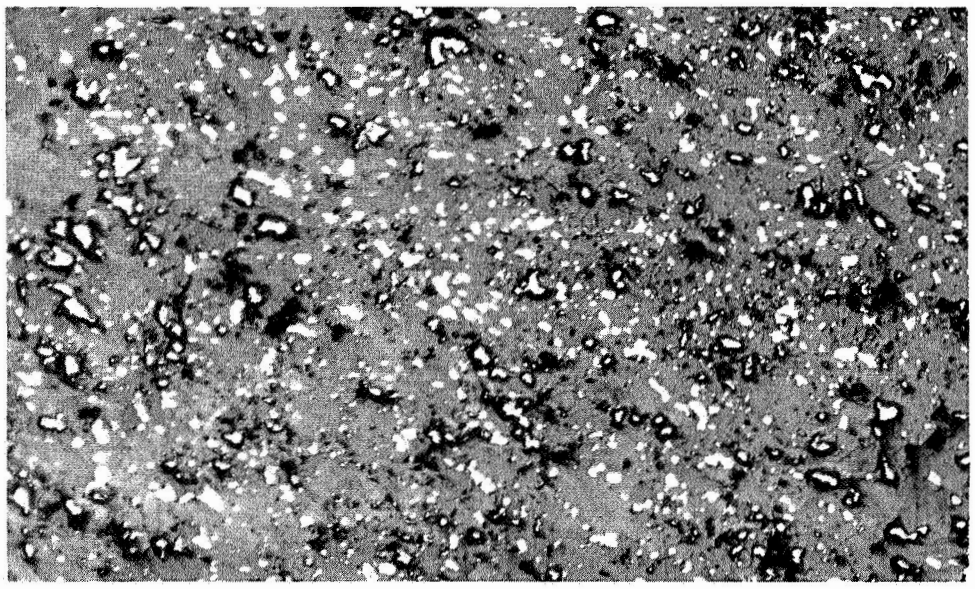

FIG 3 - MICROSTRUCTURE OF 50WT% W-GRAPHITE PRESSED AT 3000°C (320x)

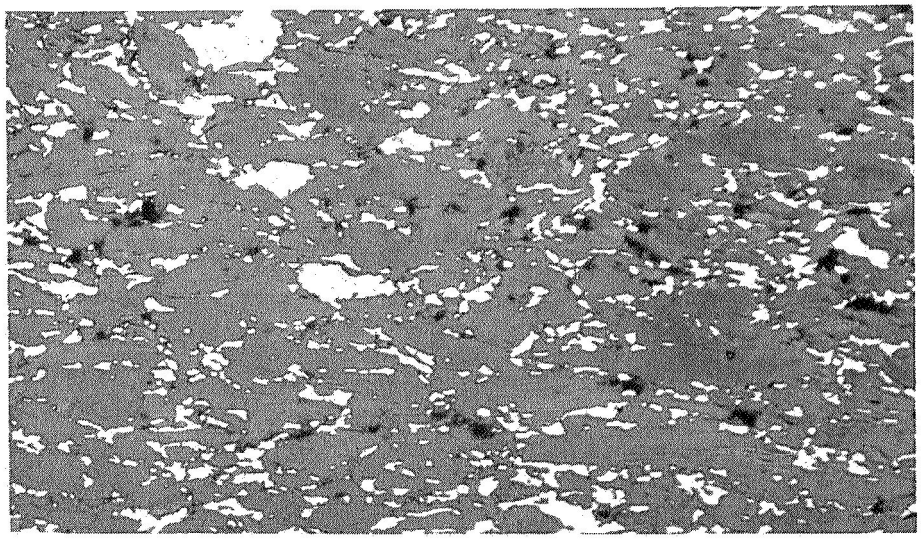

FIG 4 - MICROSTRUCTURE OF 50 WT% Ta-GRAPHITE PRESSED AT 3100°C (320x)

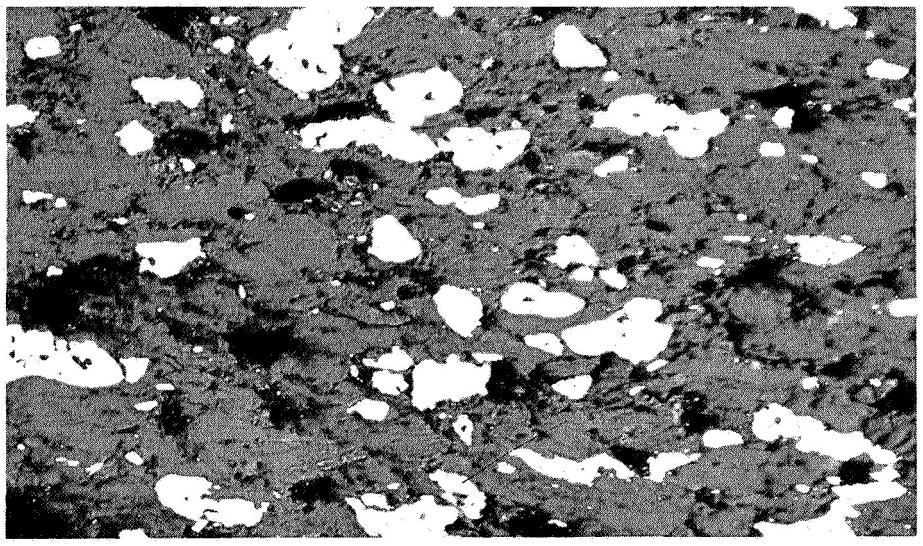

FIG 5 - MICROSTRUCTURE OF 50 WT% Ta-GRAPHITE PRESSED AT 3000°C (320x)

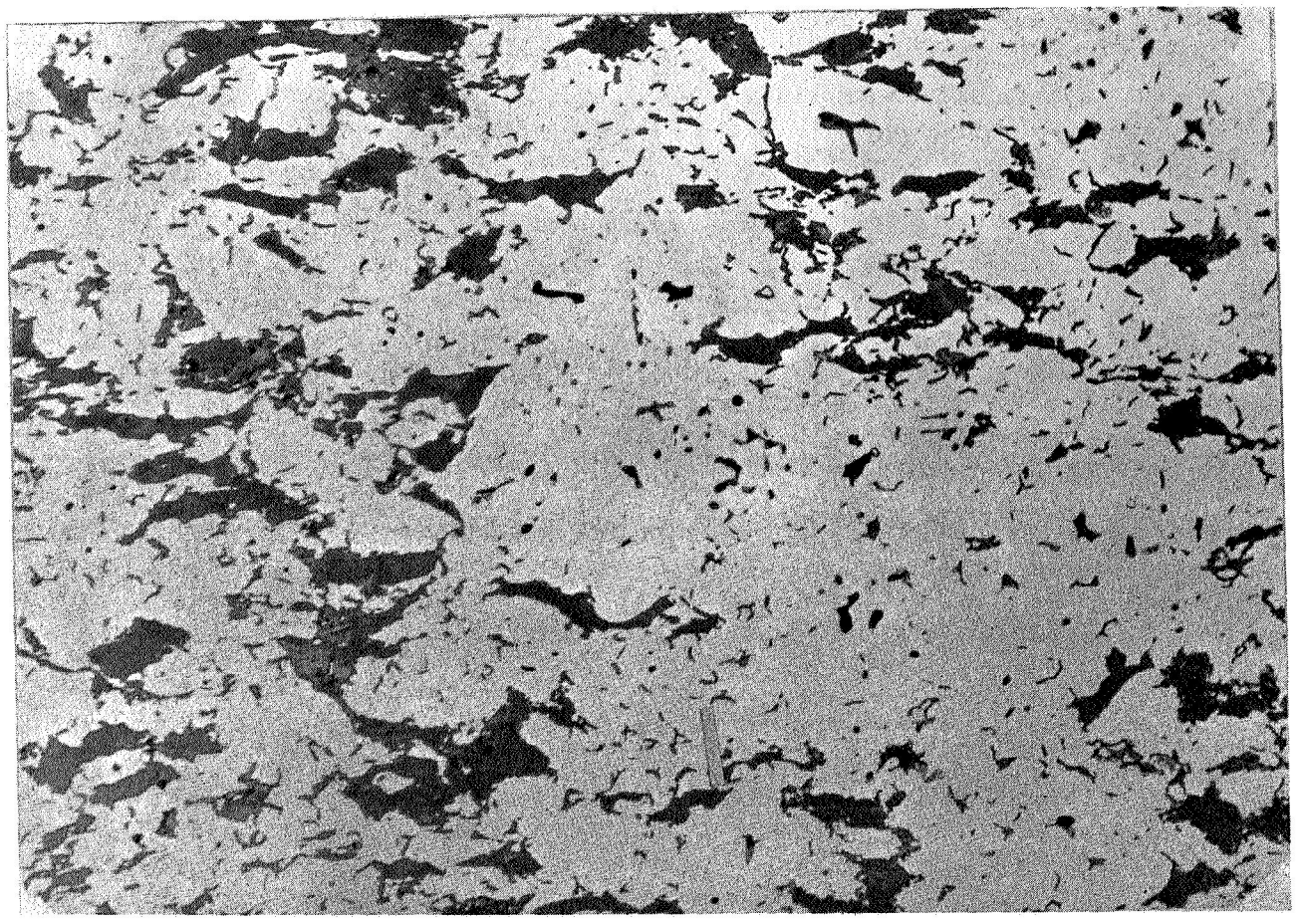

FIG 6 - MICROSTRUCTURE OF 80 WT% Nb-GRAPHITE
PRESSED AT 3000°C (x320)

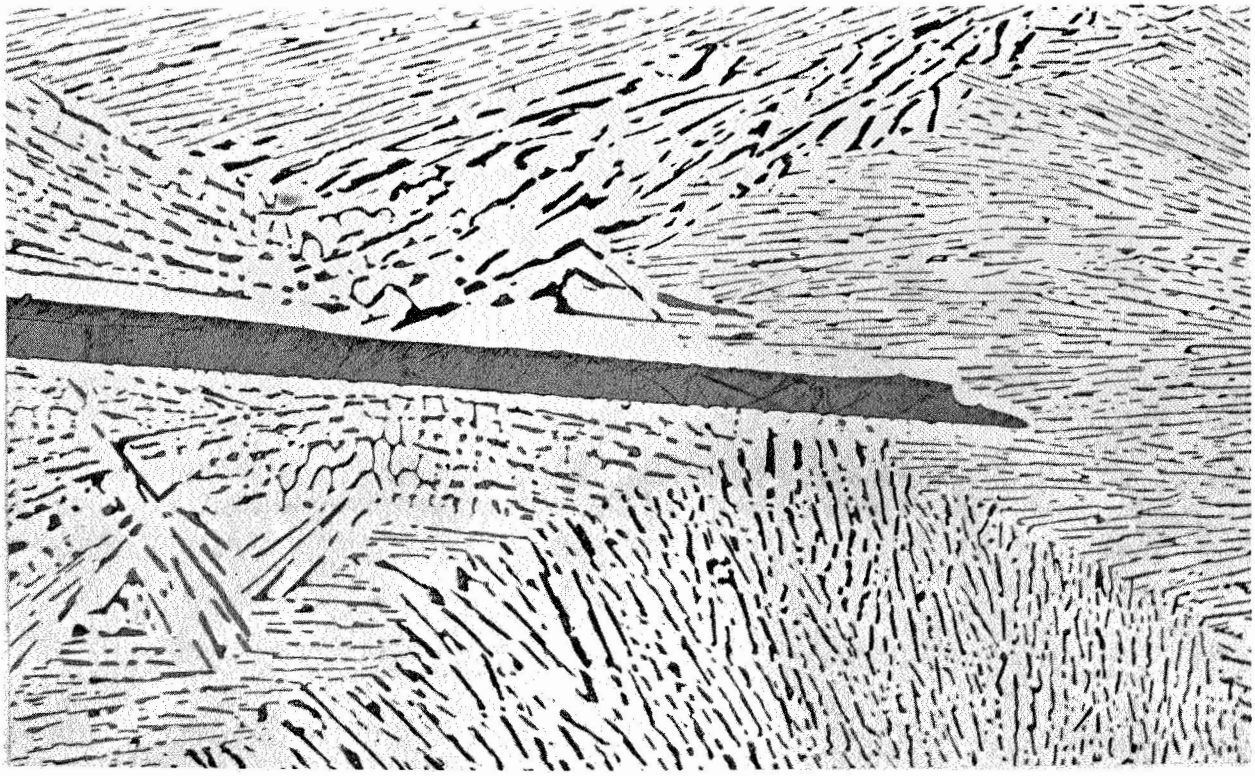

FIG 7 - MICROSTRUCTURE OF ZONE OF RECRYSTALLIZED MELT IN 80 WT% Nb PRESSED AT 3100°C SHOWING EUTECTIC STRUCTURE (x200)

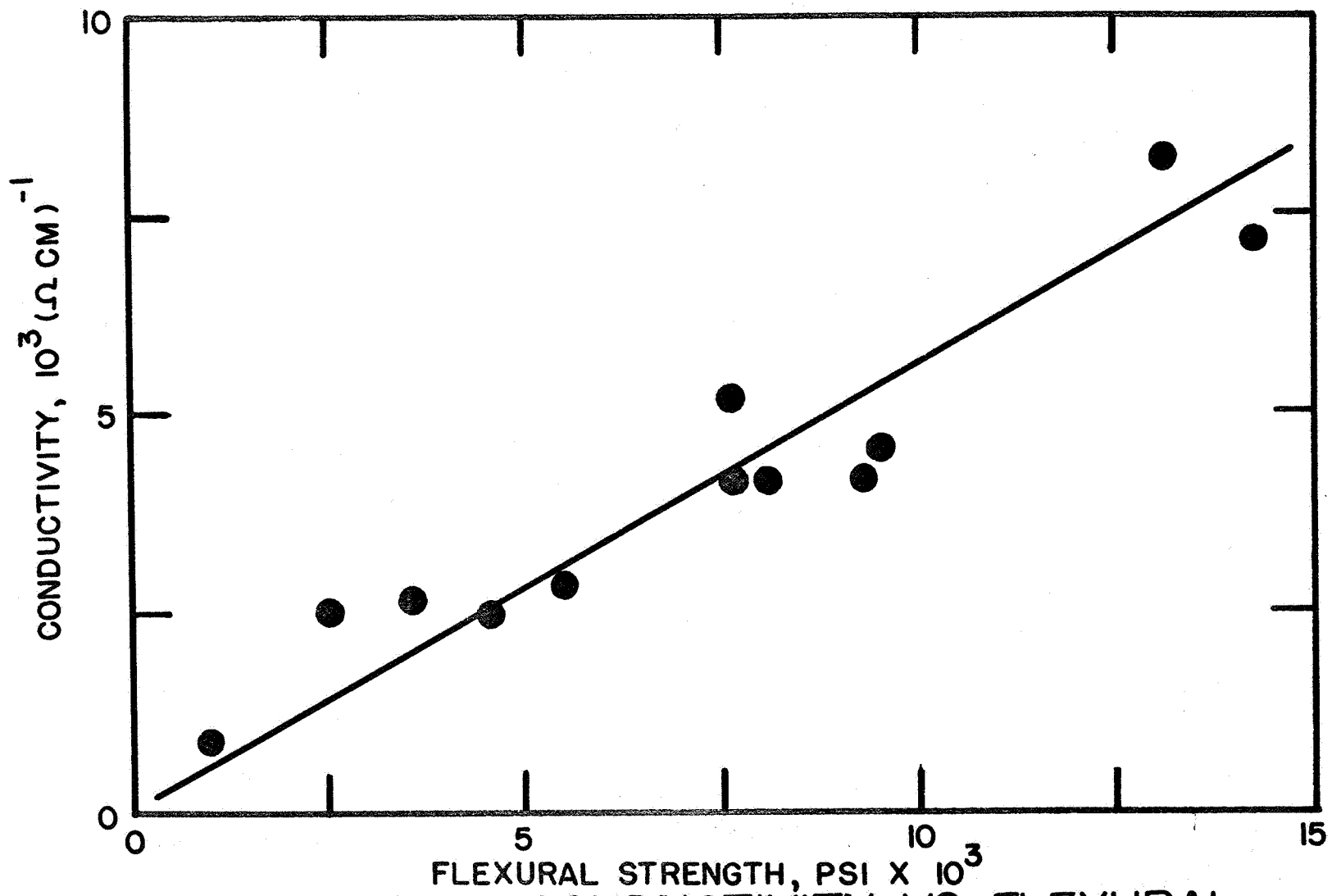

FIG 8 - ELECTRICAL CONDUCTIVITY VS FLEXURAL STRENGTH FOR Mo-C COMPOSITES

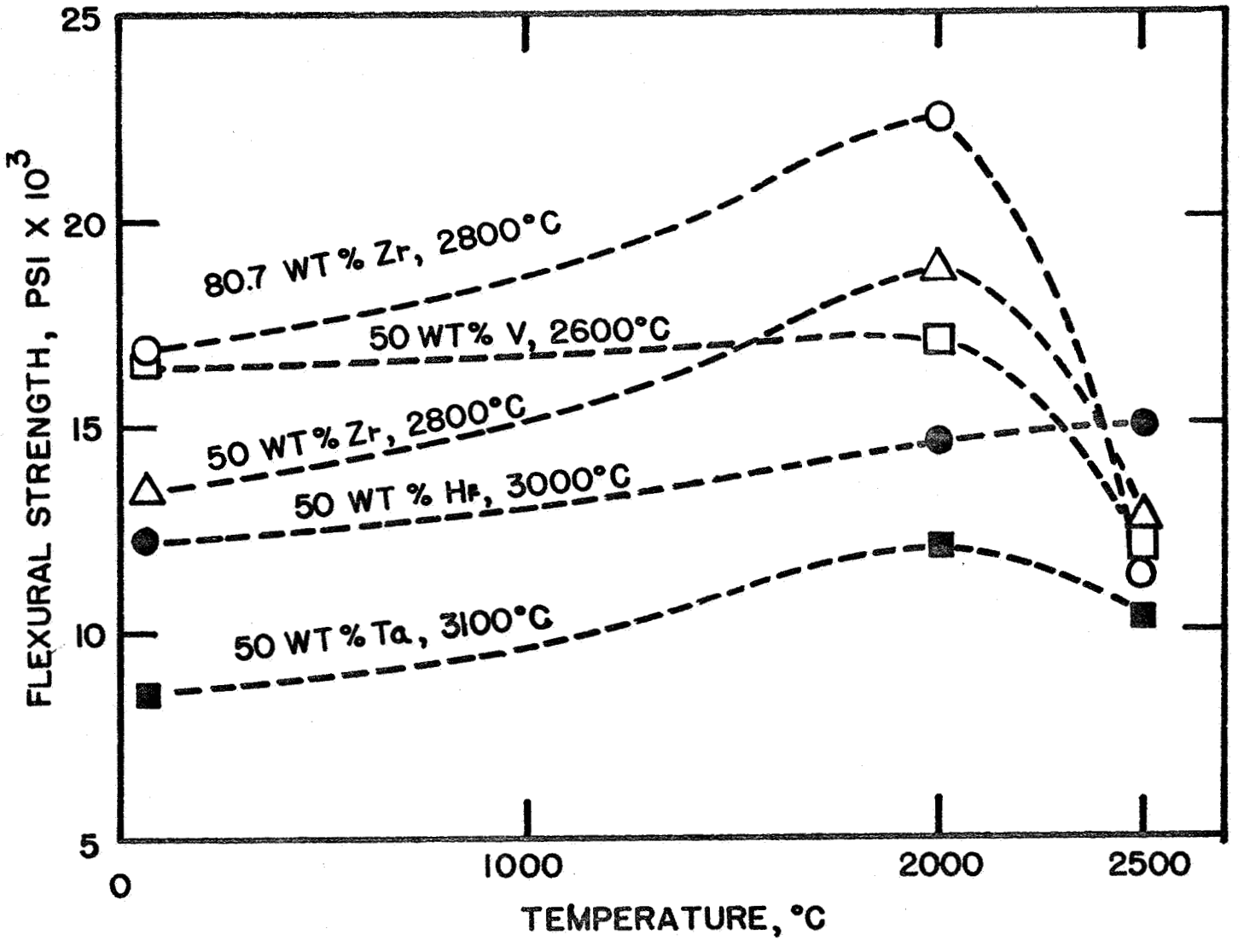

FIG 9 - FLEXURAL STRENGTH OF M-C COMPOSITES

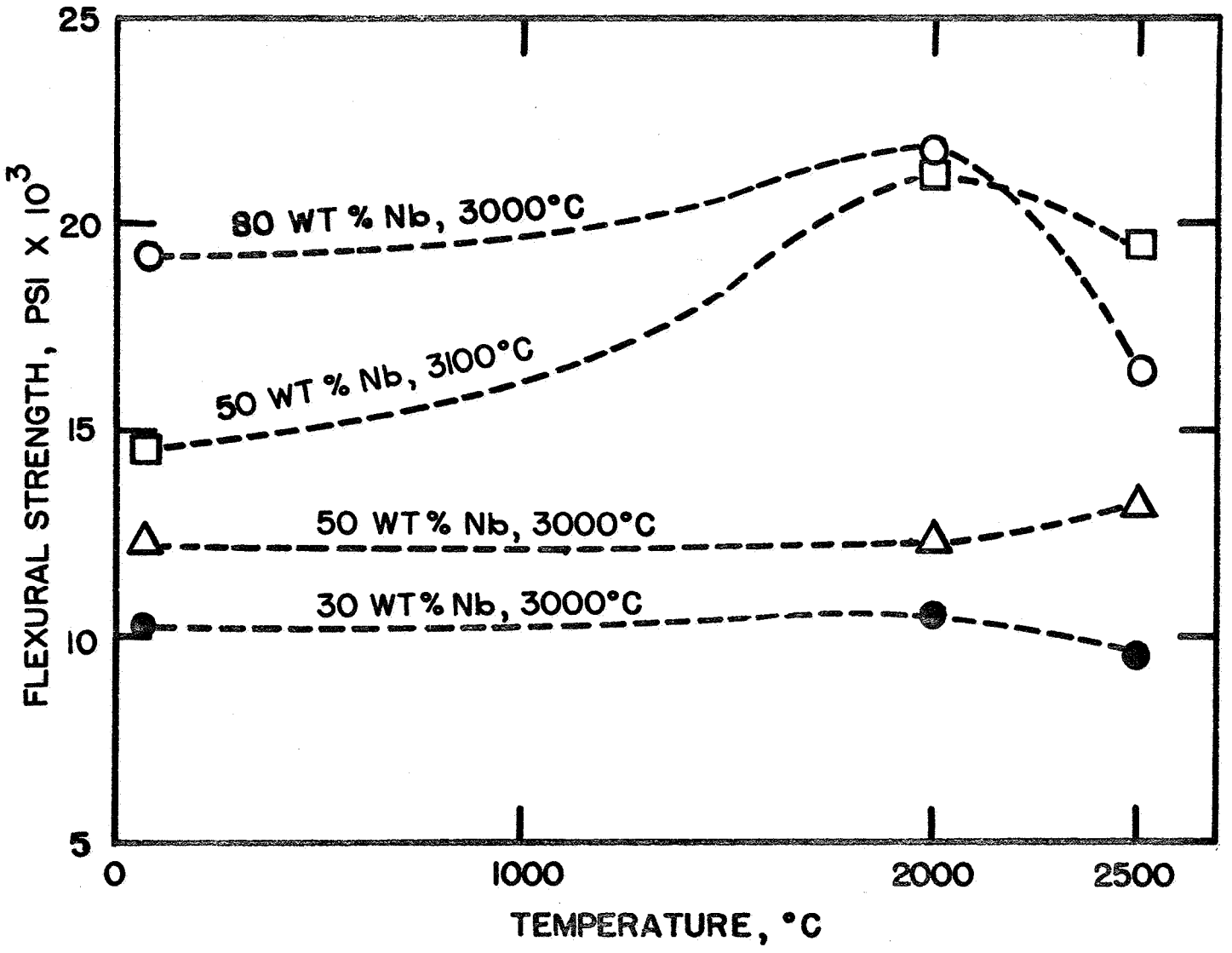

FIG 10 - FLEXURAL STRENGTH OF Nb-C COMPOSITES

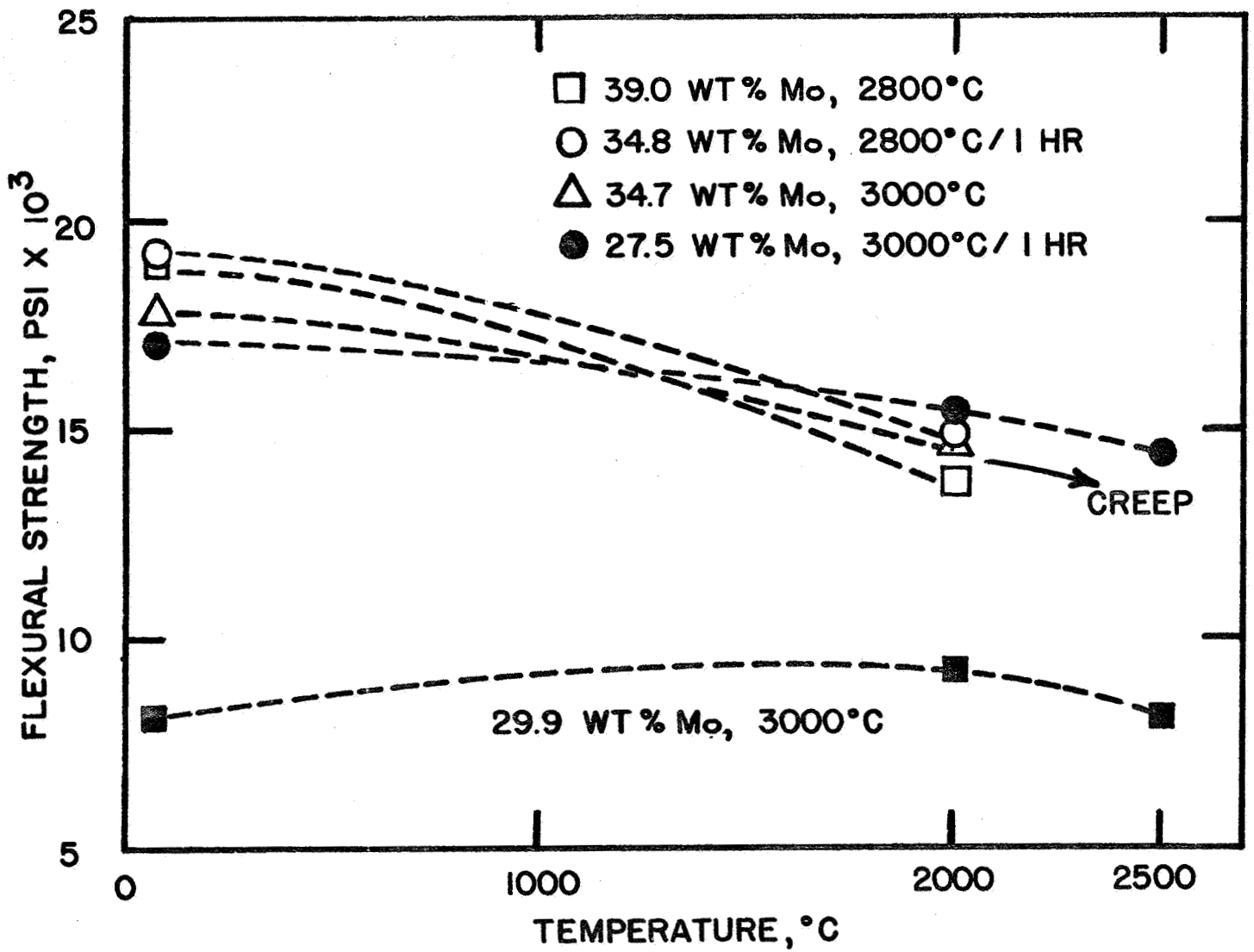

FIG 11 - FLEXURAL STRENGTH OF Mo-C COMPOSITES

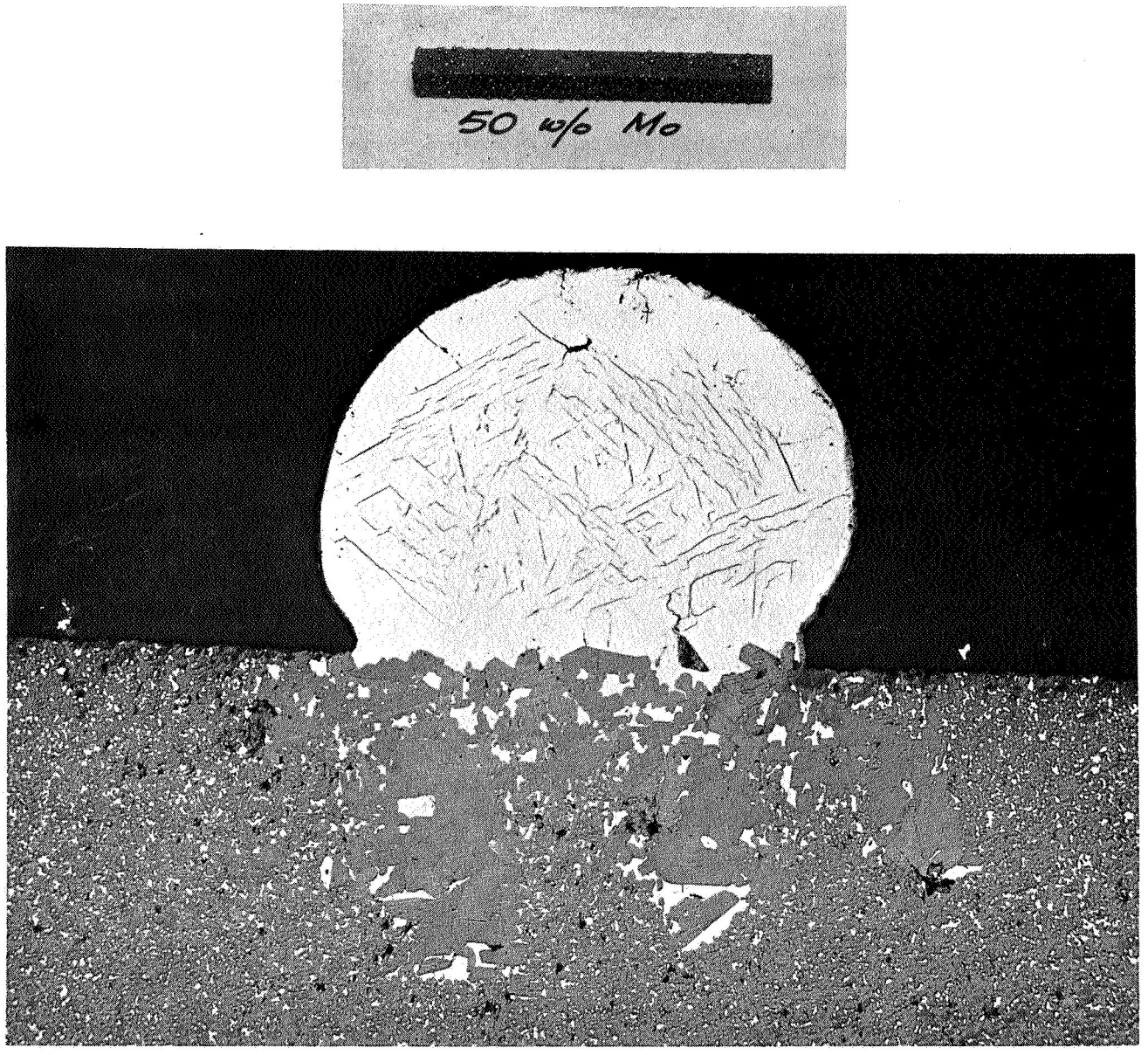

FIG 12 - MICROSTRUCTURE OF "SWEATED" AREA IN 50 WT% Mo-GRAPHITE SAMPLE HEAT TREATED AT 2600°C/2 HOURS (x100)

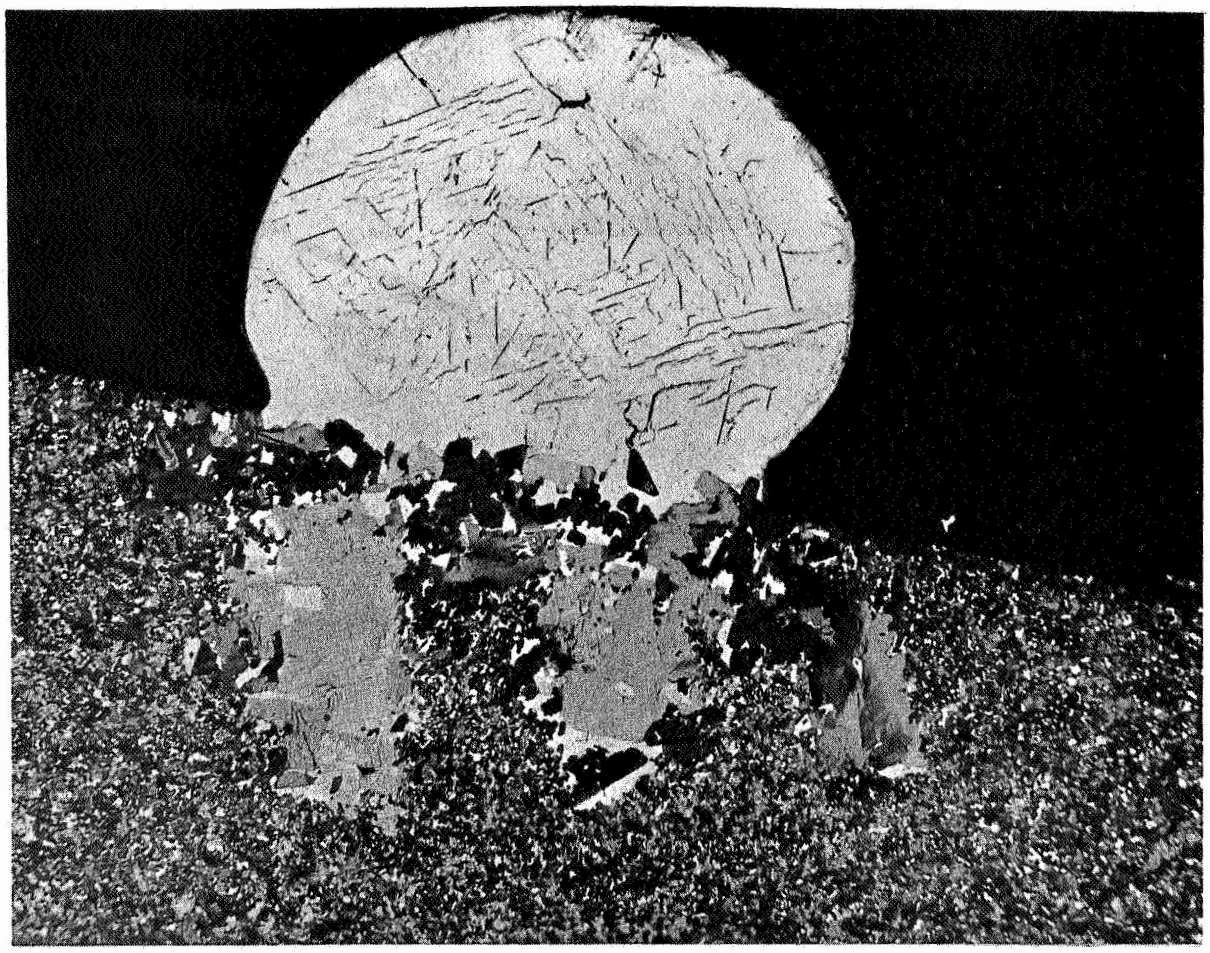

FIG 13 - MICROSTRUCTURE OF "SWEATED AREA
IN 50 WT% Mo-GRAPHITE SAMPLE
HEAT TREATED AT 2600°C/2 HRS
(POLARIZED LIGHT° x100)