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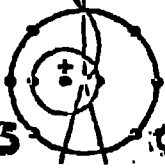
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PREPARATION OF FIBER REINFORCED TITANIUM
DIBORIDE AND BORON CARBIDE COMPOSITE BODIES*

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ABSTRACT

A process is described for uniformly infiltrating woven carbon cloth with either titanium diboride or boron carbide at reduced pressure (15-25 torr). The effects of deposition temperature on the uniformity of penetration and on coating rate are described for temperatures from 750 - 1000°C and deposit loadings from 20 - 43 vol. %. For the boron carbides, boron composition is discussed and evidence is presented suggesting that propene is the dominant rate controlling reactant.

I. INTRODUCTION

A major materials problem encountered in the development of Tokamak fusion reactors is the lack of satisfactory heat sink materials for use in limiters, wall armor, beam stops, etc. Preferably these components should contain only low-atomic number elements to minimize plasma quenching by beam-induced, sputtered products, in addition to having a high melting temperature and good thermal fatigue resistance. Of the monolithic ceramic materials available, only graphite meets these criteria; however it has an unacceptably high erosion rate due to its high chemical reactivity with the charged hydrogen isotopes in the beam. Coating monolithic graphite shapes with refractory, low atomic-number carbides or borides for protection from the Tokamak atmosphere has been proposed to lessen these problems; however, because of the differences in thermal expansion and conductivity (between graphite and the coatings), spallation of the coat (exposing the graphite surface) may occur during operation.

Riley, et al have suggested that the spallation problem could be essentially eliminated by combining the graphite and protective coating in the form of a filament reinforced composite. This could be accomplished by the chemical vapor deposition of carbides or borides on graphite cloth in such a way as to encase each individual filament, followed by hot pressing a stack of the coated cloths into a fully

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dense plate(1). The resultant structure would show a continuous network of carbide or boride reinforced with graphite filaments, essentially eliminating adherence and spalling problems. If the coating is ruptured, the damage would be restricted to the individual filaments involved, and attack of the graphite by hydrogen or by sputtering minimized. Further, the filament reinforced composite should have superior strength properties and should exhibit excellent thermal shock and thermal fatigue properties(2,3).

In this study we describe a technique for preparing such graphite filament reinforced titanium diboride and boron carbide composites.

II. EXPERIMENTAL PROCEDURES

All the coating prepared in this study was deposited on Union Carbide WCA cloth with an areal density of 0.0244 g/cm^2 , woven from yarn containing 1440 filaments each $7 \mu\text{m}$ in diameter. Circular pieces of cloth $\sim 16 \text{ cm}$ in diameter were stretched over a 13.3 cm o.d. graphite holding hoop, and held in place by compressing the excess circumferential material down over the hoop with an external graphite compression ring. Several of these disks are then stacked in a 17 cm i.d. coating chamber in such a manner that the reactant gases flow through the cloths in series. Four graphite baffles placed above the cloths and separated by spacers served to heat the coating gases to the deposition temperature. The TiB_2 deposition, and a few early boron carbide depositions were carried out in a smaller apparatus whose design was similar to that described above except that the cloths were oriented parallel to the reactant gas flow.

Deposition was carried out at a reduced pressure of 15 to 25 torr in order to enhance diffusion of the coating gases into the interior of the yarn strands to promote uniform deposition on all filaments. The reduced pressure is achieved by means of a high speed centrifugal pump using water as the pumping fluid. For the CVD, gaseous chlorides of boron and titanium were generated by direct chlorination of the elements at 575° and 400° , respectively. The BCl_3 and/or TiCl_4 were mixed with hydrogen down stream from the chlorinators and then introduced into the coating chamber. For the boron carbide coating, C_2H_6 was added to the hydrogen as a carbon source.

Analysis of the deposited material for boron content was carried out as described in Ref. 4, with the exception that fusion was done in a mixture of Na_2CO_3 and Na_2O_2 .

Hot pressing was carried out in a graphite-lined, graphite die with pressure gradually applied during heat up.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The primary emphasis of this study was to determine sets of coat-

ing parameters for TiB_2 and boron carbide deposition which would allow uniform coating of the filaments within the cloth assemblage.

TITANIUM DIBORIDE COATED CLOTH. Table 1 shows the process gas flow rates used to prepare titanium diboride coatings. Since x-ray analy-

Table 1. Titanium diboride deposition parameters

Chlorine flow to boron chlorinator (cm^3/min)	201
Chlorine flow to titanium chlorinator (cm^3/min)	134
Hydrogen flow (cm^3/min)	6000
Deposition temperatures ($^{\circ}C$)	700-1000
Deposition times (min)	240-445

sis showed only TiB_2 , and since TiB_2 has a very small homogeneity range, no analysis for boron composition was carried out (5).

The effect of deposition temperature on the uniformity of deposit thickness across the yarn strand is shown by the photomicrographs in Fig. 1. At $800^{\circ}C$ (Fig. 1c) the interior filaments in the yarn strand has less TiB_2 than the outer ones; at $1000^{\circ}C$ (Fig. 1e) the strand has been "canned" with TiB_2 excluding the coating gas from the interior filaments. Close examination of the photomicrographs in Figs. 1a and 1b suggest that the uniformity of the cloth coated at $700^{\circ}C$ might be slightly better than that at $750^{\circ}C$, however, both look satisfactory for hot pressing. Figure 2 shows the effect "canning" has on the deposition rate as a function of temperature. Above $800^{\circ}C$ the surface area accessible to the coating gas decreases so rapidly that it overcomes an exponentially increasing deposition rate resulting in an apparent maximum in the observed deposition rate. This is confirmed by the change with temperature of the fraction of the coat deposited on the cloth (weight increase of cloth/weight increase of cloth + graphite fixture) shown in Fig. 3. As the interior of the cloth becomes sealed at higher deposition temperatures, the surface area of the fixture becomes increasingly significant. The ratio of the surface area of cloth to the surface area of the graphite fixture is ~ 115 , hence at the lower deposition temperatures where metallographic examination showed that uniform deposition was obtained on all filaments, one would expect $\sim 1\%$ of the weight to be on the fixture, if the deposition rate was the same for fixture and cloth. However, Fig. 3 shows that the fraction is 10%, indicating that the deposition rate within the cloth is 1/10 of the rate outside the cloth. A similar relationship has been found for boron carbide.

HOT PRESSED TITANIUM DIBORIDE. A single hot pressed billet, prepared from material coated at $750^{\circ}C$, and containing 38 vol. % TiB_2 and 62 vol. % graphite fiber was densified at $2350^{\circ}C$ and 28 MPa. The measured properties of this billet are shown in Table 2 and its microstructure is shown in Fig. 4. While excellent compaction was achieved, the graphite fibers underwent reorganization with a resulting loss of

Table 2. Properties of TiB₂/C composite material

Composition (vol. % TiB ₂)	38
Density (g/cm ³)	2.83
Flexure strength (MPa)	108
TiB ₂ lattice spacings	
before hot pressing	a ₀ = 3.039 Å, c ₀ = 3.207 Å
after hot pressing	a ₁ = 3.039 Å, c ₁ = 3.232 Å

integrity. Irrespective of whether this was caused by incipient melting at the pressing temperature, or a solid state reaction, it is detrimental to the flexure strength. While the flexure strength shown in Table 2 is higher than that for TiB₂-C particulate composites, the value should have been significantly higher if reorganization could have been avoided.

BORON CARBIDE COATED CLOTH. Table 3 give a typical set of process parameters used for deposition of boron carbide. Since x-ray

Table 3. Typical boron carbide deposition parameters

Chlorine flow to boron chlorinator (cm ³ /min)	323
Propene flow (cm ³ /min)	14.8
Hydrogen flow (cm ³ /min)	10100
Deposition temperature (°C)	900
Deposition time (min)	600

diffraction analysis of the deposited material showed an amorphous structure, boron analyses were made to determine the composition of the deposited material as a function of temperature and other process variables. Boron content variation with deposition temperature is shown in Fig. 5. The data for 850, 900, and 950 °C represent the means (with one standard deviation) for 2-6 different coated cloths, while that at 1000 °C was determined from a single, coated cloth. Analysis of the boron content as a function of cloth stack position at 900 °C showed that the B:C ratio was essentially constant (~2), whereas the B:C ratio in the gas was ~4 at the top of the first cloth and ~6 at the bottom of the last cloth in the stack. Another run at 900 °C where the initial B:C ratio in the gas was ~5, again, resulted in a B:C ratio of 2 in the top cloth. These observations suggest that for a given deposition temperature, the B:C ratio in the deposited material is relatively insensitive to the B:C ratio in the gas for the ranges investigated.

To achieve the maximum microstructural uniformity in the final hot pressed sample, it is essential to determine the range where uniform penetration of the fiber bundles is achieved. Shown in Fig. 6 are photomicrographs characteristic of the inner regions of yarn strands coated at 850, 900, and 1000 °C, respectively. Uniformity of penetration is somewhat better at 850 °C than 900 °C, although both

appear quite adequate for the hot pressing. At 1000 °C a definite lack of uniform penetration is evident and the coated cloth is unacceptable. Based on these observations, the optimum coating temperature is in the range of 850 to 900 °C.

Figure 7 shows the variation of deposition rate as a function of cloth position in the stack for 850 and 900 °C, respectively. Over the limited range of deposition rates studied; this variation is nearly linear, which allows the production of uniformly loaded sets of cloth by reversing the stack sequence for a second coating run with the same coating time duration. For 5 cloths, this procedure produces a loading uniformity of $\pm 4\%$ and for 8 cloths $\pm 7\%$.

In order to better understand the variation of deposition rate with BCl_3 and C_3H_6 concentrations, four coating runs were made where these parameters were varied independently (Table 4). The ratio of the

Table 4. Effects of BCl_3 and C_3H_6 on deposition rate

Run	Deposition temp. (°C)	BCl_3 (moles/min)	C_3H_6 (moles/min)	Deposition rate (cloth 1) (g/min)
1	950	0.00488	0.000329	0.01320
2	950	0.00250	0.000329	0.01093
3	900	0.00838	0.000714	0.01053
4	900	0.00838	0.000567	0.00897

deposition rates on the first cloths in Runs 1 and 2 was proportional to the cube root of the ratio of the respective BCl_3 flow rates. Similarly, the ratio of the deposition rates on the first cloths in Runs 3 and 4 was proportional to the $2/3$ power of the ratio of the respective C_3H_6 flow rates. These results suggest that the deposition rate, r , on the n^{th} cloth in a stack could be given by

$$r(n) \propto P_{\text{BCl}_3}^{1/3}(n) \cdot P_{\text{C}_3\text{H}_6}^{2/3}(n) \quad (1)$$

where $P_{\text{BCl}_3}(n)$ and $P_{\text{C}_3\text{H}_6}(n)$ are the average partial pressures of the reactants. These partial pressures can be calculated iteratively from the initial reactant concentrations at the entrance to the coating chamber, the cumulative weight of material deposited up to the n^{th} cloth, the weight deposited on the n^{th} cloth, and the composition of the deposited material as inferred from Fig. 5. The average partial pressures of BCl_3 and C_3H_6 are taken as the mean of the values before and after the n^{th} cloth. Data from four coating runs at 900 °C are combined in Fig. 8 as a test of Eq. 1. The runs chosen were those which covered the widest range of deposition rates to provide the largest spread of data. The line shown through the data points is a linear least squares fit which was not constrained to pass through the origin.

While the data shown follow the functional dependence of Eq. 1, it is important to note that the runs all had very similar starting conditions. Undoubtedly there is a functional dependence on the partial pressures of HCl and H₂, but these dependencies were not decipherable in the range of parameters investigated. However, for this range the dominant rate controlling reactant is C₃H₆.

BORON CARBIDE-CARBON HOT PRESSED BILLETS. Two hot pressed billets containing 27 and 43 vol. % boron carbide, respectively, were prepared at 2100 °C and 32 MPa. These samples were made from cloth coated at 1000 °C. As discussed in the previous section, material prepared at this temperature lacks satisfactory homogeneity, and future samples prepared from material deposited at 850 and 900 °C are expected to have a better microstructure and improved properties. The microstructure of the 27 vol. % sample is shown in Fig. 9. Excellent compaction was achieved, but, as in the case of TiB₂/C hot pressing, the integrity of the graphite fibers appears to have been damaged by reaction with the boron carbide. The data presented in Fig. 5 suggest that the B:C ratio in these samples is ≈ 5. Since the B-B₄C eutectic is approximately 2075 °C, liquid phase may have been present during hot pressing leading to reorganization of the graphite fibers. This is not expected to be a problem for hot pressings prepared from material coated in the range of 850 to 900 °C, since the B:C ratio is < 4 and the B₄C-C eutectic temperature is approximately 2375 °C(5). X-ray diffraction measurements on the hot-pressed samples showed that the amorphous deposit had transformed to hexagonal B₄C (a₀ = 5.621 Å, c₀ = 12.093 Å). The electrical conductivities of both hot pressed billets are shown in Table 5.

Table 5. Electrical properties of B₄C/C composites

Composition (vol. % B ₄ C)	Density (g/cm ³)	Electrical Conductivity (Ω ⁻¹ cm ⁻¹)
27	1.71	441
43	1.87	204
100*	2.47	28

*B₄C powder hot pressed at 2050 °C and 21 MPa.

IV. CONCLUSIONS

The materials discussed in this study demonstrate the capability for preparing a homogeneous fiber reinforced structure, with the choice of ceramic and its proportion relative to carbon fiber adapted to the particular use. It is clear, however, that additional work is required to establish the correct hot pressing conditions for both TiB₂/C and B₄C/C. In addition, the effects of composition over the boron carbide range from BC to B₅C might be expected to have a substantial effect on plasma erosion resistance. The most significant problem, at present, seems to be the rather limited amount of data available on this rela-

tively new material, and especially a complete lack of empirical information on how it will actually behave when exposed to a Tokamak plasma.

ACKNOWLEDGMENTS

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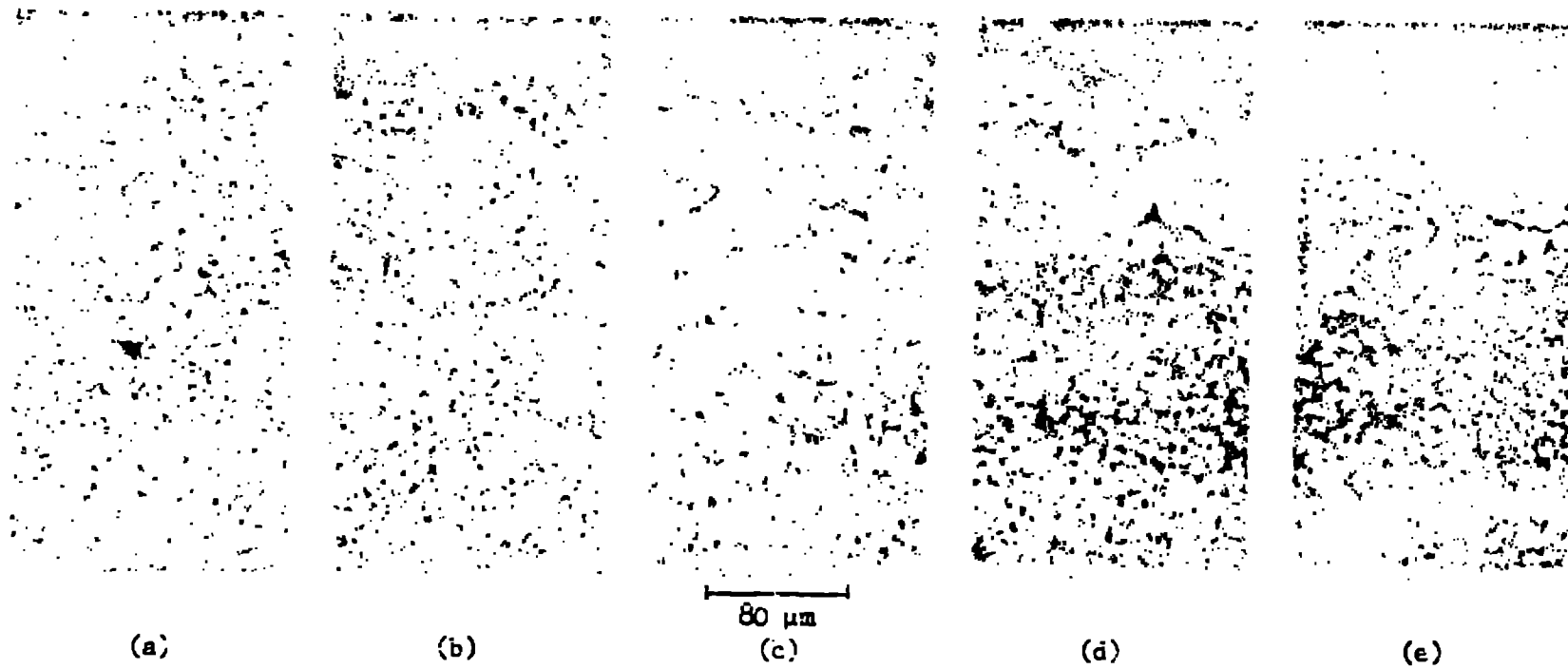


Fig. 1. Titanium diboride coated carbon cloth as deposited at a) 700°C, b) 750°C, c) 800°C, d) 900°C and e) 1000°C.

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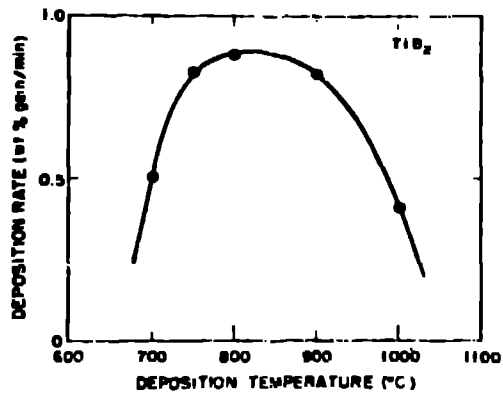


Fig. 2. TiB₂ deposition rate as a function of temperature.

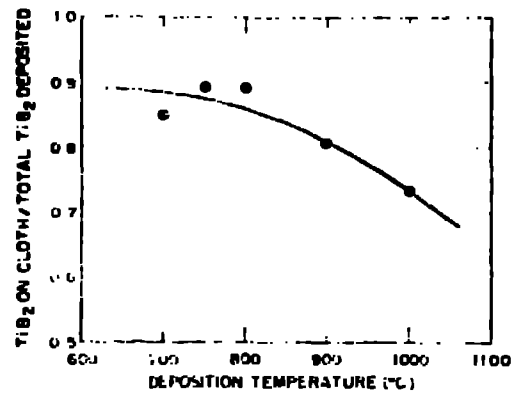


Fig. 3. Fraction on cloth of total TiB₂ deposited, as a function of temperature.

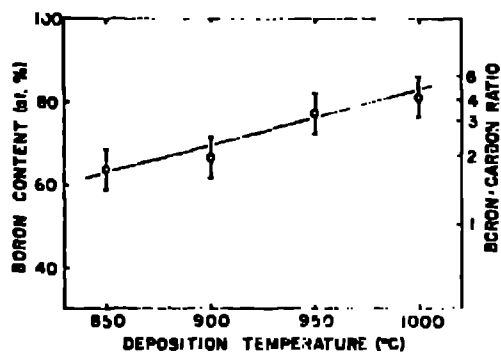


Fig. 5. Composition of boron carbide deposits as a function of temperature.

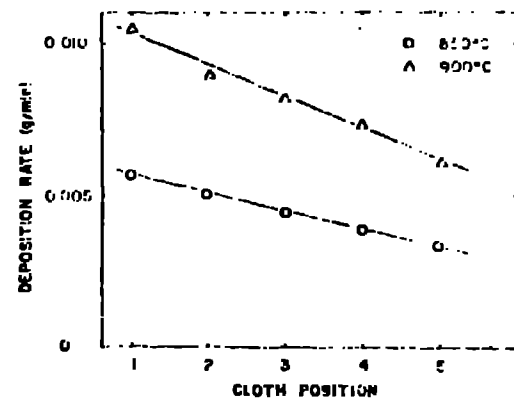


Fig. 7. Boron carbide deposition rate as a function of cloth position.

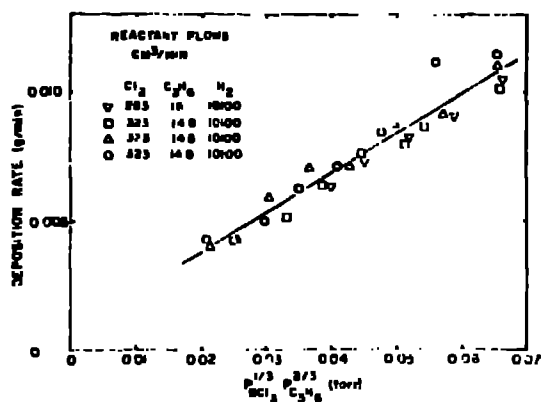


Fig. 8. Boron carbide deposition rate as a function of reactant partial pressures.

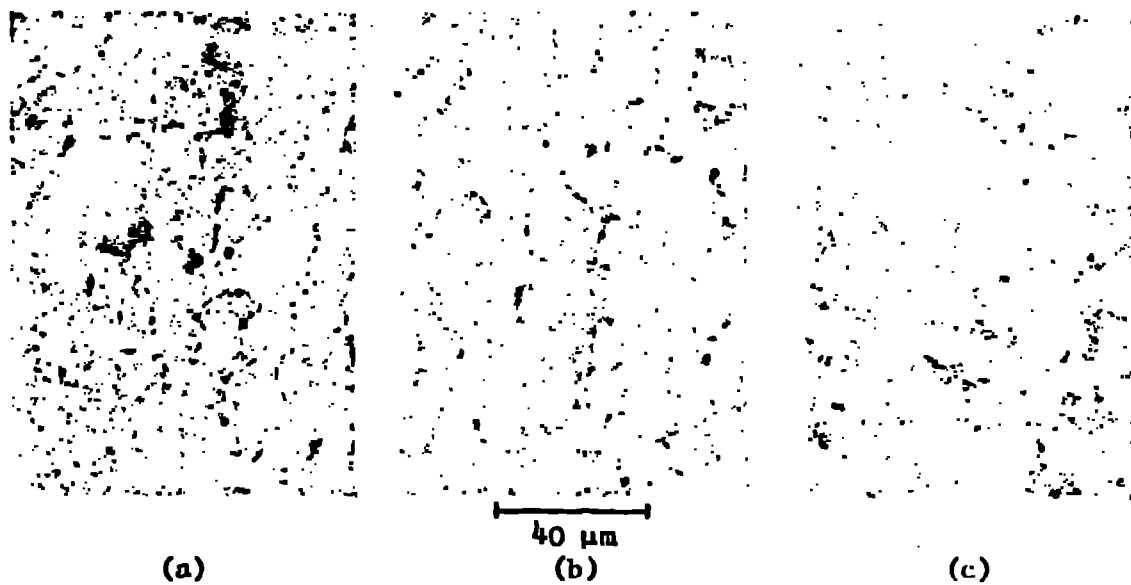


Fig. 6. Boron carbide coated carbon cloth as deposited at a) 850°C, b) 900°C and c) 1000°C.

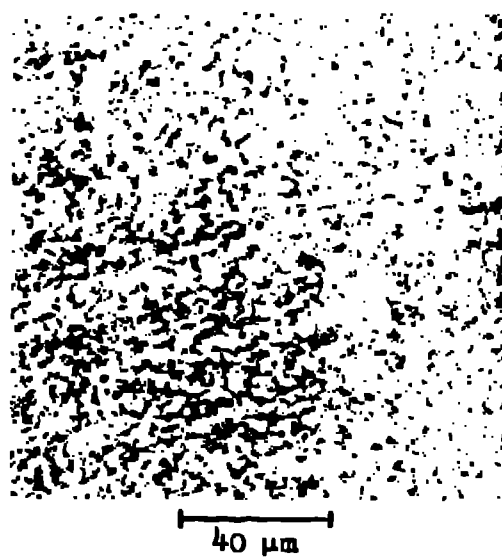


Fig. 4. Hot pressed TiB₂/C sample containing 38 vol.% TiB₂, 62 vol.% C.

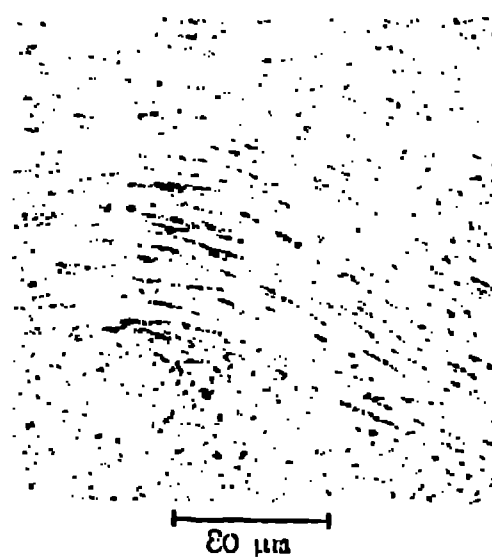


Fig. 9. Hot pressed boron carbide-carbon sample containing 27 vol.% boron carbide.