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FABRICATION OF DENSE FINE GRAINED CERAMIC MATERIALS

FINAL REPORT

by

D. Kalish
E. V. Clougherty
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November 1966

ManLabs, Inc.
21 Erie Street
Cambridge, Mass.

Contract DA-19-066-AMC-283(x)

U. S. ARMY MATERIALS RESEARCH AGENCY
WATERTOWN, MASSACHUSETTS 02172

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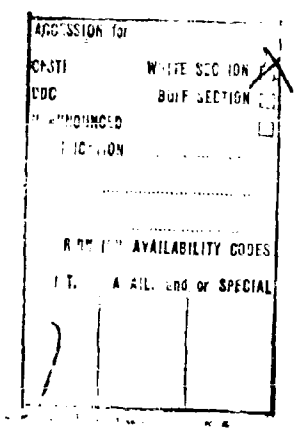

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ABSTRACT

High pressure hot pressing was used to prepare dense, crack free billets of boron carbide, silicon carbide, titanium carbide and titanium nitride. These materials were fabricated from high purity powders without the additions of densification promoters. Fabrications were generally performed in the vicinity of 1800°C at 120,000 psi for 10 minutes. Reactive high pressure hot pressing of boron carbide and elemental boron carbide was investigated with different atomic ratios of boron to carbon. Microstructures and mechanical property evaluations were obtained for selected materials prepared by this technique. The results obtained for high pressure hot pressed boron carbide and silicon carbide materials were compared with results of similar evaluation performed on conventionally fabricated samples of boron carbide and silicon carbide.

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1. INTRODUCTION AND SUMMARY

The objectives of this program were (1) to perform fabrication studies employing high pressure hot pressing, hereafter referred to as HPHP, on several selected ceramic type compounds, (2) to obtain mechanical property data on materials fabricated by this method where the materials evaluated would be representative of a class of materials, e.g., TiC, TiN, and the mechanical property data would be obtained as a function of temperature and where feasible stoichiometry and (3) to scale up the size of the billets currently being fabricated by this method.

The HPHP procedure was previously used to prepare sound billets of materials composed of refractory metal diborides and mixtures of diborides with various additives designed to improve oxidation resistance and/or to alter the boron to metal ratio in the original diboride powder (1,2,3)*. This fabrication procedure employs pressures of the order of 100,000 psi, temperatures in the range 1700° to 2000°C and times of 5 to 20 minutes. The sample material is enclosed in a boron nitride container; the system is completely closed. The experimental conditions produce increased rates of densification and full densification can be obtained at significantly lower temperatures than those employed in conventional hot pressing procedures carried out at 2,000 to 6,000 psi. The fabrication time is also considerably reduced in high pressure hot pressing. These conditions of lower temperature and shorter fabrication time and the hydrostatic component of the applied pressure retard diffusion processes and grain growth is inhibited or eliminated. Further, chemical reactions of the base powder material being fabricated with container material and/or gases present, or produced in the conventional hot pressing experiments are eliminated.

The materials selected for this program were B_4C, SiC, TiC and TiN. High purity powders were procured and characterized. After a series of fabrication screening experiments on each material, selected structures of each material were prepared for mechanical property evaluations. The latter included transverse bend strength as a function of test temperature, room temperature microhardness as a function of indenter load and room temperature modulus of elasticity. Several lots of conventionally hot pressed B_4C and SiC were obtained and evaluated for comparison with the HPHP materials. Reactive high pressure hot pressing of the B_4C powder and elemental boron powder produced single phase boron carbide material with B/C atomic ratios, significantly higher than four. Limited evaluations were carried out for such materials but it was established that the microhardness does substantially increase as B/C increases from 4 to 5.5. The size of the billet fabricated by high pressure hot pressing was scaled up from 0.3 inch diameter by 1 inch long to 1 inch diameter by 1 inch long.

*Underscored numbers in parentheses designate References given at end of report.

II. EXPERIMENTAL PROCEDURES

A. Materials: Selection, Procurement and Characterization

The material selection for this program was based in part on the available physical and mechanical property data obtained on samples fabricated by high pressure hot pressing. Chemical, physical and mechanical property data were obtained for the diborides of titanium, zirconium and hafnium in previous studies in this laboratory (1-4). Mechanical property data were obtained by Vasilos and others (4,5) on oxide materials. Other fabrications employing high pressure hot pressing were reported by Vahldiek and Lynch (7) who studied refractory oxides and borides and by Brandmayr (8) who prepared barium titanate for electrical applications. High pressure hot pressing has also been used to reactively fabricate various refractory compounds from elemental powders (1,9). Material selection was also based on the current needs of the Army Materials Research Agency as regards lightweight ceramic materials with high elastic moduli. Thus, boron carbide, silicon carbide, titanium carbide, and titanium nitride were selected for evaluation in this program.

High purity powders of the selected materials were procured and characterized. In addition, boron carbide and silicon carbide billets prepared by conventional fabrication procedures were obtained for direct comparison of characterization results and mechanical property evaluations with the high pressure hot pressed materials. Pertinent procurement information and characterization results are summarized in Tables 1 through 6.

B. Fabrication by High Pressure Hot Pressing

The essential components of the high pressure fabricating equipment include: (1) a simple piston cylinder high pressure apparatus which is capable of generating pressures up to 45,000 psi on a 0.40 inch diameter specimen, (2) a cylindrical graphite tube furnace which heats the specimen at pressure to temperatures up to 2000°C with boron nitride electrical insulators to prevent contamination of the specimen from the graphite furnace and (3) support equipment including a 1,000 ton press, a 10kv power supply and precompacting apparatus. A schematic diagram of the die and furnace assembly is shown in Figure 1.

In the pressure range used for this study, 60,000 to 150,000 psi, relatively inexpensive high pressure equipment can be employed. Previous studies (1,2) indicated that higher pressures necessitating more sophisticated equipment which would severely reduce the size of fabricated samples and increase the cost of the fabrication was not necessary to achieve high relative densities. The temperatures employed were in the range 1600° to 1900°C. Temperature calibration data for this assembly, hereafter identified as System 1, was previously established (2).

TABLE 1

CHARACTERIZATION OF BORON CARBIDE POWDER

Material Designation: $B_4C(2)$ Supplier: The Carborundum Company
Electrominerals Division

Characterization:

Qualitative Spectroscopic Analysis (ranges in weight per cent, w/o):
Fe, Si, 0.1-1.0; Ca, 0.01-0.1; all other metals except B < 0.01

Quantitative Spectroscopic Analysis (w/o):
Fe, 0.40; Si, 0.13; Ca, .012

Experimental Quantitative Analysis (w/o):
B, 77.9 (ManLabs); C, 20.4 (MIT); Pyrohydrolysis Residue 1.0

Atomic Ratio:
B/C = 4.24

Phase Identification by X-ray Methods:
B_4C (principal phase); BN or Graphite (second phase)

Particle Size:
6-7μ average

Remarks:
Metallographic results provided in Figures 7 and 8 and complementary X-ray results show that the $B_4C(2)$ powder contained free graphite even though the boron to carbon ratio of 4.24 showed the material boron rich relative to B_4C.

Material Designation: $B_4C(2A)$ Supplier: The Carborundum Company
Electrominerals Division

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Si, .01-0.1; all other metals except B ≤ 0.01

Experimental Quantitative Analysis (w/o):
B, 75.0; C, 21.9 (MIT); B, 75.0 (Ledoux)

Atomic Ratio:
B/C = 3.8

Phase Identification by X-ray Methods:
B_4C (principal phase); BN or Graphite (second phase)

Remarks: Metallographic and X-ray results show this powder contained free graphite.

TABLE 2

CHARACTERIZATION OF "HD" BORON CARBIDE

Material Designation: $B_4C(1)$ Supplier: The Carborundum Company
New Products Branch

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Si, Ca, Fe, 0.01-0.1; all other metals except B < 0.01

Experimental Quantitative Analysis (w/o):
B, 74.6; C, 23.13 (MIT) Ca, .027; Fe, 0.35; Si, 0.002 (Jarrell-Ash)

Atomic Ratio:
B C = 3.58

Phase Identification by X-ray Methods:
B_4C (principal phase); BN or Graphite (second phase)

Density:
2.45 g/cm^3

Grain Size:
10μ

Remarks:
Second phase is graphite; microstructure is shown in Figure 12.

Material Designation: $B_4C(1A)$ Supplier: The Carborundum Company
New Products Branch

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Ca, Al, Fe, Si, 0.01-0.1; all other metals except B ≤ 0.01

Experimental Quantitative Analysis (w/o):
B, 73.8; C, 22.5; N, 0.18 (MIT); B, 75.0; C, 22.8 (Ledoux);
Ca, 0.007; Al, 0.25; Si, 0.35 (Jarrell-Ash)

Atomic Ratio:
B/C = 3.64

Phase Identification by X-ray Methods:
B_4C (principal phase); BN or Graphite (second phase)

Density:
2.50 g/cm^3

Grain Size:
13μ

Remarks:
Second phase is graphite; microstructure is the same as obtained for B_4C (1), Figure 12.

TABLE 3

CHARACTERIZATION OF MISCELLANEOUS SAMPLES OF HOT PRESSED BORON CARBIDE

Material Designation: B_4C(II) Supplier: AMRA (Up-graded Technical Grade)

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Al, Si, Cr, Fe, 0.1-1; Ca, 0.01-0.1; all other metals except B < 0.01

Experimental Quantitative Analysis (w/o);
B, 72.9; C, 21.8; O, 0.23 (MIT); B, 74.5-76.5 (Supplier's Information)
Al, 0.57; Si, 0.06; Fe, 0.3; Cr, 0.27 (Jarrell-Ash)

Atomic Ratio:
B/C = 3.71

Phase Identification by X-ray Methods:
B_4C (principal phase); BN or Graphite (second phase)

Density:
2.48 g/cm^3

Grain Size:
17μ

Remarks:
Received one bar 1/2 inch wide x 5/8 inch thick x 2-1/2 inch long. Preliminary metallographic investigation revealed a band, high in second phase, approximately 0.15 inch deep along one of the 5/8 inch by 2-1/2 inch surfaces. Chemical analysis and metallographic results, Figure 14, show that the second phase is graphite.

Material Designation: B_4C(III) Supplier: AMRA (High Purity Grade)

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Al, Sn, 0.1-1.0; Pb, Ca, Si, 0.01-0.1; all other metals except B < 0.01

Experimental Quantitative Analysis (w/o):
B, 75.0; C, 21.9; O, 0.19 (MIT); B, 76-78 (Supplier's Information);
Al, 0.36; Sn, 0.17 (Jarrell-Ash)

Atomic Ratio:
B/C = 3.81

Phase Identification by X-ray Methods:
B_4C (principal phase); BN or Graphite (second phase)

Density:
2.49 g/cm^3

Grain Size:
18μ

Remarks:
Received one bar, 1/2 inch wide x 5/16 inch thick, 2 inches long. Second phase was evenly dispersed throughout the bar. Chemical analysis and metallographic results, Figure 15, show that the second phase is graphite.

TABLE 3 (CONT)

CHARACTERIZATION OF MISCELLANEOUS SAMPLES OF HOT PRESSED BORON CARBIDE

Material Designation: B_4C(IVA) Supplier: AMRA (Plate A)

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Ca, 1.0-10.0; Si, 0.1-1.0; Fe, As, 0.01-0.1; all other metals except B< 0.01

Experimental Quantitative Analysis (w/o):
B, 74.7; C, 22.4; O, 0.24; N, 1.04 (MIT); Fe, 0.06; Ti, 0.012 (MIT); Ca, 0.053; Si, 0.09 (Jarrell-Ash)

Atomic Ratio:
B/C & 3.70

Phase Identification by X-ray Methods:
B_4C (principal phase); BN or Graphite (second phase); Several unidentified lines observed

Density:
2.20 g/cm^3

Grain Size:
23μ

Remarks:
Received one plate, 6 inches square x 3/8 inch thick. Chemical analysis and metallographic results, Figure 16, show that the second phase is graphite.

Material Designation: B_4C(IVB) Supplier: AMRA (Plate B)

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Ca, 1.0-10.0; Si, 0.1-1.0; Al, Fe, Sn, 0.01-0.1; all other metals except B< 0.01

Experimental Quantitative Analysis (w/o):
B, 75.3; C, 22.5; N, 1.38 (MIT); Ca, 0.086; Si, 0.13 (Jarrell-Ash)

Atomic Ratio:
B/C = 3.71

Phase Identification by X-ray Methods:
B_4C (principal phase); BN or Graphite (second phase)

Density:
2.30 g/cm^3

Grain Size:
23μ

Remarks:
Received one plate, 6 inches square x 3/8 inch thick. Microstructure is similar to that of B_4C(IVA). Chemical analysis and metallographic results show that the second phase is graphite.

TABLE 4

CHARACTERIZATION OF SILICON CARBIDE

Material Designation: SiC(3)* Supplier: The Carborundum Company
Electrominerals Division

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Ti, 0.1-1.0; Ca, V, Zr, 0.01-0.1; all other metals except Si < 0.01

Experimental Quantitative Analysis (w/o):
Si, 69.5; C, 29.4 (MIT); Ti, 0.24 (Jarrell-Ash)

Atomic Ratio:
Si/C = 1.01

Phase Identification by X-ray Methods:
SiC (principal phase); several unidentified lines observed

Particle Size:
6μ

Material Designation: SiC(I)* Supplier: The Carborundum Company

Characterization:

Qualitative Spectroscopic Analysis (w/o):
B, Al, Ti, Fe, Zr, 0.1-1.0; Ca, Cr, Mn, 0.01-0.1; all other metals except Si < 0.01

Experimental Quantitative Analysis (w/o):
Si, 68.9; C, 29.2 (MIT)

Atomic Ratio:
Si/C = 1.01

Phase Identification by X-ray Methods:
SiC (principal phase); Si (second phase)

Densities:
3.07 g/cm^3

Remarks:
Microstructural features which include the presence of free silicon and graphite are shown in Figure 20.

*SiC(3) - Powder material; SiC(I) - KT silicon carbide.

TABLE 5

CHARACTERIZATION OF TITANIUM CARBIDE POWDER

Material Designation: TiC(2)

Supplier: Titanium Alloy Manufacturing Co.
Research Department

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Zr, 0.1-1.0; Si, 0.01-0.1; all other metals except Ti< 0.01

Quantitative Analysis (w/o):
Ti, 78.4; C, 19.03; free C, 0.19 (Supplier's Data)

Experimental Quantitative Analysis (w/o):
Ti, 80.2; Total C, 19.2 (MIT)

Atomic Ratio:
Ti/C = 1.05

Phase Identification by X-ray Methods:
TiC, no additional lines observed

Particle Size:
5μ Average

TABLE 6

CHARACTERIZATION OF TITANIUM NITRIDE POWDER

Material Designation: TiN(1) Supplier: Titanium Alloy Manufacturing Co. Research Department

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Mn, Fe, Mg, 0.1-0.001; all other metals except Ti < 0.01

Quantitative Analysis (w/o):
N, 14.23 (Supplier's Data)

Experimental Quantitative Analysis (w/o):
Ti, 82.5; N, 13.4 (MIT)

Atomic Ratio:
Ti/N = 1.80

Phase Identification by X-ray Methods:
TiN (principal phase); TiO_2 (minor amounts)

Particle Size:
-200 Mesh (as received)

Remarks:
Material is metal rich relative to TiN

Material Designation: TiN(2) Supplier: Titanium Alloy Manufacturing Co. Research Department

Characterization:

Qualitative Spectroscopic Analysis (w/o):
Fe, 0.01-0.1; Si, Zr, 0.001-0.01; all other metals except Ti < 0.01

Quantitative Analysis (w/o):
N, 18.7 (Supplier's Data)

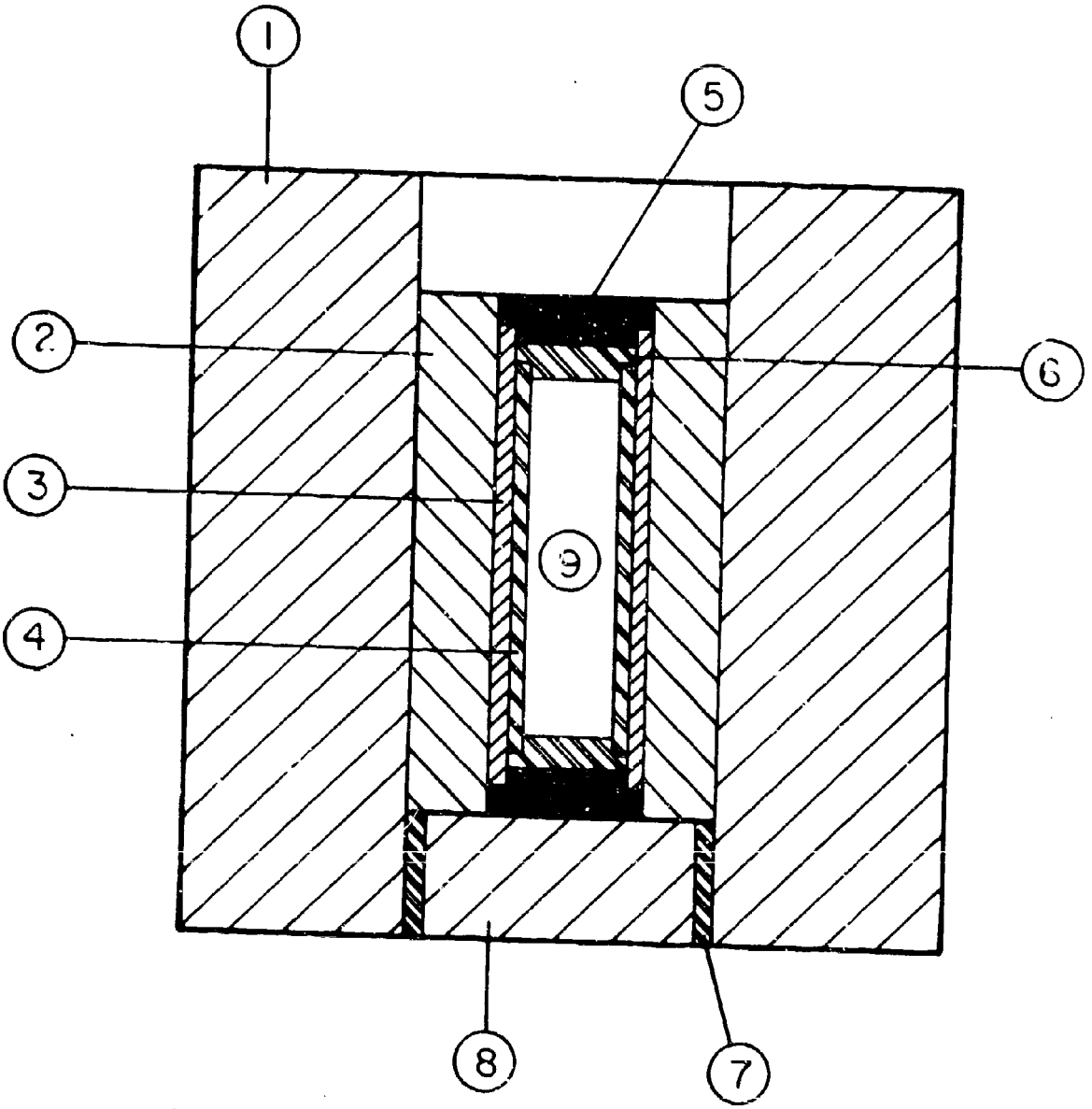
Experimental Quantitative Analysis (w/o):
Ti, 80.2; N, 19.2 (MIT)

Atomic Ratio:
Ti/N = 1.22

Phase Identification by X-ray Methods:
TiN (principal phase); Ti (second phase)

Particle Size:
60 Mesh

Remarks:
Material is metal rich relative to TiN; second phase is shown metallographically in Figures 27 and 29.



1. Die (Tungsten Carbide)
2. Outer Insulation (Lava)
3. Furnace (Graphite)
4. Boron Nitride Liner
5. Carbon Pad
6. Boron Nitride Pad
7. Lava Sleeve
8. Closure (Hardened Steel)
9. Compact Chamber (0.40 inch diam. x 1.0 inch long)

Figure 1. High Pressure Hot Pressing Components for System.

The powder material for fabrication was stored in a laboratory vacuum oven at 110°C. The powders were cold compacted at room temperature and 100,000 psi by either a double acting or a single acting hand operated hydraulic press. The cold compact was placed inside the boron nitride insulator and degassed at 5×10^{-5} torr at 1000°C for one hour. The degassing procedure was incorporated as part of the standard fabricating procedure in a previous study of borides (1); this modification decreased the incidence of cracks in the as fabricated billets and improved the subsequent thermal mechanical stability. The degassed compact in the boron nitride insulator was placed in the high pressure apparatus and pressurized at room temperature. Then, the temperature was raised to the fabricating condition and maintained for the desired time interval. Finally, the billet was cooled to ambient temperature with some simultaneous reduction in pressure. A typical heating cycle is provided in Figure 2.

In order to increase the size of the fabricated billets, the high pressure apparatus, Figure 1, was scaled up to provide a specimen 1.0 inch diameter. The schematic drawing for the larger high pressure assembly, hereafter identified as System 2, is shown in Figure 3. The length of billet was altered by adding boron nitride pads to each end of the compact. Equipment limitations prevented the degassing of compacts to be fabricated in System 2.

A power temperature calibration of System 2 was performed in order to provide a means of determining the fabrication temperature. This calibration was carried out up to 1400°C by using a thermocouple imbedded in a dummy specimen. Above 1400°C, the thermocouple failed due to the consolidation of the cell parts at the high temperatures and pressures. The power thermocouple temperature curve, Figure 4, was extrapolated above 1400°C. The extrapolation was substantiated through the use of "melting" specimens of different metals inserted in the high pressure cell next to the specimen chamber. Following each experiment the buttons were examined metallographically in order to determine if melting occurred. Buttons of three metals, platinum, chromium and iron chosen for their melting temperatures, were used for each experiment. The data points, determined on a melt/no melt basis, are also plotted in Figure 4.

C. Metallography

The polishing procedure given in Table 7 was found to produce the best results for the ceramic materials of interest in this program.

Various etchants were employed; they are presented with each micrograph. It was observed that chipping and pulling out of grains due to improper grinding often contributed to an apparent porosity. This condition led to conflicting results when the metallographic porosity was compared to bulk density measurements or when the reproducibility of a microstructure for a given set of fabrication conditions was examined.

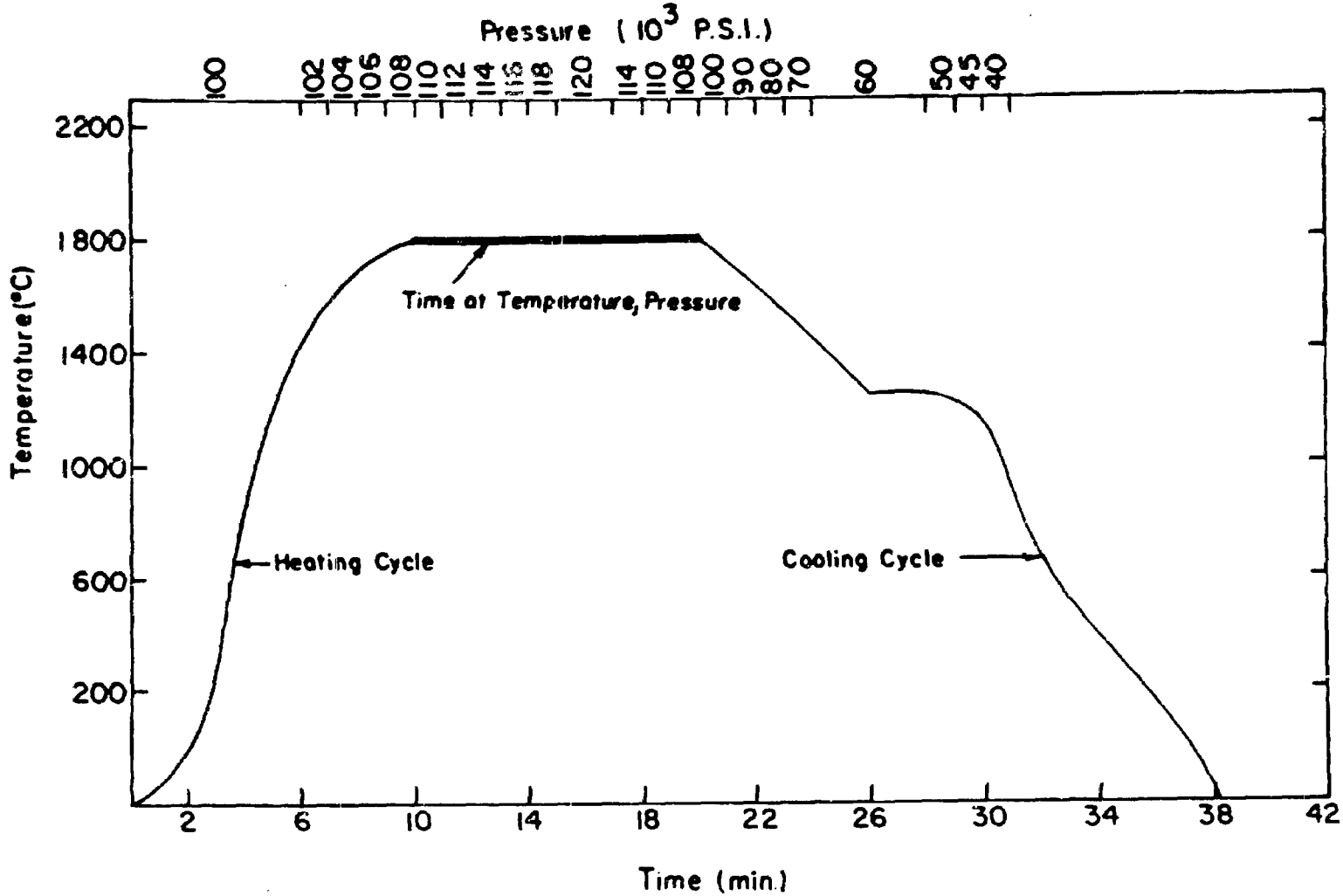
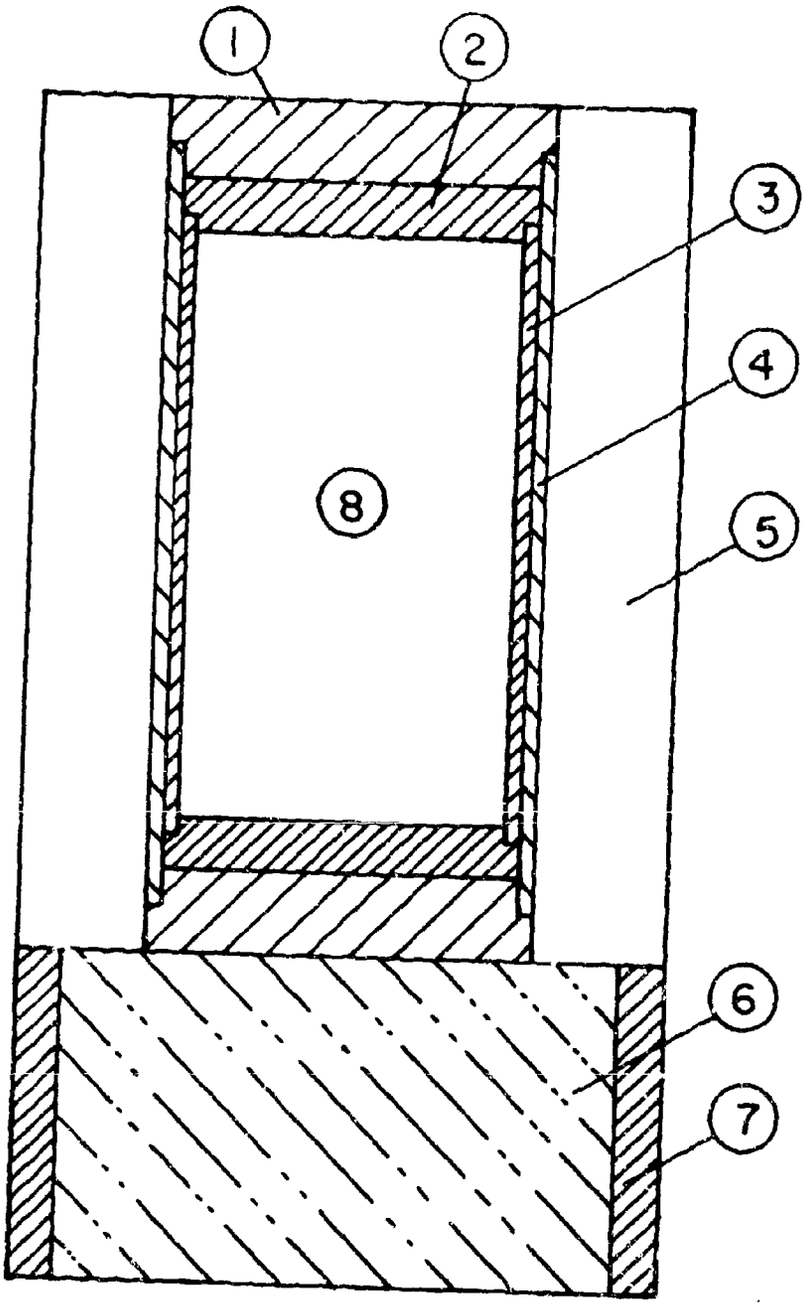


Figure 2. Time Temperature Pressure Cycle for High Pressure Hot Pressing in System 1.



1. Furnace Contact Pad(Carbon)
2. Elec. Insulating Pad (BN)
3. Elec. Insulating Liner (BN)
4. Graphite Furnace
5. Thermal Insulator (Lava)
6. OL. FM. Closure
7. Closure Electrical Insulator (Lava)
8. Compact Chamber (1.0 inch diam. x 2.5 inches long)

Figure 3. High Pressure Hot Pressing Components for System 2.

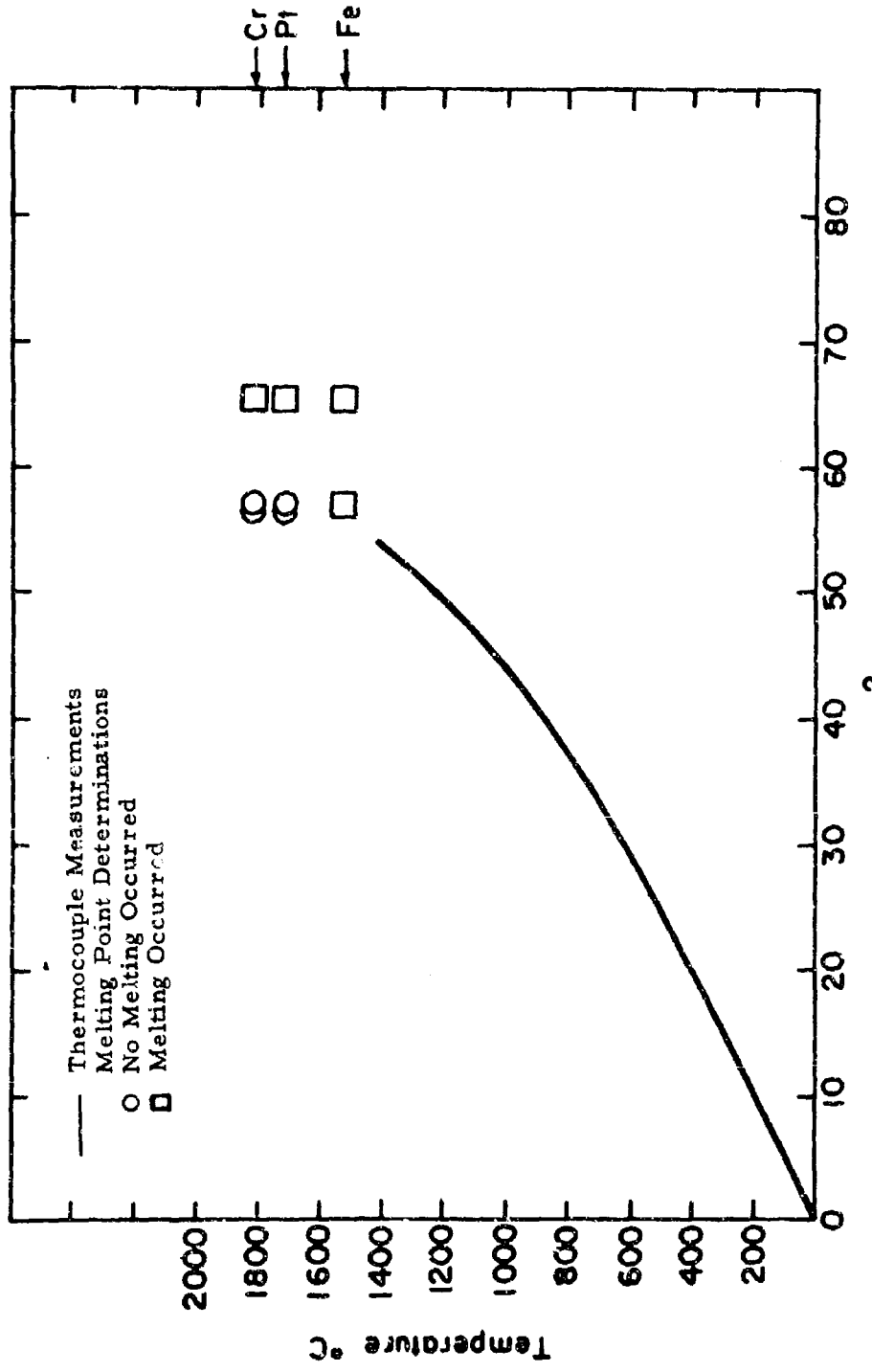


Figure 4. Temperature Calibration Curve for System 2.

TABLE 7

POLISHING PROCEDURE FOR METALLOGRAPHIC PREPARATION

Status*	Station	Polishing Paste	Lubricant	Time
Rough Grind	70 grit resin bonded diamond grinding disc		Tap Water	
Intermediate Grind	240 grid SiC paper	30μ diamond	Kerosene	15 min.
	320 grit SiC paper	15μ diamond	Kerosene	10 min.
	Canvas cloth	9μ diamond	Kerosene	5 min.
	Buehler "Metcloth"	6μ diamond	Kerosene	10 min.
Final Polish	Pellon cloth	0.3μAl_2O_3	Distilled Water	2 min.
	Buehler "Microcloth"	0.6μAl_2O_3	Distilled Water	30 min.

*Rough and intermediate grinding steps are done on automatic polishing machines. Final polishing is done manually. The times reported here are approximate and may change with individual specimens.

D. Hardness

Hardness measurements were made using a Leitz Durimet Microhardness Tester and a Knoop Diamond Indenter. The Knoop configuration was chosen for testing these materials since it was specifically designed to minimize stress induced cracking in hard, brittle materials. The reported data were obtained from symmetrical, crack free indentations.

Since the Knoop hardness for brittle materials is usually inversely proportional to the indenter load, at the lower loads, the hardness was measured at a series of loads in order to experimentally define this relation.

E. Transverse Bend Strength

The primary interest in the bend testing phase of the program was to determine the room temperature strength. However, high temperature strength properties were measured in several cases in anticipation of possibly determining the temperature range for the onset of gross plastic deformation. This information would be useful to assist in the design of hot pressing processes and thereby to enhance the mechanical properties.

1. Specimen Preparation

The dimensions of the transverse bend strength specimens were: 0.80 inch long x 0.20 inch wide x 0.10 inch thick. These specimens were obtained from fabricated sample materials prepared by high pressure hot pressing and by conventional hot pressing. The exterior of the as fabricated materials were ground in order to remove surface contamination. Materials prepared by high pressure hot pressing were then heated in argon at 1500°C prior to further machining. The cylindrical billet was then cut into two rectangular bars by diamond abrasive cutting. Final dimensions and surface preparation were obtained by a series of precision grinding operations using a Sanford Surface Grinder and selected Norton diamond abrasive wheels containing the following nominal size diamond particles: 23μ, 16μ, 4-8μ. Optional hand lapping procedures using 0.1-1.0μ alumina usually induced surface flaws which led to premature failures. Following the final grinding step, the surfaces were examined for cracks and grain pull outs. The four longitudinal edges were ground to a radius of 5-10 mils by hand lapping using 3μ diamond paste on a cast iron lapping wheel.

When the room temperature strength of a given material was established, a room temperature proof stress level was chosen for specimens to be tested at elevated temperatures. The proof stress levels employed are 25,000 psi for SiC, 25,000 psi for TiC and 35,000 psi for B_4C. If the specimen survived this proof test, the load was released and the specimen was used for tests at elevated temperatures. This procedure gave added confidence to strength levels observed at higher temperatures.

2. Apparatus and Testing Procedure

The procedure and apparatus described below was used for all measurements performed at elevated temperature. After completion of the proof test, the chamber in the apparatus shown schematically in Figure 5 was filled with dry argon and the temperature was raised under flowing argon to the desired testing temperature at a rate of approximately 1000°C per hour. The specimen was maintained at the test temperature for 15 minutes, then the load was applied to produce a strain rate of 3×10^{-4} in/in/min until fracture occurred. The temperature was lowered to ambient at the rate of 1000°C in 30 minutes.

The high temperature apparatus, Figure 5, employed a three point loading system. The load was applied and measured with a Baldwin Tensile Tester. The specimen was heated by radiation from a tungsten element supported by boron nitride insulators. The temperature was measured with a micro optical pyrometer (disappearing filament type). The reported temperatures for the bend tests are not corrected for emissivity nor for the prism used for sighting onto the tension side of the specimen. Room temperature transverse strength measurements were made in a similar three point loading apparatus. In the latter, the sapphire supports were replaced by tungsten carbide.

The transverse bend strength was calculated from the load at fracture according to Eq. (1) for a three point load system:

$$\sigma\,(\text{psi}) = \frac{1.5\,Pl}{bh^2} \qquad (1)$$

where P is the load, in pounds, at fracture, l is the distance, in inches, between bottom supports, b and h are the width and thickness, in inches, of the specimen, respectively.

F. Modulus of Elasticity

The standard dimensions of specimens used for determining modulus of elasticity were: 0.20 inch wide, 0.038 inch thick and 0.850 inch long. The specimens were prepared in the same manner as the bend strength specimens.

The measuring apparatus consists of two units: the loading unit and the deflection measurement unit, Figure 6. The specimen was loaded in either 3 or 4 point bending through a proving ring, strain gage type dynamometer vertically mounted in a brass frame. Squared type bushings (guides) were incorporated into the design in order to provide one degree of freedom for the dynamometer movements (vertical direction) and also to insure smooth frictionless motion. The resistance strain gage type circuit is excited with a stabilized D.C. constant voltage (18 volts). The output signals from the dynamometer are measured with a digital type millivolt meter. The working range of the dynamometer is 0 to 200 pounds and the accuracy is $\pm$ 0.5 pounds ($\pm$ 0.25%) for the entire range.

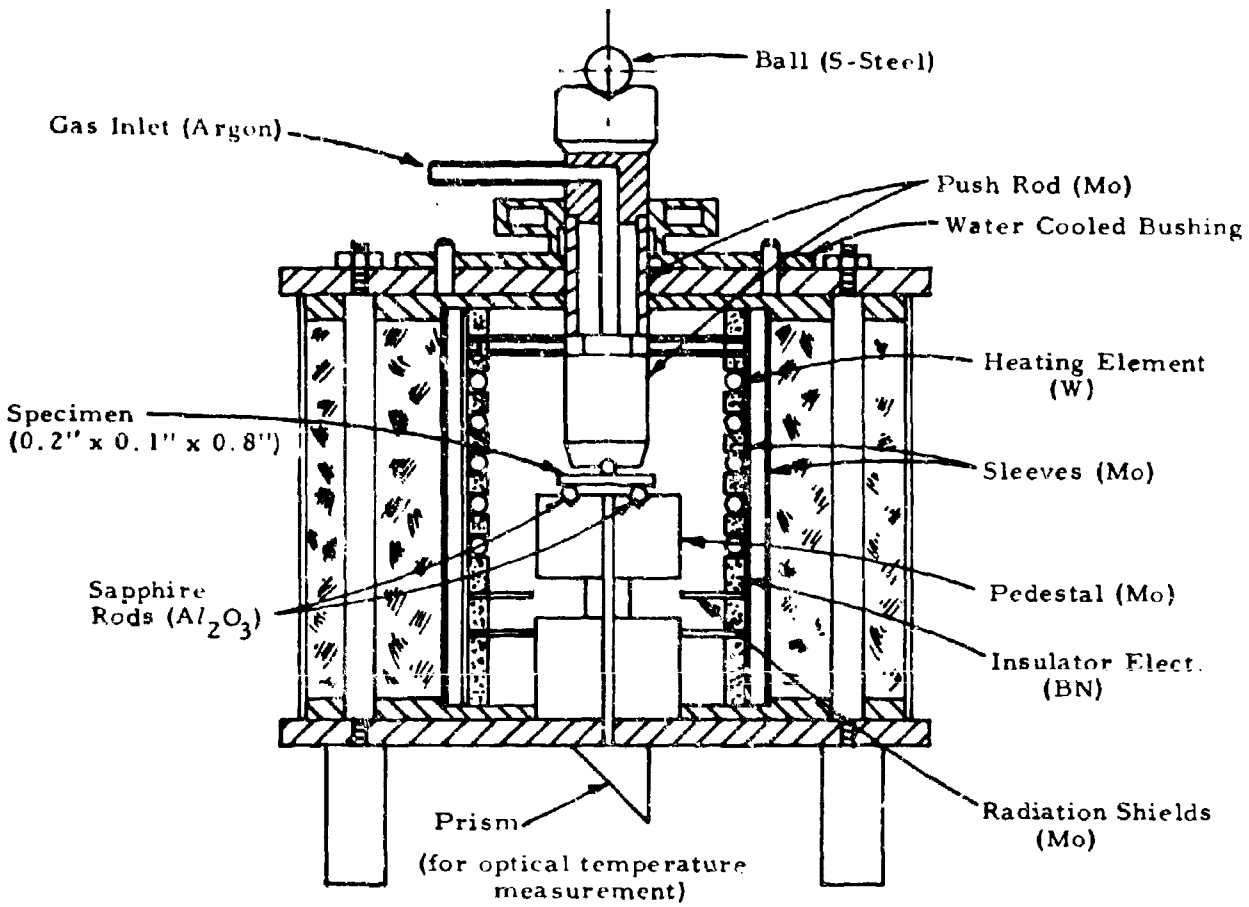


Figure 5. Schematic Diagram of Elevated Temperature Bend Test Apparatus.

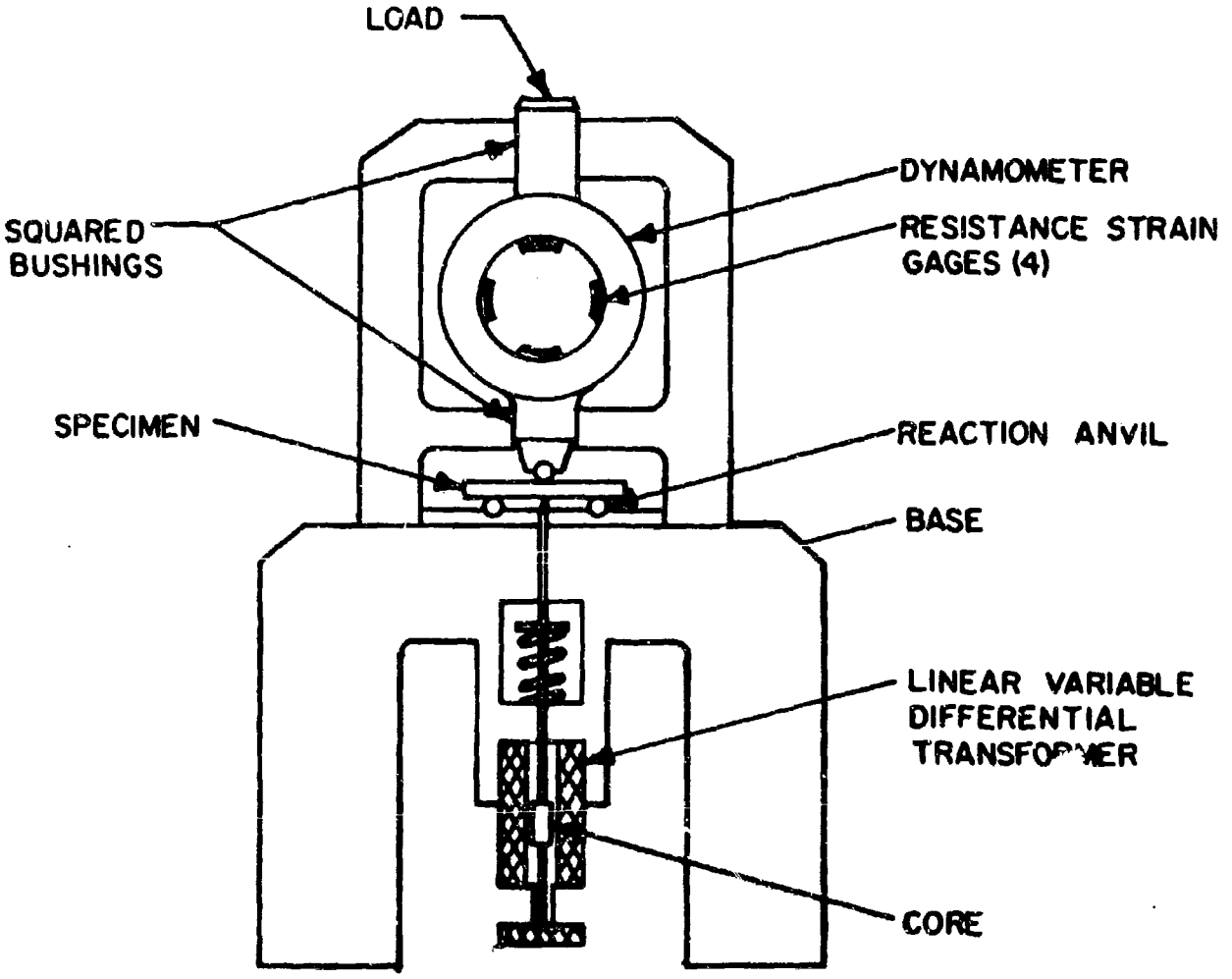


Figure 6. Schematic Diagram of Apparatus for Measuring Elastic Modulus.

The specimen deflection is measured with a linear variable differential transformer (L.V.D.T.). The deflections are transmitted to the L.V.D.T. through a brass pusher rod which is spring loaded against the specimen. A transformer core is mounted on the lower end of the rod. The relative mounting of the linear differential transformer in respect to the pusher rod core unit was adjustable. The primary coil of the L.V.D.T. was energized with an A.C. voltage source (4 volts, 2000 cps) and the secondary coil was connected to the digital millivolt meter. The linear working range of L.V.D.T. is 0.005 inch and the accuracy read out is 50×10^{-6} inch ($\pm$ 1%).

G. Electron Fractography

The fracture surfaces of broken bend specimens were examined by electron fractography. The surface structures were replicated using a preshadowed two stage replication technique. This procedure requires (1) wetting the fracture surface with acetone and placing cellulose acetate tape on the surface, (2) stripping the dried tape from the surface and statically shadowing the surface replica side with chromium at 60°, (3) evaporating carbon on to the chromium and (4) dissolving the cellulose acetate tape with acetone. The preshadowed positive carbon replicas were then examined in the electron microscope at magnifications from 1700 to 15000X.

III. RESULTS AND DISCUSSION

A. Boron Carbide

1. High Pressure Hot Pressed Material

Fabrication experiments designed to produce boron carbide by reactively hot pressing elemental boron and graphite powders were unsuccessful. Pressing these powders at 1800°C and 100,000 psi for 10 minutes produced incomplete densification and a highly inhomogeneous structure.

High pressure hot pressing the as received $B_4C(2)$ powder in System 1 produced a material containing excess graphite, Figure 7. Addition of boron powder to the $B_4C(2)$ powder followed by reactive high pressure hot pressing produced an essentially single phase material, Figure 8. This was accomplished by mixing ten weight per cent, w/o, boron powder with the $B_4C(2)$ powder. Examination of the reactively hot pressed specimen by X-ray diffraction indicated a single phase material. However, metallographic examination revealed the presence of small amounts of a second phase. A close inspection of Figure 8 shows fine grained areas which contain annealing twins. Other areas containing larger grains apparently formed as a result of recrystallization and grain growth. These observations indicate that deformation has occurred in the high pressure hot pressing. In view of the apparent success of initial "reactive" hot pressing experiments, involving boron carbide and boron powders additional fabrications were performed. The as received composition of boron carbide powder was reactively hot pressed with different amounts of boron powder. Samples with compositions in the range $B_{4.8}$ to $B_{12}C$ were fabricated. Billets were produced for several compositions within this range; however, some of these billets cracked during subsequent grinding. Metallographic examination indicated a powder mixing problem existed for compositions with additions above 19 w/o boron; the higher boron additions produced inhomogeneous structures which tended to crack. Successful fabrications included additions to the B_4C of 10, 12, 14, 16 and 19 w/o boron. Bend test results for HPHP specimens for several of these compositions and HPHP as received $B_4C(2A)$ powder are presented in Table 8. Bend strengths from 50,000 to 60,000 psi were obtained over the entire range of compositions evaluated. Elastic modulus measurements for B_4C with O, 12 and 16 w/o B additions gave a value of approximately 50×10^6 psi. A typical fracture surface for HPHP boron carbide is shown in Figure 9. Both intergranular and transgranular fracture facets are observed.

The addition of boron to B_4C tended to refine the grain size for compositions up to 19 w/o boron additions. This effect is demonstrated for the $B_4C(2)$ powder in Figures 7 and 8. The $B_4C(2A)$ powder as pressed possessed a finer grain size than the (2) powder. The effect of adding 12, 14 or 16 w/o boron to $B_4C(2A)$ is illustrated in Figure 10.

The limited amount of bend strength and modulus data in Table 8 shows no change in these properties with composition. However, the hardness of the matrix does increase with increasing boron content and goes through a maximum at B/C = 5.0. Microhardness data for the various compositions

Plate No.
7718

As Polished 500X

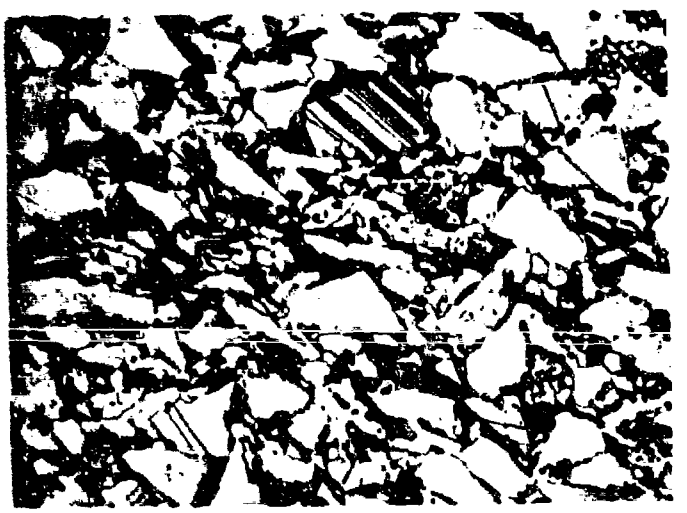


Plate No.
7750

Etched 500X

NOTE:

Specimen No.: 64226
Fabrication Conditions: 1800°C, 120,000 psi, 10 min.
Hardness: Reliable impressions could not be obtained
Etchant: 20% potassium hydroxide (electrolytic)
Grain Size: 50μ (average of larger grains)
B/C ratio: (4.24)

Figure 7. Microstructure of High Pressure Hot Pressed Boron Carbide Prepared from B_4C(2) Powder.

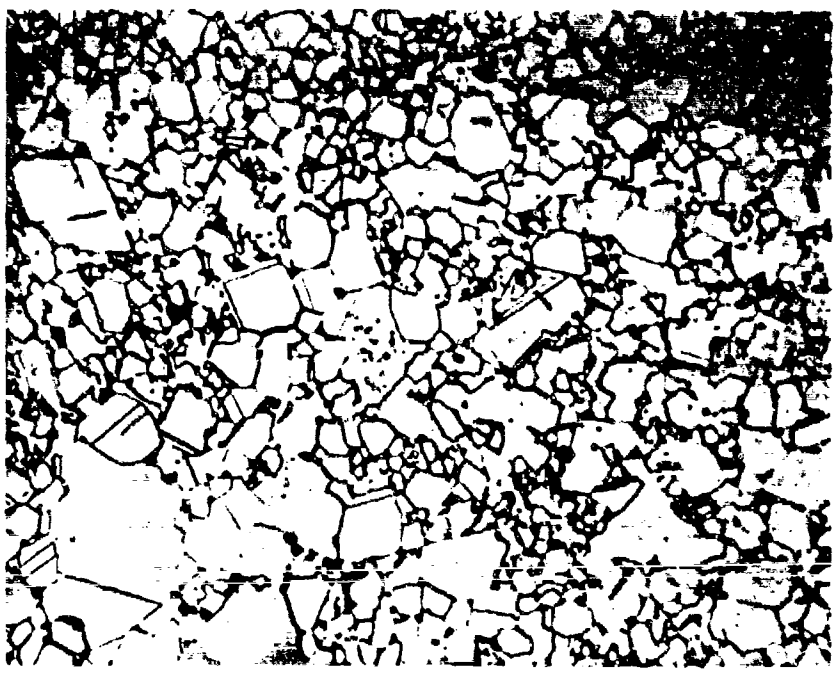


Plate No.
7681

Etched 1000X

NOTE:

Specimen No.: 68000
Fabrication Conditions: 1800°C, 120,000 psi, 10 min.
Hardness: KHN (200 grams) = 3000 kg/mm^2
Etchant: 20% potassium hydroxide (electrolytic)
Grain Size: 7μ
B/C Ratio: 4.79

Figure 8. Microstructure of High Pressure Hot Pressed Boron Carbide, Prepared from B_4C(2) + Ten Weight Per Cent Boron.

Plate No.
3603A

10,000X

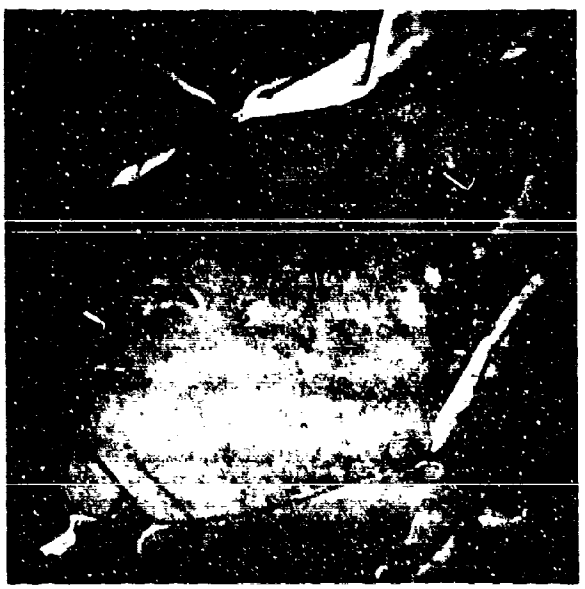
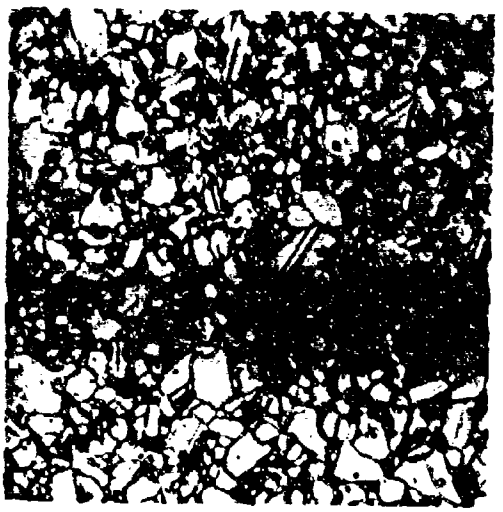


Plate No.
3602B

10,000X

Figure 9. Electron Replica Fractography of High Pressure Hot Pressed Boron Carbide. Specimen No. 6831B, Fabrication Conditions; 1800°C, 10 min., 112 x 10^3 psi.

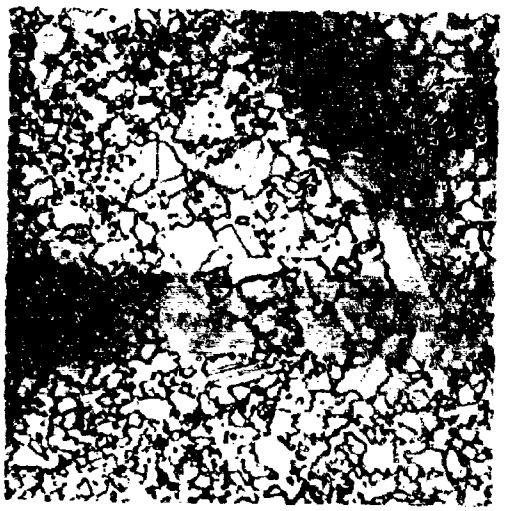
Plate No. 8309



Etched 1000X

As Received 2A

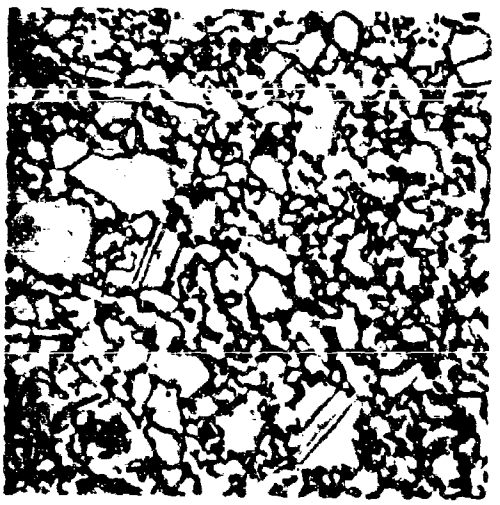
Plate No. 7854



Etched 1000X

10 w/o B Added

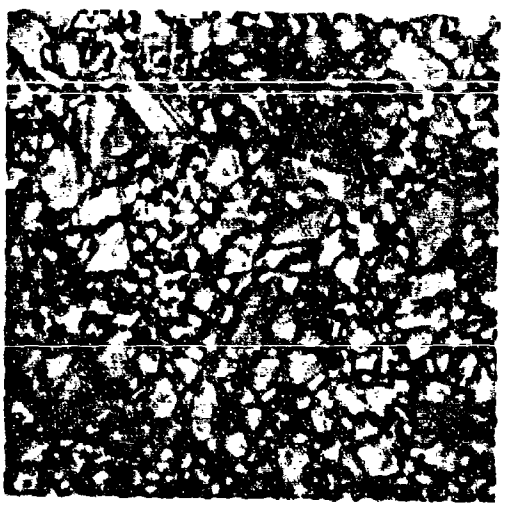
Plate No. 8296



Etched 1500X

12 w/o B Added

Plate No. 8359



Etched 1500X

16 w/o B Added

Figure 10. Light Micrographs of High Pressure Hot Pressed Boron Carbide Fabricated from B_4C(2A) Powder, As Received and with 12, 14 and 16 w/o B Added.

TABLE 8

TRANSVERSE BEND STRENGTH OF HIGH PRESSURE HOT PRESSED BORON CARBIDE

Material*	Specimen No.	Bend Strength psi	Modulus of Elasticity 10^6 psi
B_4C	78435A	53,700	49.3
(B/C = 3.81)	78435B	57,000	50.8
B_4C + 12 w/oB	68314A	53,500	
(B/C = 4.89)	68314B	78,000	
	68315A	57,700	
	68315	66,500	
B_4C + 12 w/oB	71027A	53,000	54.1
(B/C & 4.89)	71027B	50,000	46.4
(System 2)			
B_4C + 16 w/oB			
(B/C = 5.11)	68463A	49,400	51.2
B_4C + 19 w/oB	72358A	58,500	
(B/C = 5.5)	72358B	56,400	

*Powder B_4C (2A) used.

of boron carbide are tabulated in Table 9 and presented graphically in Figure 11. Apparently, the bend strength is not a sensitive measure of the inherent strength of the boron carbide matrix. The bend strength may be more influenced by factors such as grain size, surface preparation, residual stresses from the hot pressing operation, or stress corrosion. Although less modulus data are reported, similar factors would also effect this parameter.

2. Scale Up of Billet Size in High Pressure Hot Pressing

Boron carbide was high pressure hot pressed in System 2 with height to diameter ratios of 1/2, 1/4 and 1/8; the diameter in each case was 1.0 inch. The experiments with h/D = 1/4 and 1/8 were unsuccessful possibly due to a lack of heat penetration along the radius of the sample. The experiment with h/D = 1/2 was performed without difficulty. The resulting 1/2 inch high x 1.0 inch diameter specimen was sectioned and several bend specimens were obtained. The bend test results are included in Table 8. The modulus determined for two of the specimens was within the expected range, which suggests that the density was comparable to billets produced in System 1.

The feasibility of fabricating fully dense fine grained high purity boron carbide by high pressure hot pressing was demonstrated. The properties and structure of boron carbide can be altered and improved by reactive hot pressing. The addition of elemental boron powder to B_4C powder yields single phase materials with a wide range of B/C ratios. The "stoichiometric" B_4C may contain free graphite which is eliminated in reactive high pressure hot pressing. A scale up of the billet size of boron carbide that can be prepared by reactive HPHP was achieved; billets 0.4 and 1.0 inches in diameter were fabricated.

3. Conventionally Hot Pressed Material

Conventionally hot pressed boron carbide was obtained in four lots. The first lot, a commercial grade labeled B_4C "HD", was received from Carborundum Company in two shipments (designated in this program as B_4C(I) and B_4C(IA)). The typical microstructure for this material is presented in Figure 12. Bend tests were carried out at room and elevated temperatures. These data are reported in Table 10. The bend strength at 25°C appeared slightly higher for B_4C(I), 68,600 psi, than for B_4C(IA), 56,300 psi, although their chemistry and microstructure did not differ markedly. Modulus of elasticity measurements were made on B_4C(IA) material; average of 52.5×10^6 psi was obtained. Specimens from both shipments displayed predominantly transgranular cleavage fracture, Figure 13. Twinning is also observed in the electron fractographs of Figure 13. Elevated temperature bend tests on B_4C(I) maintained a strength of 68,000 psi up to 1300°C.

The three remaining lots of conventionally hot pressed B_4C were supplied by AMRA. The second and third lots of hot pressed boron carbide were labeled as an "up graded technical grade" and a "high purity grade"; these lots were respectively designated B_4C(II) and B_4C(III). Bend specimens of B_4C(II) and B_4C(III) were cut with two orientations; the loading direction being

TABLE 9

MICROHARDNESS OF HIGH PRESSURE HOT PRESSED BORON CARBIDE

Material*	Specimen No.	No. of Readings	$KHN_{(200)}$	Standard Deviation
B_4C (B/C = 3.80)	78378	10	3002	± 30
B_4C + 10 w/oB (B/C = 4.78)	68498	10	2966	± 40
B_4C + 12 w/oB (B/C = 4.89)	68437	30	3053	± 60
B_4C + 14 w/oB (B/C = 5.00)	68445	30	3216	± 80
B_4C + 16 w/oB (B/C = 5.11)	68464	30	3142	± 80
B_4C + 18 w/oB (B/C = 5.21)	68475	30	3193	± 95
B_4C + 19 w/oB (B/C = 5.5)	72447	20	3150	± 50
B_4C + 56 w/oB (B/C = 12)	72419	20	2924	± 40

*Powder B_4C(2A) used.

TABLE 10

TRANSVERSE BEND STRENGTHS OF CONVENTIONALLY HOT PRESSED B_4C

Material	Specimen No.	Test Temperature °C	Bend Strength psi	Modulus of Elasticity 10^6 psi
B_4C(I)	65002	25	61,300	
	65003	25	73,000	
	65004	25	59,000	
	65005	25	80,000	
	65006	25	71,600	
	65008	1000	60,200**	
	65007	1300	78,500**	
	65009	1300	57,600**	
B_4C(IA)	74008	25	49,000	59.5
	74009	25	64,000	48.1
	74010	25	47,600	52.6
	74011	25	57,300	49.8
B_4C(II)*	75003 (L)	25	15,700	
	75004 (L)	25	13,300	
	75005 (L)	25	49,500	
	75006 (L)	25	37,400	
	75009 (T)	25	67,500	
	75010 (T)	25	58,400	
	75013 (L)	25	49,500	
	75014 (L)	25	60,200	
	75007 (L)	1200	55,300**	
	75011 (T)	1200	55,600**	
	75008 (L)	1350	58,000**	
	75012 (T)	1350	59,500**	
B_4C(III)*	76004 (L)	25	51,400	
	76005 (L)	25	67,300	
	76006 (L)	25	73,700	
	76013 (T)	700	51,300**	
	76011 (T)	1000	51,600**	
	76009 (L)	1200	57,800**	
	76010 (T)	1200	61,500**	
	76007 (L)	1350	48,000**	
	76008 (T)	1350	47,000**	

TABLE 10 (CONT)

TRANSVERSE BEND STRENGTHS OF CONVENTIONALLY HOT PRESSED B_4C

Material	Specimen No.	Test Temperature °C	Bend Strength psi	Modulus of Elasticity 10^6 psi
B_4C(IVA)	77040	25	36,000	26.3
	77041	25	30,000	28.7
	77042	25	31,200	30.9
	77025	25	30,300	
	77026	25	28,400	
	77027	25	29,000	
	77028	25	29,000	
B_4C(IVB)	77039A	25	39,200	33.0
	77039B	25	39,700	36.0

*Bend specimens stressed parallel to the hot pressing direction denoted by (L); specimens stressed normal to the hot pressing direction denoted by (T).

**Proof tested at 25°C to a stress of 35,000 psi.

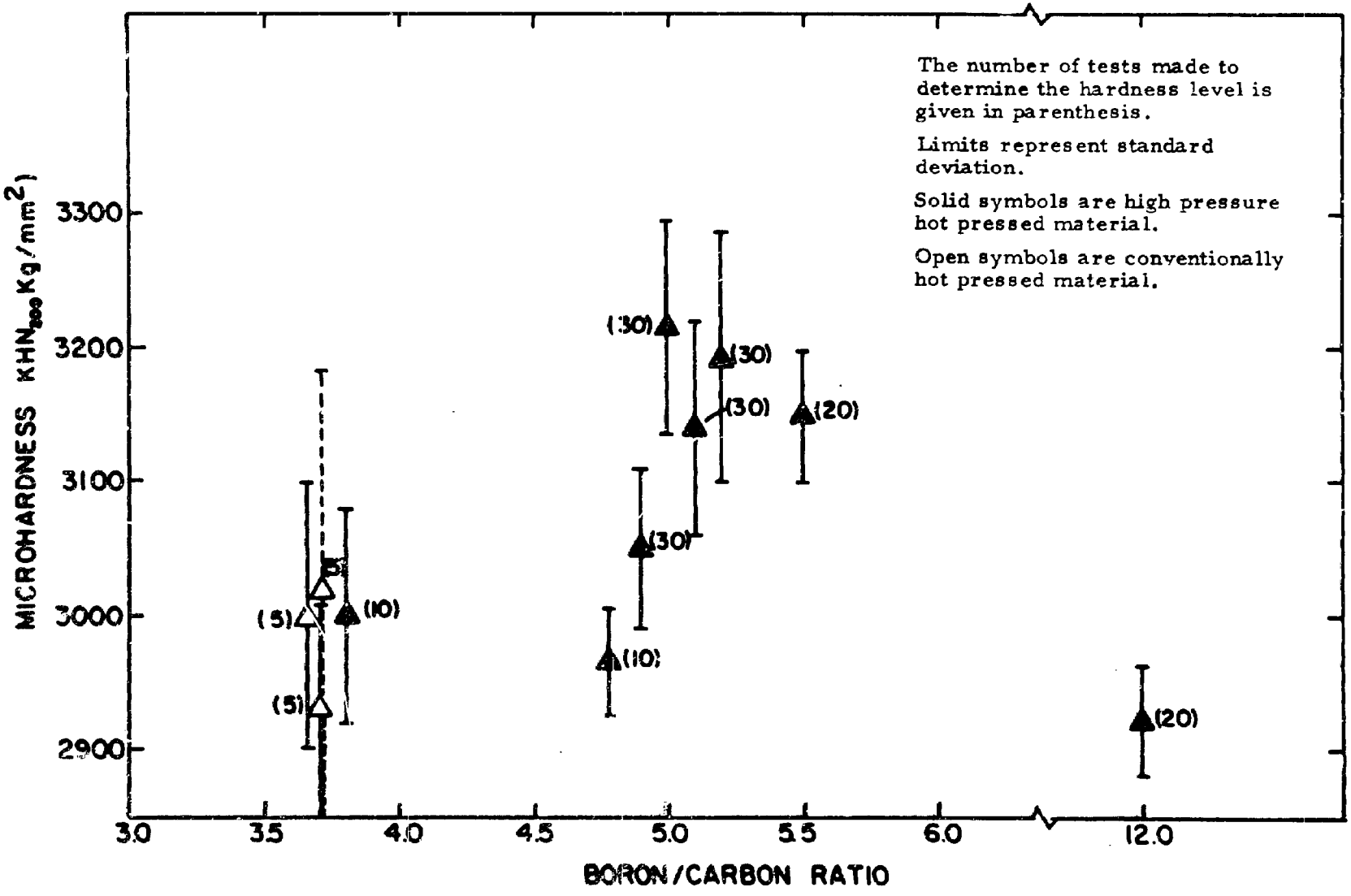


Figure 11. Microhardness as a Function of Boron/Carbon Ratio in High Pressure Hot Pressed Boron Carbide.

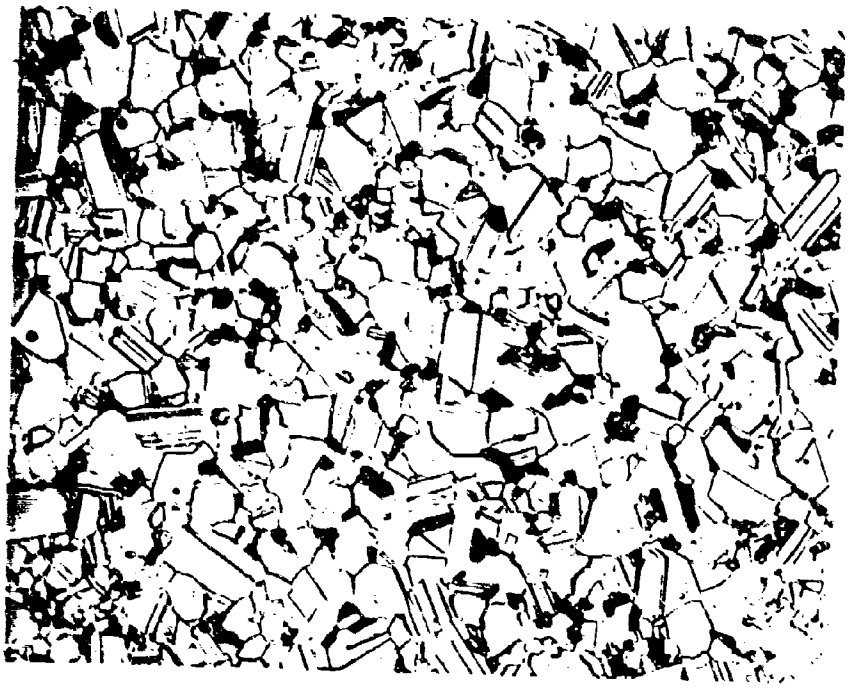


Plate No.
7752

Etched

1000X

NOTE:

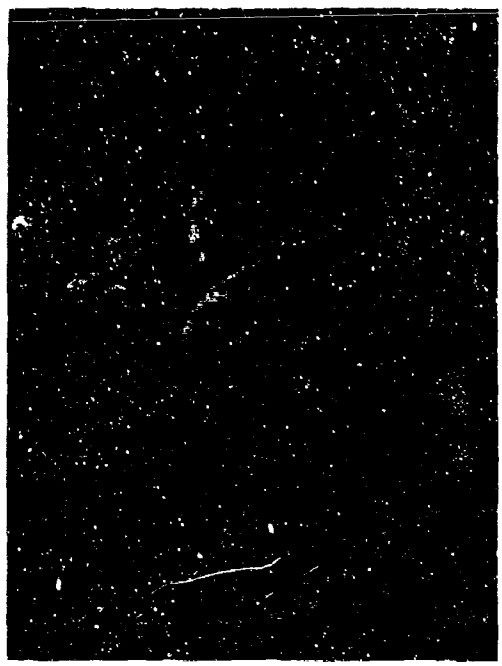
Specimen No.: 67003
Hardness: KHN (200 gms) = 3070 kg/mm^2
Etchant: 20% KOH (electrolytically)
Grain Size: 10μ
B/C Ratio: 3.58

Figure 12. Light Micrograph of Conventionally Hot Pressed "HD" Boron Carbide Supplied by Carborundum Company, B_4C(I).

Plate No. 3653A

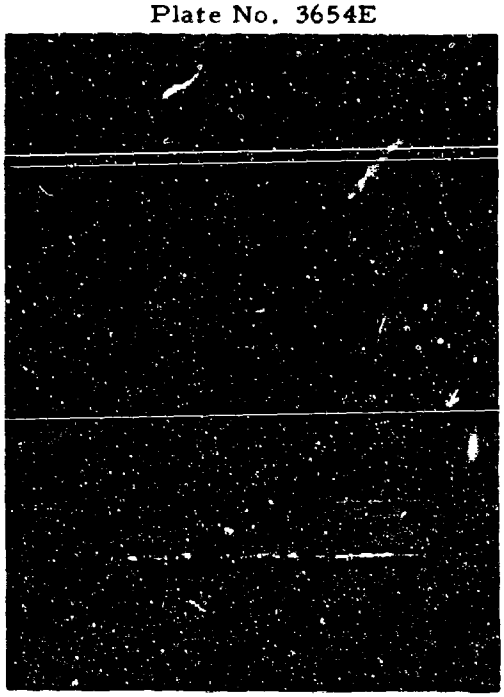
6500X

Plate No. 3653B



4500X

Plate No. 3654E



6500X

Figure 13. Electron Fractography of B_4C(IA) Tested Bend Specimens.

either parallel or normal to the hot pressing direction (although in both cases the bending tensile stresses were normal to the pressing direction). The as received plate dimensions prevented cutting bend specimens such that the outer fiber tensile stress would be parallel to the original hot pressing direction. The data given in Table 10 indicates no strength difference between the two specimen orientations. However, the up graded technical grade, B_4C(II) contained a large proportion of second phase near one of the original surfaces of the hot pressed plate. The depth of this layer rich in second phase was approximately 0.150 inch. X-ray diffraction and metallography revealed that this second phase was graphite. Specimens 75003, 75004, 75005 and 75006 were taken from this graphite rich region. Presumably, the high graphite content causes the low bend strength, 29,000 psi of these specimens. The B_4C(II) material, Figure 14, has an average room temperature bend strength of 58,900 psi if the results obtained on the specimens from the graphite rich region are neglected. The B_4C(III), Figure 15, material has a slightly higher room temperature strength of 64,000 psi. The B_4C(II) maintains its strength up to 1350°C while the B_4C(III) exhibits a small decrease in strength when the test temperature is raised from 1200°C to 1350°C. Electron fractography indicated equal amounts of transgranular and intragranular fracture modes.

The fourth lot of hot pressed boron carbide contained two 6 inch square plates; these were designated B_4C(IVA) and B_4C(IVB). The microstructure of B_4C(IVA), Figure 16, indicates that more than one impurity phase is present. Impurity phases of boron nitride or graphite were indicated by X-ray diffraction. Chemical analysis revealed the presence of more than 1 w/o nitrogen (Table 3). The impurity phase content of this lot is much higher than in B_4C(II) and B_4C(III) and the bend strengths are lower. The average bend strengths of B_4C(IVA) and B_4C(IVB) were 30,500 psi and 39,500 psi respectively. Electron fractography of tested specimens revealed an almost entirely transgranular fracture mode, Figure 17. A second phase was observed as large islands in the grain boundaries. Microhardness values determined for the conventionally hot pressed materials are presented in Table 11. Symmetrical indents were difficult to obtain with the B_4C(IVB) material.

TABLE 11

MICROHARDNESS VALUES FOR CONVENTIONALLY HOT PRESSED BORON CARBIDE

Material	Specimen	No. of Readings	$KHN_{(200)}$	Standard Deviation
B_4C(IA) (B/C = 3.66)	74006	5	3000	± 100
B_4C(II) (B/C = 3.71)	75001	5	2931	± 80
B_4C(IVB) (B/C = 3.72)	77037	5	3020	± 200

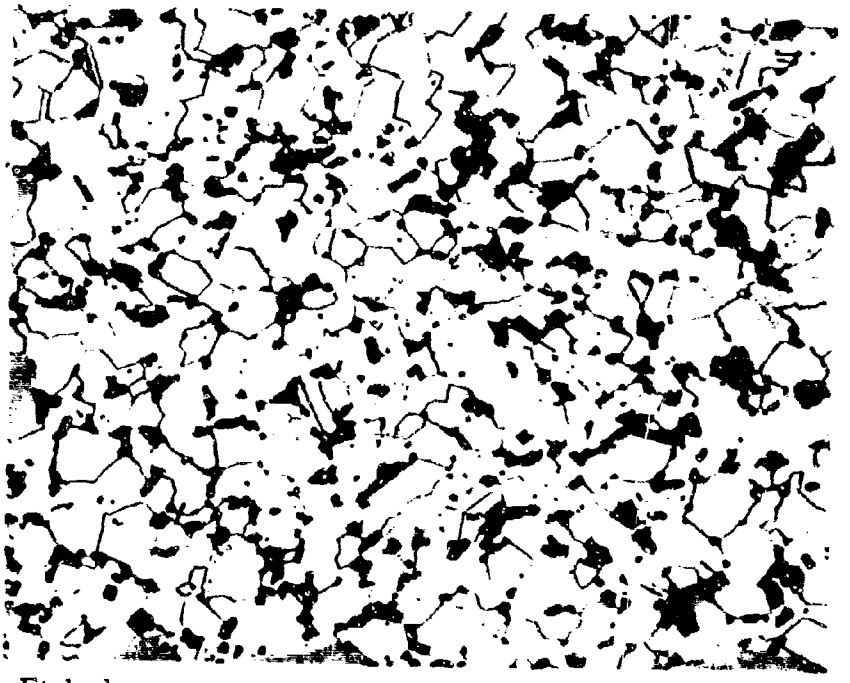


Plate No.
7739

Etched

500X

NOTE:

Specimen No.: 75001
Hardness: KHN (200 grams) = 3120 kg/mm^2
Etchant: 5% KOH (electrolytically)
Grain Size: 17μ
B/C Ratio: 3.71

Figure 14. Light Micrograph of Conventionally Hot Pressed Boron Carbide Supplied by AMRA, Up Graded Technical Grade, B_4C(II).

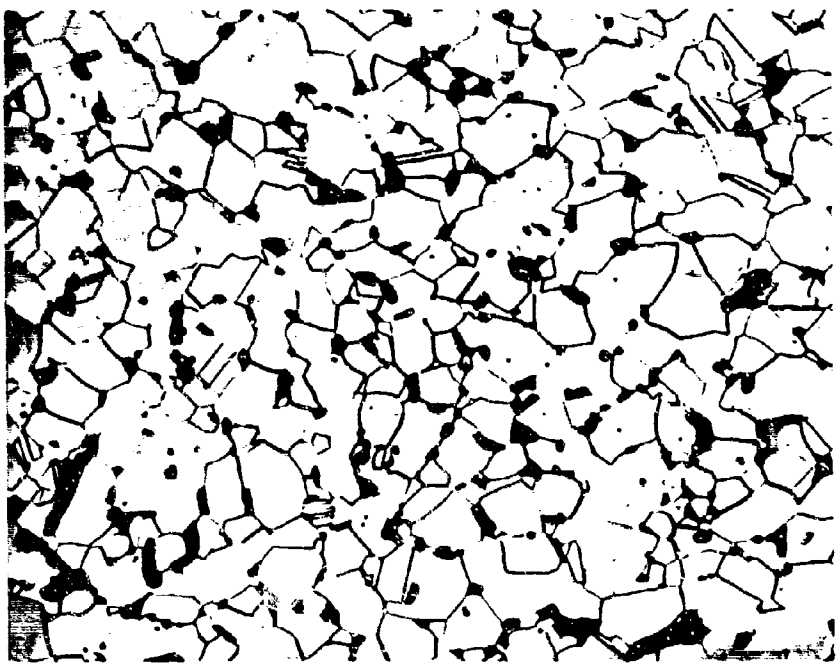


Plate No.
7741

Etched 500X

NOTE:

Specimen No.: 76003
Hardness: KHN (200 grams) = 3177 kg/mm^2
Etchant: 5% KOH (electrolytically)
Grain Size: 18μ
B/C Ratio: 3.81

Figure 15. Light Micrograph of Conventionally Hot Pressed Boron Carbide Supplied by AMRA, High Purity Grade B_4C(III).

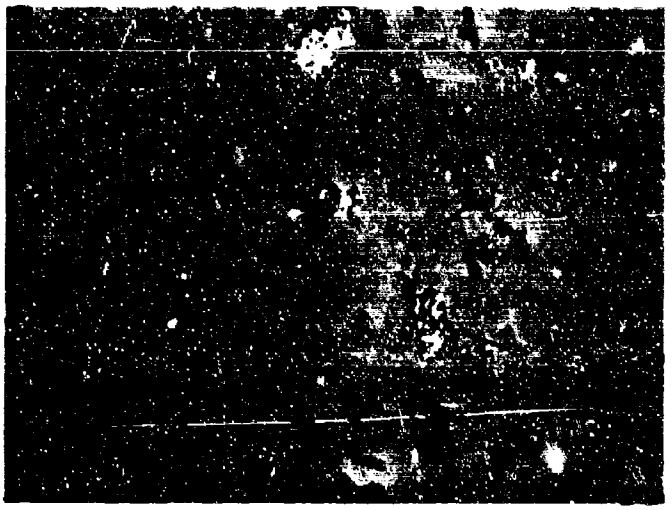


Plate No.
7949

As Polished 500X

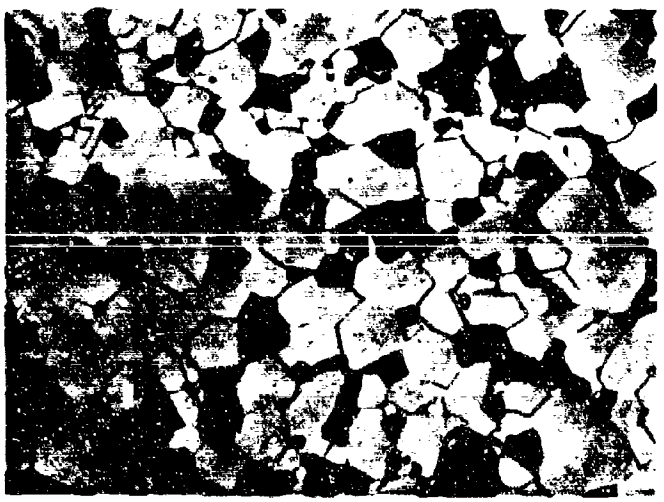


Plate No.
7896

Etched 500X

NOTE:

Specimen No.: 77009A
Hardness: KHN (200 grams) = 2980
Etchant: 5% KOH (electrolytically)
Grain Size: 20μ
B/C Ratio: 3.70

Figure 16. Microstructure of Conventionally Hot Pressed Boron Carbide Supplied by AMRA, B_4C(IVA).

Plate No. 3665A

6500X

Plate No. 3665D

6500X

Plate No. 3659A

6500X

Figure 17. Electron Fractography of B_4C(IVA).

The microhardness results show that the hardness of the boron carbide matrix is not related to the bend strength of the entire body (which contains boron carbide plus impurity phases). This lack of correlation of bend strength and microhardness was also found for the high pressure hot pressed material. In the case of the conventionally hot pressed boron carbide, the fracture initiation process and consequently the bend strength appears to be controlled by the presence of impurity phases, principally graphite. The microhardness of the conventionally hot pressed materials, plotted in (Figure 9) is comparable to HPHP boron carbide with a similar B/C ratio of 3.7.

The effect of extremes in microstructure on the mechanical properties of boron carbide are demonstrated by B_4C(IA) and B_4C(IVB). The bend strength, modulus of elasticity and microhardness of these materials are compared in Table 12. Although the microstructures were quite different, the chemistry and microhardness are similar. The lower strength and elastic modulus of B_4C(IVB) is attributed to the high second phase content.

TABLE 12

COMPARISON OF MICROSTRUCTURE AND MECHANICAL PROPERTIES FOR TWO CONVENTIONALLY HOT PRESSED BORON CARBIDE MATERIALS

Material	Grain Size	Second Phase Vol. %	Microhardness KHN_{200}	Bend Strength psi	Modulus of Elasticity psi
B_4C(IA) (B/C = 3.66)	13μ	11	3000	54,500	52.5×10^6
B_4(IVB) (B/C = 3.72)	23μ	35	3020	39,500	34.5×10^6

B. Silicon Carbide

1. High Pressure Hot Pressed

Silicon carbide powder, SiC(3), was initially high pressure hot pressed at 100,000 psi and 1800°C for 10 minutes. These fabrication conditions yielded billets 0.4 inch diameter x 0.9 inch long with no apparent defects. The microstructure of this material, Figure 18, is virtually free of elemental silicon. A small amount of porosity or holes produced by second phase pull out during polishing is observed. Inspection of the ends of the compacts revealed regions of high porosity. The highest porosity zone was associated with the end of the compact which was at the top of the high pressure cell. The top end of the high pressure cell contains the moveable piston which could act as a large heatsink

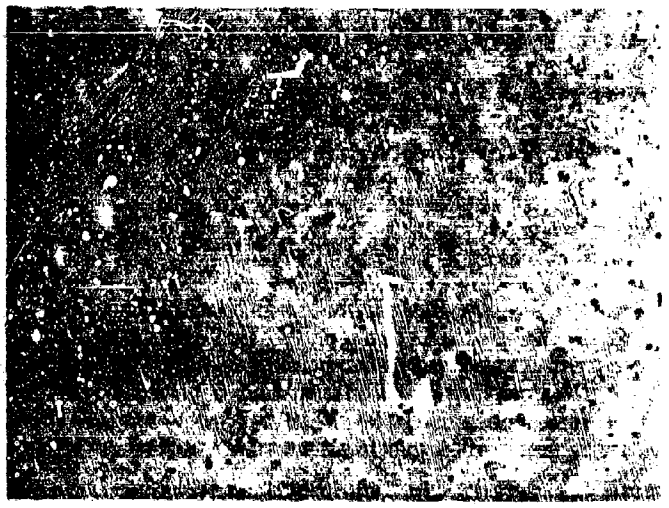


Plate No.
7486

As Polished (a) 500X

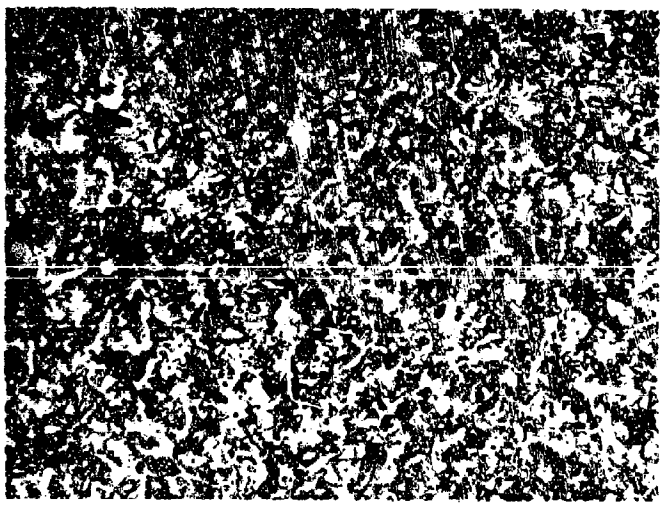


Plate No.
7585

Etched (b) 500X

NOTE:

Specimen No.: 66205
Fabrication Conditions: 1800°C, 100,000 psi, 10 min.
Hardness: KHN (200 grams) = 2826
Grain Size:
Etchant: 20% potassium hydroxide (electrolytically)

Figure 18. Light Micrographs of High Pressure Hot Pressed Silicon Carbide.

and thereby prevent that end of the compact from reaching the fabrication temperature. Temperatures of up to 1900°C and higher fabricating pressures (150,000 to 250,000 psi) were employed in efforts to reduce the region of high porosity. Compacts fabricated at 250,000 psi were fractured into at least 5 sections. Compacts fabricated at 150,000 psi contained numerous circumferential cracks, although the compact was whole. In both cases, the region of high porosity was not significantly reduced. The fabrication conditions selected for the SiC(3) powder were 1900°C and 100,000 psi for ten minutes. Metallographic examination showed that these latter compacts were dense and crack free over most of their length and that a high porosity region occurred at one end of the billet. Bend specimens could not be obtained from material densification fabricated this way because such specimens would leave this region of higher porosity at one end and a fully dense region at the other end.

2. Scale Up of Billet Size in High Pressure Hot Pressing

Silicon carbide powder, SiC(3), was high pressure hot pressed in System 2. Billets produced in this apparatus were 1 inch diameter x 1 inch long. Such a billet is shown in Figure 19. The microstructure at the center of this billet indicated that almost complete densification occurred, however, metallographic examination of other sections showed a radial variation in density. Additional experiments at higher temperatures and longer times did not produce complete non-porous densification. It should be noted that the cold compacts for System 2 fabrications could not be degassed in presently available facilities. Previous experience in our laboratory indicated that fully dense crack free billets could not be produced without degassing. Thus, these experiments served only to show the feasibility of scaling up the high pressure hot pressing operation. However, fully dense or uniformly dense billets could not be obtained. Modification of the high pressure apparatus to allow higher fabrication temperatures, that is greater than 1900°C, a more favorable height to diameter ratio and a reduction in end heat losses and introduction of a degassing procedure in System 2 would enhance the possibility of producing a uniformly dense, crack free billet.

3. Conventionally Fabricated Silicon Carbide

Two types of conventionally fabricated SiC were procured for evaluation in this program. The first type was "KT" SiC obtained from the Carborundum Company. This material, designated SiC(I), contains free Si and graphite and the porosity is very low as shown in Figure 20a. Etching a second lot of material was provided by Avco/RAD in the form of a hot pressed billet. This material, designated SiC(II), contains considerably less free silicon than the SiC(I). The microstructure of the SiC(II), Figure 21a, appears to show some porosity. The etched microstructure of this material, Figure 21b, reveals an extremely fine grain size. The matrix phases for both hot pressed materials have comparable microhardness. Bend strengths for the "KT" SiC and the Avco SiC are presented in Table 13. The SiC(I) has an average bend strength of 39,000 psi at room temperature and 35,600 psi at 1000°C. The SiC(II) has a similar room temperature bend strength, 39,000 psi. Modulus of elasticity measurements obtained on three of the SiC(I) specimens gave an average determination of 47.9×10^6 psi.

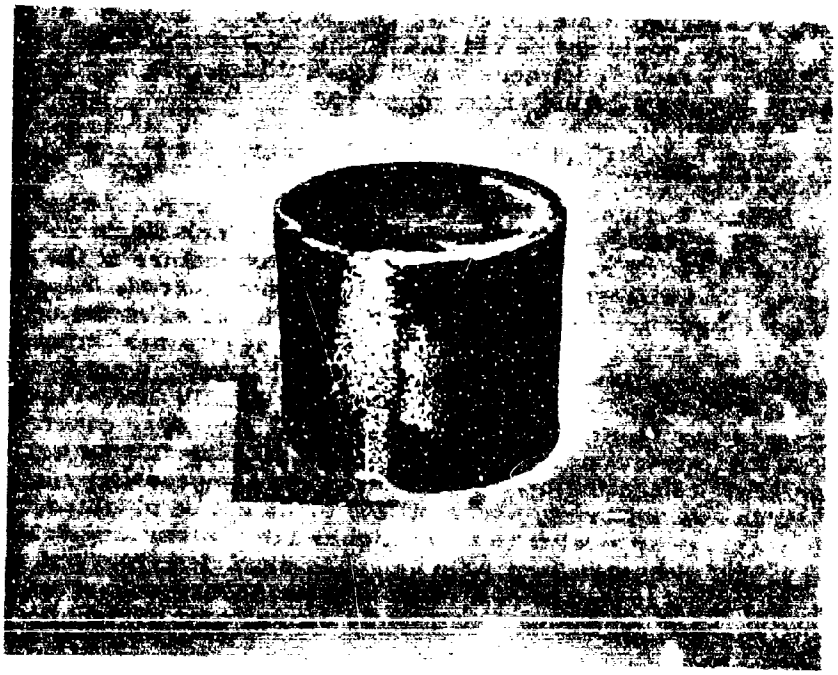


Plate No.
7493

Specimen No.: 67015
Fabrication: 1790°C, 10 min. 135,000 psi

Figure 19. Macrophotograph of Silicon Carbide Fabricated in High Pressure Hot Pressing, System 2.

Plate No.
7492

As Polished (a) 500X

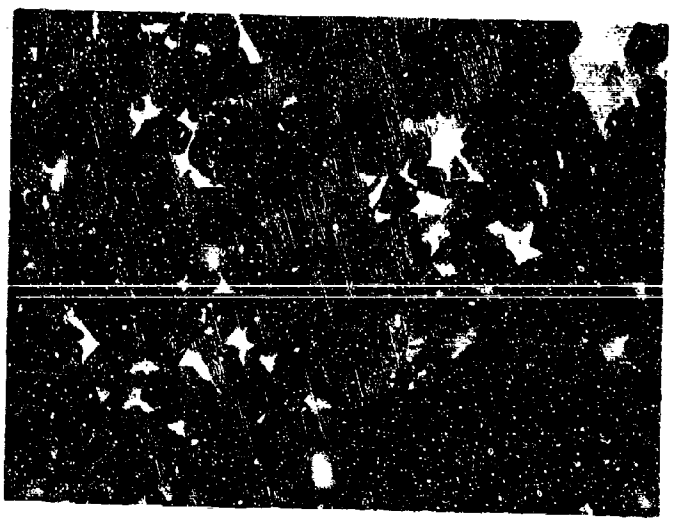


Plate No.
7616

Etched (b) 500X

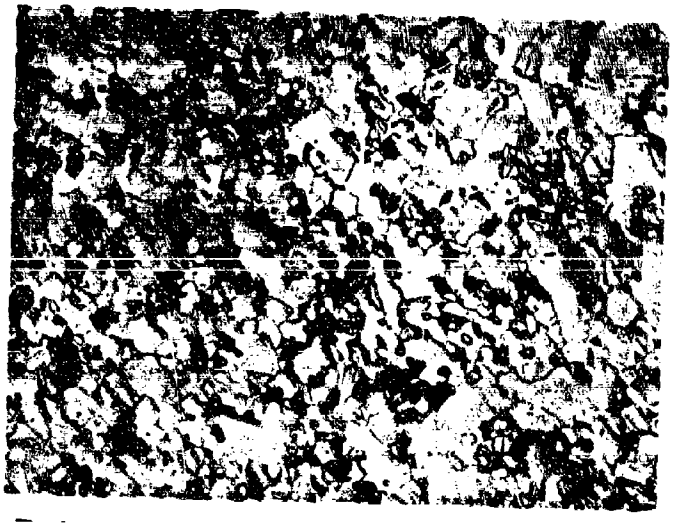
NOTE:

Specimen No.: 67000
Hardness: KHN (200 grams) = 2800 kg/mm^2 (matrix)
KHN (200 grams) = kg/mm^2 (light phase)
Etchant: 20% potassium hydroxide (electrolytically)

Figure 20. Light Micrographs of "KT" Silicon Carbide Supplied by Carborundum Company, SiC(I).

As Polished (a) 500X

Plate No. 7489



Etched (b) 500X

Plate No. 7584

NOTE:

Specimen No.: 69001
Hardness: KHN (200 grams) = 2850 kg/mm^2
Etchant: 20% potassium hydroxide (electrolytically)

Figure 21. Light Micrographs of Hot Pressed Silicon Carbide Supplied by Avco, SiC(II).

TABLE 13

TRANSVERSE BEND STRENGTH OF CONVENTIONALLY HOT PRESSED SILICON CARBIDE

Material	Specimen No.	Test Temperature °C	Strength psi	Modulus of Elasticity 10^6 psi
SiC(I)	67001	25	38,800	
Carborundum	67002	25	35,000	
Material	67006	25	44,300	
	67008	25	31,200	
	67080	25	39,200	48.2
	67081	25	37,000	47.5
	67082	25	41,200	48.1
	67010	1000	31,800*	
	67011	1000	37,500*	
SiC(II)	69002	25	26,000	
Avco	69003	25	40,400	
Material	69004	25	36,000	
	69005	25	46,300	
	69006	25	46,500	

*Proof tested at 25°C to a stress of 25,000 psi.

C. Titanium Carbide

1. High Pressure Hot Pressed Material

Titanium carbide powder was high pressure hot pressed at 1800°C and 100,000 psi for 10 minutes, into dense crack free billets 0.4 inch diameter x 0.9 inch high. The microstructure of this material, Figure 22, shows equiaxed grains, approximately 16 microns in diameter and a small amount of second phase. In the early part of this program, the fabricated compacts of this material were sectioned by electrical discharge machining (EDM) and finish ground to provide mechanical test specimens. Ten bend tests at 25°C gave an average strength of 33,900 psi, Table 14. Two tests at 1000°C showed that the bend strength was maintained; the average strength was 35,000 psi. One test at 1390°C gave a dramatic drop in strength to 38,000 psi. The elevated temperature test specimens were proof tested at 25°C and 25,000 psi. Metallographic examination of the fractured bars disclosed that fine transverse cracks developed when specimens were machined by the electrical discharge method. Sixteen bend specimens prepared by diamond cutting and grinding gave an average strength of 64,800 psi at 25°C, Table 15, thus the specimens machined only with diamond tools showed an increase in bend strength of better than 90 per cent over those cut by EDM. The data in Table 15 also shows that fabrication pressure has little or no effect upon the strength of nearly fully dense titanium carbide. In view of these results it was presumed that localized heating during the EDM process caused microcrack formation and an accompanying loss of strength. Chronologically, TiC was the first material studied. Therefore all additional bend test specimens in this program were machined and ground using diamond cutting and grinding tools.

Knoop hardness values of HPHP TiC were obtained as a function of indentations load and are presented in Figure 23. The microhardness depends upon the indentation load. A load of 50 grams gave a hardness of 3400 kg/mm^2. Increasing the indentor load to 500 grams reduces the measured microhardness to about 2100 kg/mm^2. It is evident that reference to a microhardness value must be accompanied by a specific indentor load in order to compare numbers obtained in different investigations.

The grain size of titanium carbide was determined as a function of distance along the length of the high pressure hot pressed billet; the results are summarized in Figure 24. The grain size is smallest at the ends with a maximum occurring at approximately 3/5 the distance from the top of the billet. This variation is probably due to uneven temperature distribution along the length of the compact. (Indications of such an uneven temperature profile were discussed in the section on HPHP SiC.) A more favorable height to diameter ratio in the fabrication was found to reduce both the grain size variation and the over-all grain size to 8μ, Figure 25.

Two additional billets of TiC were prepared by high pressure hot pressing at 110,000 psi and 1800°C for 10 minutes. These billets were machined into 4 bend test specimens using diamond cutting procedures after receiving a post fabrication vacuum treating treatment at 1500°C for one hour.

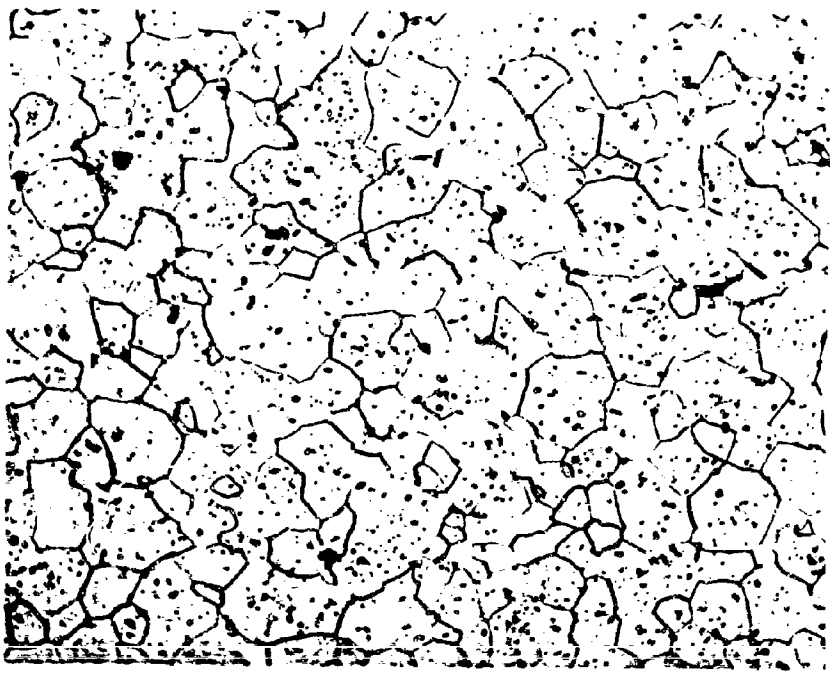


Plate No.
7468

Etched 500X

NOTE:

Specimen No.: 62187
Fabrication Conditions: 1800°C, 110,000 psi, 10 min.
Hardness: KHN (200 grams) = 2850 kg/mm^2
Etchant: 10 ml. HNO_3 + 10 ml. glycerine + 2 dps. HF

Figure 22. Light Micrograph of High Pressure Hot Pressed Titanium Carbide.

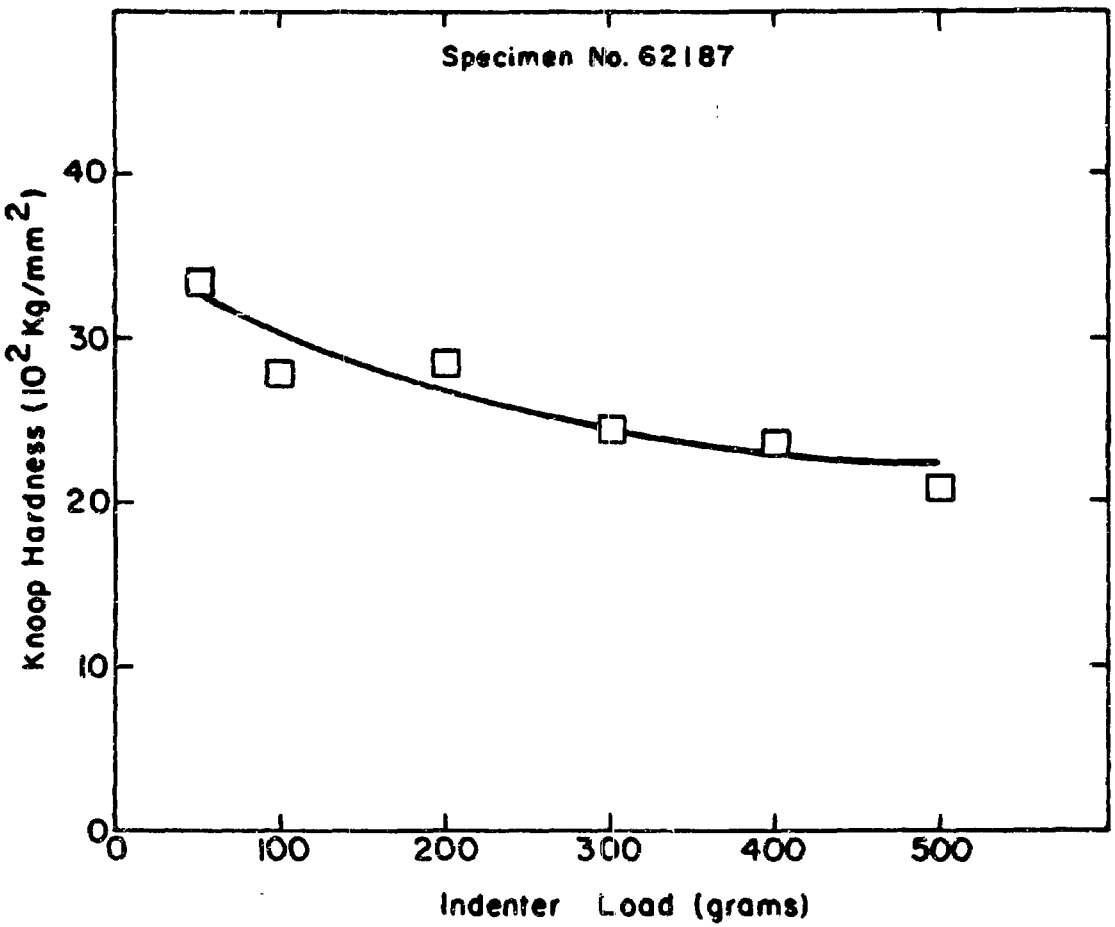


Figure 23. Knoop Hardness vs. Load for High Pressure Hot Pressed Titanium Carbide.

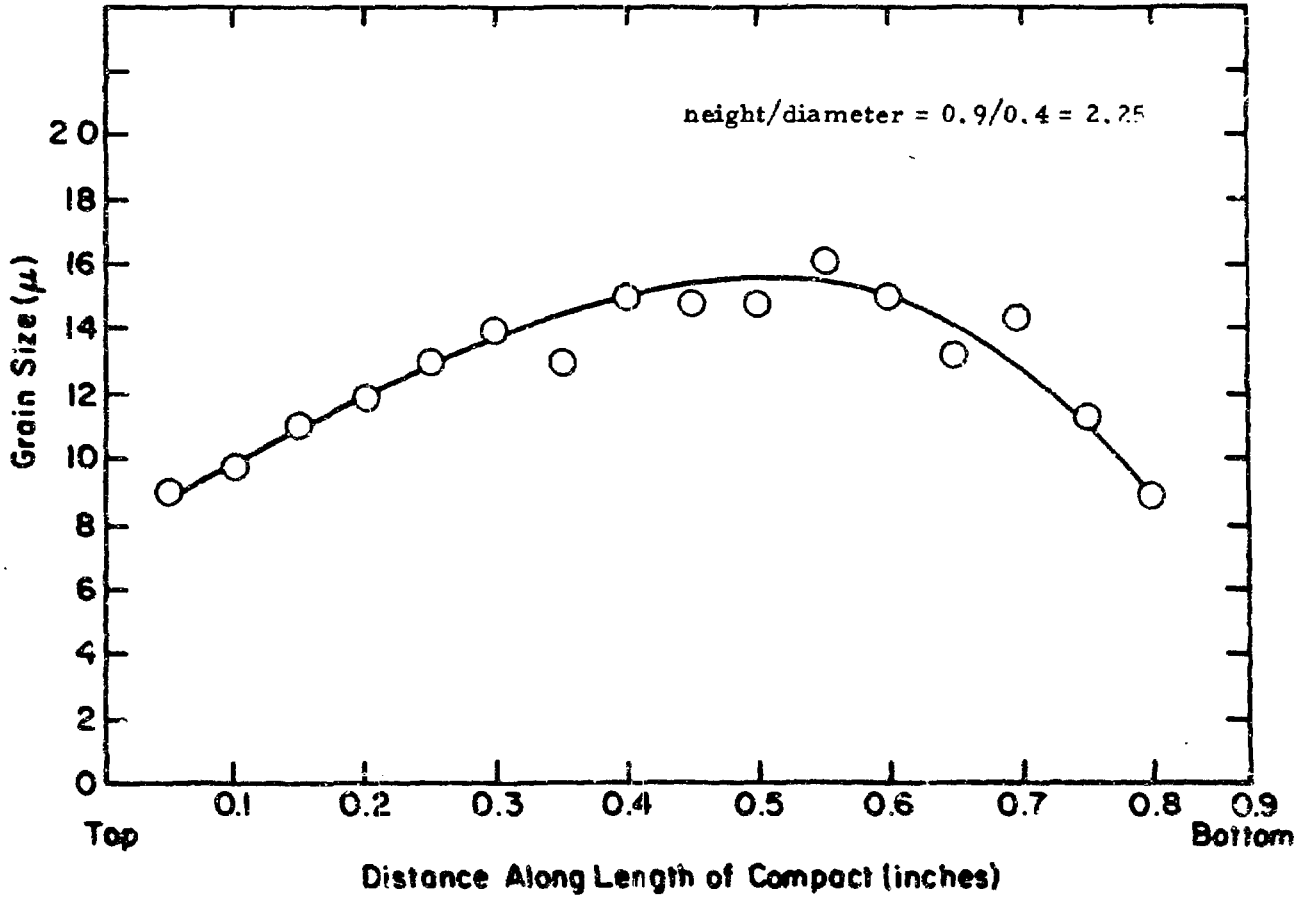


Figure 24. Grain Size Variation Along the Length of a High Pressure Hot Pressed (System 1) TiC Billet.

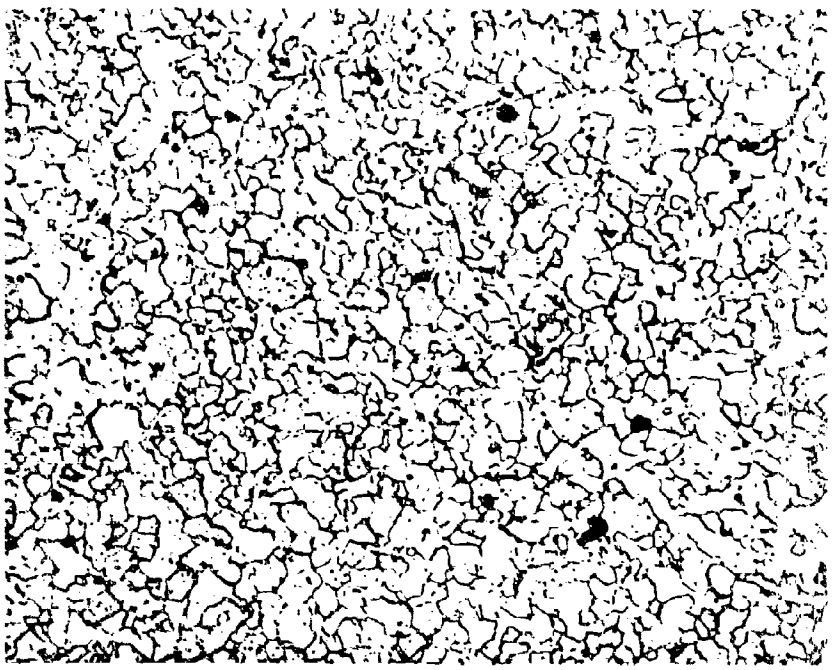


Plate No.
8179

Etched 500X

NOTE:

Specimen No.: 62417
Fabrication Conditions: 1800°C, 130 x 10^3 psi, 10 min.
Etchant: 10 ml. HNO_3 + 10 ml. glycerine + 2 dps. HF
Grain Size: 8μ
Compact Size: 0.4 inch diameter x 0.4 inch long

Figure 25. Light Micrograph of High Pressure Hot Pressed Titanium Carbide, Fabricated in System 1 with h/d = 1.

TABLE 14

TRANSVERSE BEND STRENGTH OF TITANIUM CARBIDE SPECIMENS PREPARED BY ELECTRICAL DISCHARCE MACHINING

Specimen No.*	Density gm/cm^3	Bend Strength psi	Test Temperature °C
40016A	4.80	46,200	25
62208B	4.80	46,200	25
62209A	4.89	Broke in EDM	
62209B	4.89	Broke in EDM	
62215B	5.00	46,100	25
62216A	4.90	22,600	25
62216B	4.90	26,900	25
62284A	5.04	83,800	25
62322A		53,000	25
62322B		10,000	25
62323A		25,800	25
62323B		28,600	25
62208A	4.80	42,000	1000**
62284B	4.80	28,000	1000**
62215A	5.00	3,800	1390**

*Fabricated at 1800°C, 110,000 psi, 10 min.

**Proof tested at 25°C to a stress of 25,000 psi.

TABLE 15

TRANSVERSE BEND STRENGTH AT 25°C OF TITANIUM CARBIDE SPECIMENS PREPARED BY DIAMOND MACHINING

Specimen No.	Fabrication Pressure* psi	Bend Strength psi	Density g/cm^3
62363A	60,000	73,500	4.87
62363B	60,000	83,000	4.87
62416A	60,000	58,700	
62416B	60,000	54,600	
62330A	110,000	62,300	
62330B	110,000	75,000	
62331A	110,000	64,100	
62331B	110,000	61,900	
62359A	100,000	84,000	4.88
62359B	100,000	82,000	4.88
62253A	100,000	30,000	
62253B	100,000	70,000	
62442A	100,000	60,200	
62442B	100,000	65,700	
62360A	235,000	53,500	4.87
62360B	235,000	58,000	4.87

*Fabrication conditions 1800°C, 10 min.

The bend test results are given in Table 16. Three of the four specimens broke below 50,000 psi while only one of the previous 16 specimens obtained from billets which were not subjected to post fabrication heating, Table 15, failed below 50,000 psi. These results showed that no benefit was derived from the heating conditions and in fact, post fabrication heating at 1500°C can be detrimental to the strength at room temperature. This conclusion could be qualified by the introduction of improved degassing procedures which coupled with post heating at 1500°C or possibly higher could lead to improved mechanical property behavior.

TABLE 16

TRANSVERSE BEND STRENGTH AT 25°C OF TITANIUM CARBIDE HEATED IN VACUUM AT 1500°C (1 HOUR)

Specimen No.*	Density gm/cm^3	Bend Strength psi
62415A	4.90	78,000
62415B	4.90	41,000
62385A	4.87	1?,000
62385B	4.87	20,000

*Fabrication conditions 1800°C, 110,000 psi, 10 min. Diamond machining of specimens.

However, more billets would have to be annealed at various temperatures to confirm the apparent harmful influence of annealing.

The modulus of elasticity was measured during several of the bend tests; the results are listed in Table 17. The average elastic modulus of high purity polycrystalline TiC was found to be 52.3 x 10^6 psi.

TABLE 17

MODULUS OF ELASTICITY AT 25°C OF HIGH PRESSURE HOT PRESSED TITANIUM CARBIDE

Specimen No.	Elastic Modulus 10^6 psi
62416A	49.7
62416B	49.5
62253A	52.8
62253B	52.4
62442A	59.0
62442B	50.7
Average	52.3 x 10^6 psi

2. Scale Up of High Pressure Hot Pressing

Titanium carbide was high pressure hot pressed in System 2 with a compact height of 0.5 inch. The light micrograph, Figure 26, of this material shows a fine grained structure containing a relatively high, uniformly distributed amount of porosity. The high porosity prevented obtaining bend test specimens. This compact could not be degassed prior to fabrication.

In summary, the feasibility of fabricating fully dense fine grained high purity titanium carbide was successfully demonstrated. Material with an average bend strength at 25°C of 64,800 psi was prepared. The billet size was scaled up from 0.4 to 1.0 inch diameter. Several factors in the fabrication and specimen preparation procedure were studied in order to achieve uniform structure and consistent properties.

D. Titanium Nitride

Titanium nitride powder, TiN(2), was high pressure hot pressed into dense billets, 0.4 inch diameter x 0.9 inch long. The fabricated material contains two phases, identified by X-ray diffraction as TiN and Ti metal. The fabrication produced a high density material with evidence of recrystallization and grain growth; the fabricated material is characterized by an equiaxed grain size of approximately 48μ, Figure 27. Such processes as recrystallization and grain growth would be expected of a sodium chloride type structure fabricated under the conditions temperature and pressure employed in this study. A very mildly etched microstructure of the TiN matrix which shows the second phase but not the twin structure, is provided in Figure 28. The more potent etch required to reveal the TiN grain boundaries and twins, severely attacks and

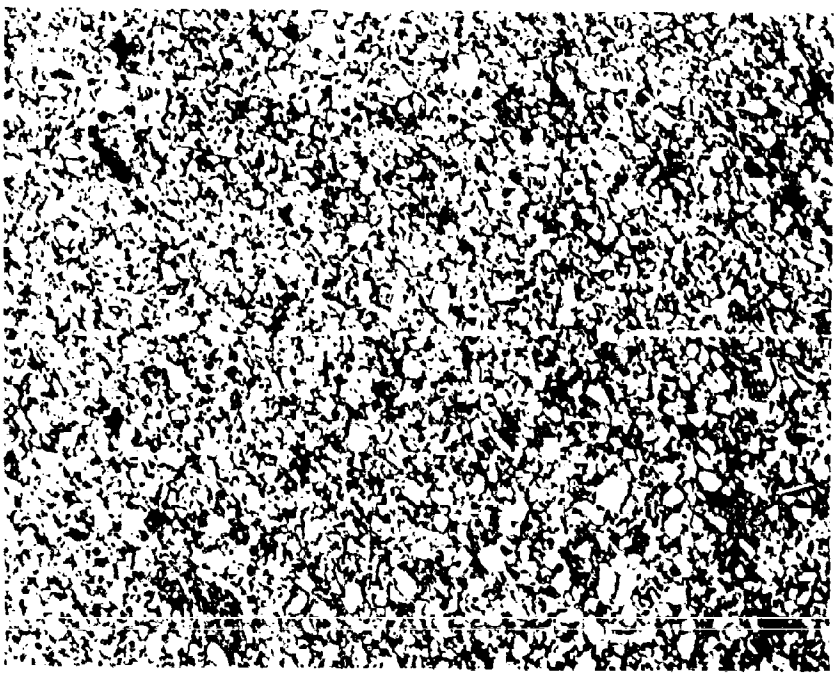


Plate No. 7620

Etched 500X

NOTE:

Specimen No.: 63016
Fabrication Conditions: 1800°C, 10 min., 110,000 psi
Etchant: 10 ml. HNO_3 + 10 ml. glycerine + 2 dps. HF
Grain Size: 4μ

Figure 26. Light Micrograph of High Pressure Hot Pressed Titanium Carbide Fabricated in System 2.

Plate No.
7465

Etched 500X

NOTE:

Specimen No.: 60185
Hardness: KHN (200 grams) matrix phase: 1852 kg/mm^2
second phase (grey): too soft to measure
Etchant: 10 ml. HNO_3 + 10 ml. glycerine + 2 dps. HF

Figure 27. Light Micrograph of High Pressure Hot Pressed Titanium Nitride with Conventional Etch.

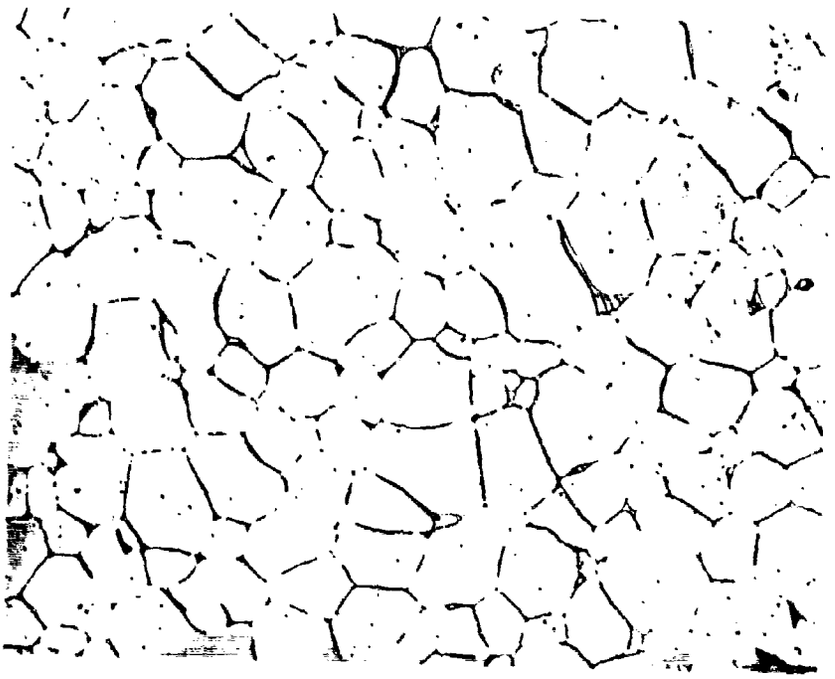


Plate No.
8011

Etched

500X

NOTE:

Specimen No.: 60371
Fabrication Conditions: 1800°C, 100,000 psi, 10 min.
Hardness: KHN (200 grams) = 1720 kg/mm^2
Etchant: 10cc Lactic acid + 10cc nitric acid, 3 dps. hydrofluoric acid
Grain Size: 48μ

Figure 28. Light Micrograph of Matrix of High Pressure Hot Pressed Titanium Nitride with a Mild Etch.

obliterates the second phase (Figure 27). The photomicrograph in Figure 29 shows a lightly etched area rich in the second phase. This structure was revealed with a titanium metal etching solution. Knoop hardness values of the matrix material determined as a function of load, Figure 30, do not show any appreciable change at loads above 200 grams. The hardness values for each phase are given with their respective photomicrograph; for comparison purposes, the matrix has a hardness of approximately 1800 kg/mm^2 while the second phase has a hardness of about 800 kg/mm^2.

Attempts to slice the HPHP billets by electrical discharge machining proved difficult and produced deep craters and cracks of the samples. Smaller size samples of TiN were easily and efficiently cut by EDM techniques, however, the long cuts (>0.8 inches) needed to obtain bend specimens were difficult to control, causing localized overheating and specimen cracking. This was similar to the problem experienced with TiC.

The fabrication of TiN(2) was carried out over a range of temperatures and pressures, Table 18. The fabrications which employed the lower pressures and high temperatures yielded crack free bars.

TABLE 18

FABRICATING CONDITIONS FOR TiN

Billet	Temp °C	Time min	Pressure 10^3 psi	Remarks
60308	1000	10	100	highly porous
60307	1500	10	100	cracked and porous
60300	1700	10	100	cracked and dense
60325	1800	10	100	cracked and dense
60344	1800	10	90	cracked and dense
60351	1800	10	80	cracked and dense
60338	1800	10	72	crack free and dense
60339	1800	10	68	crack free and dense

Bend specimens 60338A, 60338B and 60339A were tested at room temperature; the measured strengths were 21,000 psi, 20,000 psi and 16,500 psi respectively. Post test metallographic examination of these specimens showed fully dense microstructures containing a second phase. A variation in grain size was noted along the length of the compact, Figure 31. The smallest grain size was found to be at the top of the compact as it stands in the high pressure apparatus. The grain size increased to a maximum at approximately 3/5 the distance from the top. (Similar results were obtained for TiC and discussed in the previous section.)

Plate No.
7753

Etched 1000X

NOTE:

Specimen No.: 60280
Fabrication Conditions: 1800°C, 100,000 psi 10 min.
Hardness: Second phase KHN (200 grams) = 7 8 kg/mm^2
Etchant: 20cc water + 1 drp. hydrofluoric aci

Figure 29. Light Micrograph of High Pressure Hot Pressed Titanium Nitride with Selected Second Phase Etch.

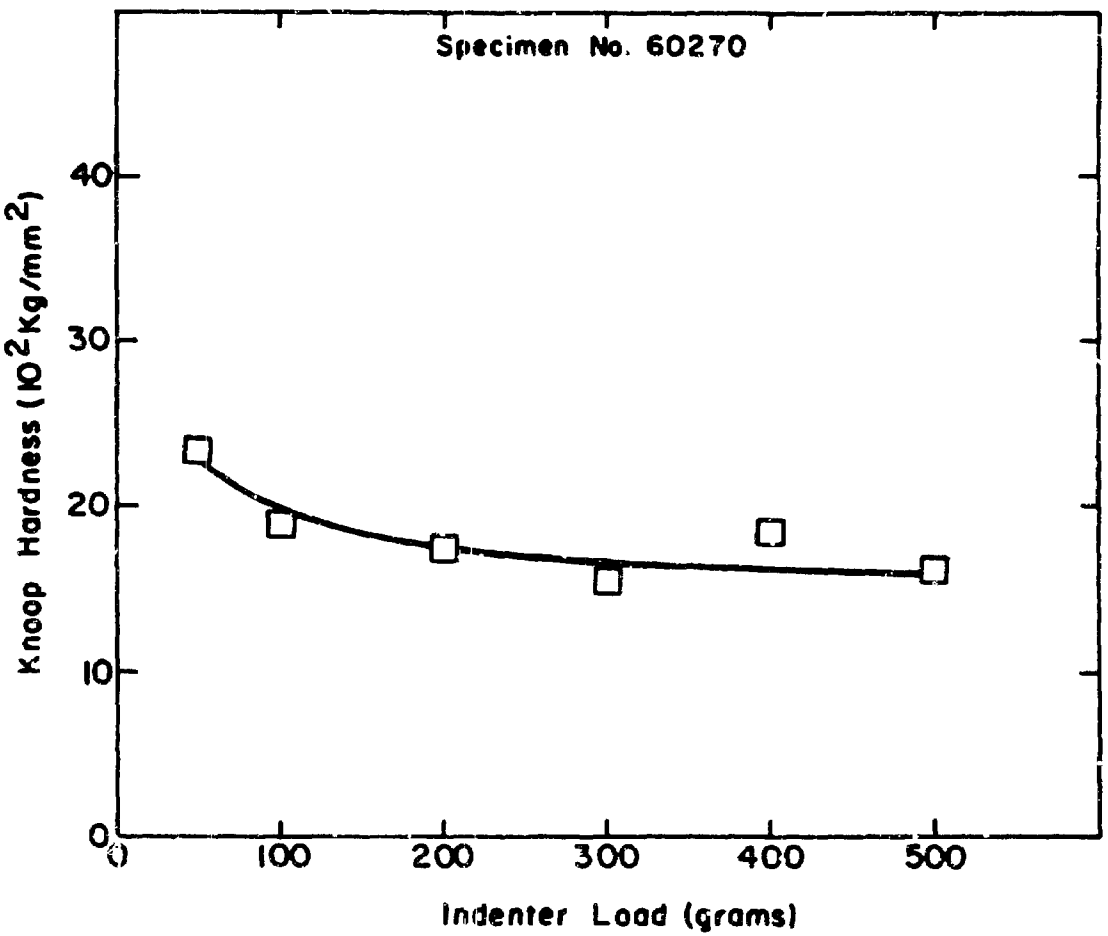


Figure 30. Knoop Hardness vs. Load for High Pressure Hot Pressed Titanium Nitride.

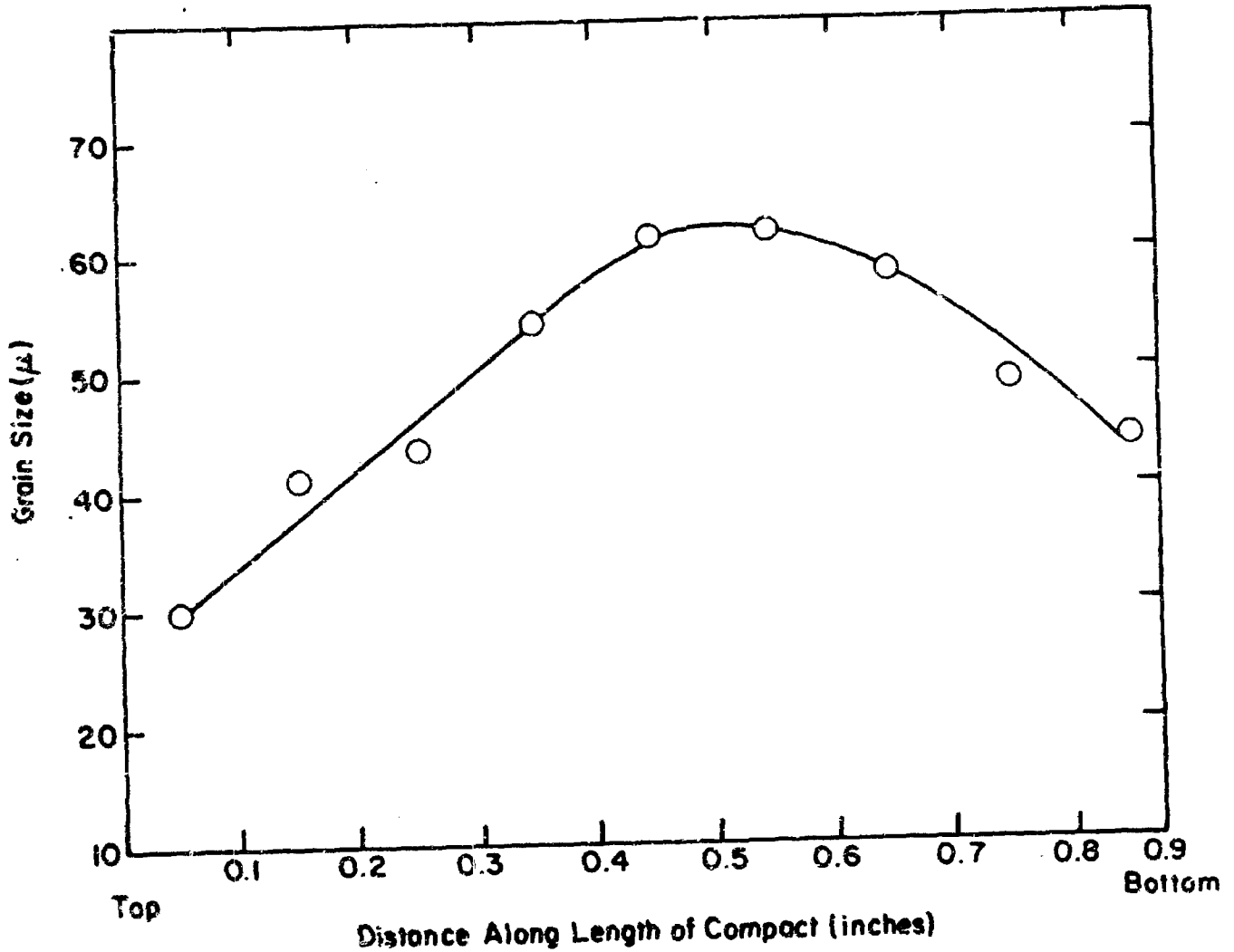


Figure 31. Grain Size Variations Along the Length of a High Pressure Hot Pressed TiN Compact.

The fracture surface of bend specimen 60338A showed predominatly transgranular fracture with many cleavage facets. In order to produce a more uniform cold compact, a lubricant was employed to reduce frictional stresses during loading and ejection of the compact from the die. Prior to loading, the die walls and piston surfaces were washed with a saturated solution of stearic acid in carbon tetrachloride. The influence of the lubricant was immediately noticeable. The pressure required to remove the compact from the die was reduced from 160,000 psi to 65,000 psi. The green density increased 22 per cent from 3.01 g/cc to 3.70 g/cc and the green compressive strength increased from 160 psi to 350 psi. The above experimental work was carried out only on TiN but the obvious advantage of employing a lubricant in cold compacting is applicable to all materials.

Titanium nitride was fabricated in System 2 with h/D = 1/2. The fabrication conditions were 1800°C for 10 minutes at 60,000 psi. The compacts were highly dense but contained cracks. Metallographic inspection of the high pressure cell parts revealed the lava liner was fired at high temperatures in confined areas. This would indicate that the graphite furnace was damaged during the run, causing "hot spots". As with the other materials, this size compact was not degassed prior to fabrication.

In summary, the feasibility of fabricating fully dense slightly metal rich titanium nitride was demonstrated. Evidence of recrystallization and grain growth strongly suggests that the microstructure and mechanical properties could be improved and controlled through the appropriate selection of fabrication temperatures and times. In addition, the frequency of cracking may be reduced or eliminated by fabricating at the low end of the high pressure regime (i.e., 60,000 psi) and by choosing a system with a more favorable height to diameter ratio. Introduction of degassing procedures could produce further improvement in the fabrication procedure.

IV. SUMMARY AND CONCLUSIONS

1. The feasibility of fabricating high relative density ceramics, free of metallic impurities, by high pressure hot pressing was demonstrated. Materials fabricated were boron carbide, silicon carbide, titanium carbide and titanium nitride. The difficulty of preparing fully dense materials increases from TiN to TiC to B_4C to SiC.

2. The optimum fabrication conditions for obtaining dense crack free billets involves fabrication pressures at the low end of the "high pressure regime", i.e., 60,000 psi and fabrication temperatures of at least 1800°C. (Fabrication time as a variable was not studied.) It is desirable to use a lubricant during cold compacting before fabrication. In addition, degassing the cold compact at a high temperature in vacuum, is absolutely necessary to achieve crack free billets that are mechanically stable to reheating.

3. The ability to scale up the high pressure hot pressing operation from a 0.4 inch diameter to a 1.0 inch diameter billet was demonstrated for all four materials studied.

4. The bend strength of conventionally hot pressed boron carbide is markedly effected by the presence of graphite as a second phase. Four lots of $_4C$ evaluated have average bend strengths that vary from 29,000 to 68,600 psi. In addition, the strength within one plate varies with location (and hence the amount of graphite) by a factor of two.

5. Boron carbide and boron metal powders were reactively hot pressed with a high pressure apparatus to yield a single phase nearly fully dense material free of graphite. This HPHP boron carbide has a bend strength of 57,600 psi at 25°C and an elastic modulus of 50. x 10^6 psi, independent of the B/C ratio in the absence of graphite.

6. The microhardness of the boron carbide matrix varies with the boron to carbon ratio. Conventionally hot pressed boron carbides, from several sources, have matrix microhardnesses of 3000 kg/mm^2 and B/C ratios near 3.7. Reactive HPHP can produce boron carbide with a B/C ratio up to 12. The microhardness of the matrix reaches a maximum of 3200 kg/mm^2 with a B/C of 5.0 to 5.2. Therefore, reactive HPHP may be utilized to give a higher matrix hardness and consistently high bend strengths through an increase in B/C ratio and an elimination of graphite as a second phase.

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13 ABSTRACT

High pressure hot pressing was used to prepare dense, crack free billets of boron carbide, silicon carbide, titanium carbide and titanium nitride. These materials were fabricated from high purity powders without the additions of densification promoters. Fabrications were generally performed in the vicinity of 1800°C at 120,000 psi for 10 minutes. Reactive high pressure hot pressing of boron carbide and elemental boron carbide was investigated with different atomic ratios of boron to carbon. Microstructures and mechanical property evaluations were obtained for selected materials prepared by this technique. The results obtained for high pressure hot pressed boron carbide and silicon carbide materials were compared with results of similar evaluation performed on conventionally fabricated samples of boron carbide and silicon carbide.

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