UNIVERSITY OF CALIFORNIA
DEPARTMENT OF MECHANICAL ENGINEERING
DAVIS, CALIFORNIA

**AN INVESTIGATION OF THE PARAMETERS
 INFLUENCING THE MICROSTRUCTURE
 OF HOT-PRESSED BORON CARBIDE**

**Progress Report
 November 1975**

Intramural Order 5749905

by

**Z. A. Munir, Principal Investigator
 G. R. Veerkamp, Graduate Research Assistant
 Department of Mechanical Engineering
 and the Materials and Devices Research Group
 University of California, Davis**

AN INVESTIGATION OF THE PARAMETERS
INFLUENCING THE MICROSTRUCTURE
OF HOT-PRESSED BORON CARBIDE

Progress Report

submitted to:
Inorganic Materials Division
Lawrence Livermore Laboratory

by

Z. A. Munir, Principal Investigator
G. R. Veerkamp, Graduate Research Assistant
Department of Mechanical Engineering
and the Materials and Devices Research Group
University of California
Davis, California

November, 1975

—NOTICE—
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

for

Abstract

An investigation was conducted to determine the influence of various parameters on the microstructure of hot-pressed boron carbide compacts. It was determined that a critical temperature (approximately 2200°C) was necessary to suppress exaggerated grain growth, and that exaggerated growth was also enhanced at higher pressures within the pressure range investigated. Microhardness examinations and twin density analyses were also performed, both of which demonstrated a primary dependence on grain size, with a secondary dependence occurring between microhardness and pressure and twin density and temperature.

Fracture analysis indicated a mixed intergranular-transgranular fracture mode, with transgranular fracture predominating at smaller grain sizes. Also, observed bend strengths of fracture specimens are in reasonable agreement with reported values.

Electron microprobe scanning was performed on B_4C , $B_4C + AlF_3$, and $B_4C + MgF_2$. The results indicated a solubility of Al and Mg in the lattice. X-ray analysis was also conducted on $B_4C + 10\%AlF_3$ specimens, and tended to confirm the formation of a $B_{12}C_2Al$ compound, which apparently assumes an expanded B_4C unit cell configuration.

Acknowledgements

Mr. Dean Ankeny and Dr. Gordon Smith provided valuable technical assistance. Discussions with Dr. J. Birch Holt provided continuous stimulus and encouragement. This work was supported by an Intramural Grant from the Lawrence Livermore Laboratory.

Table of Contents

	Page
Abstract	ii
Acknowledgements	iii
Table of Contents	iv
List of Figures	v
List of Tables	vii
Introduction	1
Procedure	7
Results	14
Discussion	55
Conclusions	61
References	62
Appendices	
Appendix A - Thermal histories of specimens investigated	64
Appendix B - Detail drawings of tool and die set used for rupture testing	79
Appendix C - Textronix 4010 programs used to plot data	81

List of Figures

	Page
Figure 1 Boron-Carbon equilibrium diagram of Elliott.	2
Figure 2 B_4C unit cell.	3
Figure 3 Particle size distribution of KBI powder.	9
Figure 4 Schematic of hot press interior.	10
Figure 5 Fracture apparatus.	13
Figure 6 Micrograph of B_4C pressed at 1000 psi and 2150°C.	16
Figure 7 Micrograph of B_4C pressed at 2000 psi and 2150°C.	16
Figure 8 Micrograph of B_4C pressed at 3000 psi and 2150°C.	17
Figure 9 Micrograph of B_4C pressed at 3000 psi and 2200°C.	18
Figure 10 Micrographs of B_4C pressed at 3000 psi and 2100°C.	19
Figure 11 Micrographs of B_4C pressed at 3000 psi and 2050°C.	20
Figure 12 Micrograph of $B_4C + 10\%AlF_3$ pressed at 3000 psi and 1950°C.	21
Figure 13 Micrograph of $B_4C + 10\%AlF_3$ pressed at 3000 psi and 1900°C.	21
Figure 14 Micrograph of $B_4C + 10\%MgF_2$ pressed at 3000 psi and 1900°C.	22
Figure 15 Micrograph of $B_4C + 10\%Ni$ pressed at 3000 psi and 1900°C.	22
Figure 16 Microhardness vs grain size at constant temperature and pressure.	24
Figure 17 Microhardness vs temperature at constant pressure.	25
Figure 18 Microhardness vs pressure at constant temperature.	26
Figure 19 Twin density vs temperature at constant pressure.	27
Figure 20 Twin density vs pressure at constant temperature.	28
Figure 21 Microstructure of pure B_4C rupture specimen.	30
Figure 22 Microstructure of 1% AlF_3 rupture specimen.	31
Figure 23 Microstructure of 10% AlF_3 rupture specimen.	31
Figure 24 Electron micrographs of the fracture surface of B_4C specimen showing intergranular fracture.	32
Figure 25 Inclusion in pure B_4C specimen.	33

List of Figures (continued)

	Page
Figure 26 Fracture surface of B_4C specimen showing transgranular fracture.	33
Figure 27 Electron micrographs of fracture surface of $B_4C + 1\%AlF_3$ showing predominantly transgranular fracture.	34
Figure 28 Scanning oscilloscope display of $B_4C + 10\%AlF_3$ specimen.	37
Figure 29 Scanning oscilloscope display of $B_4C + 10\%MgF_2$ specimen.	40
Figure 30 Scanning oscilloscope display of $B_4C + 10\%AlF_3$ fracture specimen.	43
Figure 31 Scanning oscilloscope display of $B_4C + 1\%AlF_3$ fracture specimen.	46
Figure 32 Scanning oscilloscope display of B_4C fracture specimen.	49
Figure 33 Diffractometer scan of B_4C specimen.	51
Figure 34 Diffractometer scan of $B_4C + 10\%AlF_3$ specimen.	53

List of Tables

	Page
Table 1 Selected Mechanical Properties of Boron Carbide at 25°C.	5
Table 2 Impurity Concentrations in KBI Powder.	8
Table 3 Specimen Pressing Parameters.	15
Table 4 Grain Size, Twin Density, and Microhardness of the Specimens Investigated.	23
Table 5 Rupture Strengths of B_4C , $B_4C + 1\%AlF_3$, and $B_4C + 10\%AlF_3$.	36

Introduction

Boron carbide, first synthesized by Moissan in 1899 by smelting a charge of boric anhydride with charcoal in an arc electric furnace,¹ is today the focus of numerous research attempts aimed at effectively utilizing its various attractive properties. After diamond and cubic boron nitride, which are both more expensive to produce, boron carbide is the hardest man-made material with a Mohs hardness of 9.5+.² In addition, its low density (2.52g/cm^3),³ high melting point (2450°C),² and large neutron capture cross-section (approximately 4000 barns),² make it an attractive material in connection with modern reactor technology.

The exact nature of the phase distribution in the boron-carbon system was not precisely determined until relatively recently. Moissan's early work had pointed to a formula of B_6C ¹ and Ridgway in 1934 concluded from his work that "the boron-carbon system consists of three phases: boron, a compound in the neighborhood of B_4C , and graphite."⁴ Various authors⁵⁻⁷ have since listed other possible compounds such as B_{13}C_2 , BC_2 and B_7C . One of these authors, Glaser,⁷ suggested that a solid solution range did indeed exist between 4 and 28 atomic % carbon. Finally, Elliott⁸ published an equilibrium diagram which was later confirmed by Kieffer et al.⁹ establishing the existence of a single carbide of composition B_4C having a solubility range of 9 to 20 atomic % carbon, with a melting temperature of 2450°C , as shown in Figure 1.

The crystal structure of boron carbide has been established^{10,11} as being rhombohedral and belonging to the space group $D_{3d}^5-\bar{R}3m$, with a lattice constant $a=5.19\text{\AA}$ and $\alpha=66^\circ 18'$. Figure 2 shows a schematic of a B_4C unit cell. In the course of their work on the structure of boron carbide, Clark and Hoard noted that when the B/C ratio was greater than 4, an expansion of the lattice occurred, and the excess boron could not be removed with aqua regia, a reagent commonly

Figure 1 - Boron-Carbon equilibrium diagram of Elliott.

Figure 2 - J_4C unit cell.

used to dissolve it, thus suggesting that boron formed a solid solution with boron carbide.¹¹ The mechanism later proposed by Zhdanov¹² for this solubility was the replacement of carbon atoms in the 1b position (Figure 2), with an upper limit corresponding to $B_{13}C_2$, a compound which, as Samsonov¹³ points out, is inclined to decompose to the stable $B_{12}C_3$ or B_4C structure via the reaction

Various authors have conducted investigations into the mechanical properties of B_4C .¹³⁻¹⁹ Table I lists a summary of these properties. Lack of microstructural uniformity of the test samples (e.g., compact density ranges from 82%¹⁴ to theoretical¹⁷ and impurity contents run between "unlisted"¹⁴ to 99.9% pure¹⁹), cast a degree of uncertainty on the significance of the reported data. The effect of microstructural variables such as porosity, grain size, purity, etc., on the behavior of any material is well documented. For instance, it was shown by Liebling¹⁷ that porosity had a strong influence on the values obtained for the Young and shear moduli of boron carbide. Young's modulus changes from 65×10^6 to 30×10^6 psi as the porosity increases from 0 to 9%, while the shear modulus decreases from approximately 30×10^6 to 20×10^6 psi over the same porosity range. Furthermore, the parameters of porosity, grain size, and impurity content are known to have a strong influence on the fracture strengths of ceramics. Various authors have investigated the dependence of fracture strength, σ_f , with grain size,²⁰ and have shown a $D^{-1/2}$ dependence, where D is the average grain size. Porosity is thought to have a similar effect in that pores can act as crack nucleation sites, thus decreasing the ultimate strength.²¹ Likewise, impurities can decrease σ_f by forming second phase particles which, as Lange²² demonstrated, will decrease strength as their size increases. It is thus quite obvious that an accurate characterization of these variables is imperative when attempting to assess the properties of a ceramic such as boron carbide.

TABLE 1: Selected Mechanical Properties of Boron Carbide at 25°C.

Property	Reported value	Reference
Bend Strength	$46.9 - 50.3 \times 10^3$ psi	(15)
Compressive Strength	25.5×10^4 psi	(13)
	40×10^4 psi	(16)
Young's Modulus	65×10^6 psi	(14,16)
	68×10^6 psi	(17)
Shear Modulus	27×10^6 psi	(14)
	29.85×10^6 psi	(17)
Bulk Modulus	37×10^6 psi	(14)
Poisson's Ratio	0.21	(14)
	0.14	(17)
Microhardness	3200 kg/mm ²	(16)
	4750 kg/mm ²	(18)

Although it is known that process variables such as temperature, pressure (in the case of hot pressing), and the presence of activators can influence the microstructure, and hence mechanical properties of sintered ceramics, little work has been performed in this area in connection with B_4C . The few results provided by Stibbs et al.,²³ Dzhencinskii et al.,²⁴ and Dutta²⁵ are incomplete. Stibbs and coworkers demonstrated that additions of up to 10% of Al, Mg, or a metallic boride (e.g., TiB_2) to B_4C gave sintered bodies with 99+% theoretical density at 2150-2250°C. Likewise, Dzhencinskii et al. sintered B_4C by adding up to 10% Ti and obtained dense bodies (97+% theoretical density) which reportedly possessed decreased brittleness. Since the major disadvantage of boron carbide is its extreme brittleness, this observation is most interesting. Dutta has published results of hot pressing B_4C using additives of iron with sodium silicate and magnesium in an attempt to lower pressing temperature and to increase densification. His results indicated that a 98.4% density was achievable when pressing was performed at 1750°C and 3500 psi.

It should be noted that the work of Prochazka and Smith²⁶ with SiC shed additional light on the importance of sintering parameters. Hot pressing and sintering of SiC using activators (to control microstructure) was performed in an attempt to produce the highest strength possible. This they were able to do using Si_3N_4 or BN additives to keep grain size small and density high. It was also noted that in the presence of minor impurities of boron and carbon (approximately 0.5% each), temperature and time of exposure must be controlled precisely to prevent exaggerated grain growth. The importance of these results, both in terms of controlling grain growth and porosity, and the degree to which sintering parameters influenced them, are substantial and provide the motivation for a similar study with B_4C .

The present investigation was concerned with determining the effect of temperature, pressure, and activators on the microstructure of hotpressed boron carbide. The overall objective is to decrease brittleness, and to reduce sintering time and temperature.

Procedure

A. Powder Characterization and Specimen Preparation

The powders used in the present investigation were high purity KBI* blends. To determine impurity levels, X-ray fluorescence and spectrochemical analyses were both conducted and the results of which are presented in Table 2. A separate analysis yielded B and C concentrations of 79.75 and 19.34%, respectively. In addition, a particle size characterization was performed, with the results presented in Figure 3.

No ball milling was performed prior to pressing except for samples which were to be used for fracture analysis. In that case, milling was conducted using 2.5 liters of reagent-grade toluene and B_4C chips fabricated from KBI powder. Milling lasted 18 hours for the samples with 10% AlF_3 addition, and 24 hours for those with 1% AlF_3 . In each instance, a weight loss of 22g from the chips used for milling occurred. Milled powder was subsequently filtered and vacuum dried at 120°C before pressing.

All powder blends were filtered through a 12 mesh nylon screen to remove agglomerates. Specimens were then briefly cold pressed at 3000 psi to provide initial densification. Final densification was achieved with a 3" hot press fitted with ATJ grade graphite dies, as shown in Figure 4. Die walls were wrapped with 4 layers of Union Carbide "Grafoil" (grade GTA, 0.015" thick) for protection, with two layers provided for ram faces.

All pressings were performed in an argon atmosphere. Temperatures were recorded with an optical pyrometer accurate to within $\pm 2^\circ C$. Specimen heat-up rates were not conducted uniformly between runs; thermal histories recorded for all runs are listed in Appendix A. Once temperature was attained, constants T and P were maintained until the observed ram travel was zero, in that

*Kawecki Berylco Industries Inc., P.O. Box 429, Hazelton, Penn. 18201.

Table 2: Impurity concentrations in KBI powder.

Impurity	Concentration (ppm)
Fe	200
Al	80
Ca	25
Co, Pb, Sb	25
Si	20
Be	15
Bi, Ge, Sn	8
Cr	5
Ni, Mg	4
Zn, Sr	3
Cu, Ag	0.8

Figure 3 - Particle size distribution of KBI powder.

Figure 4 - Schematic of hot press interior.

maximum density was the deciding criterion for all runs. After pressing, compacts were cleaned of any residual grafoil which may have adhered during densification.

Metallographic sections were prepared by first cutting specimens with a 5" diameter, 0.014" thick Norton Co. diamond cut-off wheel, and mounting them in a $1\frac{1}{4}$ " diameter Bakelite or Lucite molds. Grinding was accomplished using Lapmaster 20 μm B_4C powder on a Lapmaster grinder for 4 hours. Sections were then polished with a Buehler Automet polishing attachment using a Buehler Texmet polishing cloth impregnated with Metadi 1 μm heavy grade diamond paste. Polishing time was approximately 16 hours.

B. Quantitative Measurements

Much of the present investigation was concerned with determining the microstructural characteristics of the B_4C specimens, including grain size analysis, twin density analysis, microhardness evaluation, and electron microprobe scanning.

Grain size analysis was determined by taking photomicrographs with a Leeds photometallograph of typical regions and outlining the grain boundaries with India ink to improve contrast. These micrographs were then analyzed with an Image Analyzing Computers Ltd. Quantimet 720 to obtain mean grain diameters. Unfortunately, this method could not be employed to estimate twin densities, due to their high concentration. Estimates were made by counting distinguishable twins on 3 micrographs and averaging the results.

Microhardness measurements were obtained with a Wilson "Mo" Tukon hardness tester using a 136° diamond pyramid indenter. Ten readings on each definite grain size region were taken, and the results averaged.

Metallographic observations had shown large "pitted" areas in samples which had additions of AlF_3 or MgF_2 . In an effort to determine their cause,

electron microprobe analysis was performed with an Applied Research Laboratories model EMX-SM microprobe operated at 15 kV. The probe was adjusted to perform elemental mapping of pitted areas, a common technique described elsewhere.²⁷ In addition, supportive X-ray diffraction scans were conducted on B_4C and $B_4C + 10\%AlF_3$ specimens using a Norelco wideangle diffractometer, with Cu K α radiation and a graphite monochromator.

Rupture testing of samples activated with 1 and 10% AlF_3 , and of an unalloyed sample was performed in an attempt to further characterize the effects of microstructural variables on strength properties of hot-pressed compacts. Testing was conducted using a Tinius Olsen testing machine fitted with a tool and die set especially fabricated for this purpose (Figure 5 and Appendix B). Specimen dimensions of 2.00" x 0.75" x 0.50" were obtained by cutting hot-pressed compacts with an 8" diamond saw. All free surfaces were ground with a resonoid-bonded diamond grinding wheel to a No. 32 finish. Fracture surfaces were subsequently analyzed with a Cambridge Stereoscan electron microscope operated at 15 kV, for determination of the fracture mode.

Figure 5 - Fracture apparatus.

Results

Table 3 lists the various pressing parameters and final densities obtained for the specimens investigated. As can be seen, all densities of B_4C specimens were greater than 97.5%, with most centering around 99+%. However, B_4C + additive powders which had not been milled exhibited somewhat reduced density.

Photomicrographs of the various microstructures are presented in Figures 6-15. Figures 6-8, which show the structural change as pressure is increased from 1000 to 3000 psi while temperature is held constant, seem to indicate that exaggerated grain growth is enhanced by higher pressure. Figures 8-11 demonstrate the effect of varying temperature at constant pressure, and show enhanced, albeit localized, grain growth at lower temperatures.

Figures 12 and 13 are of B_4C + 10% AlF_3 hot-pressed specimens whose powders were not ball milled, and indicate the high degree of "pitting" encountered with this material. Furthermore, the uniform grain growth enhancement and reduction in twin density concentration encountered in this instance are to be noted. Figure 14, which is of a B_4C + 10% MgF_2 specimen, shows the same general characteristics, while Figure 15 (B_4C + 10%Ni) shows no pitting or enhanced growth.

The results of the grain size, twin density, and microhardness evaluations are listed in Table 4. Plots of microhardness vs grain size, T and P are presented in Figures 16-18, while plots of twin density vs T and P are presented in Figures 19 and 20. These graphs were constructed using the Textronix 4010 Advanced Plotting Package. Programs used are listed in Appendix C. Since microhardness readings are accurate only to within $\pm 200 \text{ kg/mm}^2$ and as much as a 25% error is possible in the twin density measurements, the trends displayed must be viewed in light of these constraints. Nevertheless, it appears

Table 3: Specimen Pressing Parameters.

Material	T(°C)	p(psi)	% of Theoretical Density
B ₄ C	2150	1000	99.2
"	2150	2000	98.0
"	2150	3000	99.0
"	2200	"	99.2
"	2100	"	97.6
"	2050	"	98.8
B ₄ C + 10%AlF ₃	1950	"	91.7
B ₄ C + 10%AlF ₃	1900	"	94.4
B ₄ C + 10%MgF ₂	1900	"	90.9
B ₄ C + 10%Ni	1900	"	97.4**
B ₄ C*	2150	"	98.8
B ₄ C + 10%AlF ₃ *	2000	"	99.2
B ₄ C + 1%AlF ₃ *	2000	"	99.6

* Specimens used for rupture testing and fracture analysis.

** Density (2.64) exceeded theoretical.

Figure 6 - Micrograph of B₄C pressed at 1000 psi and 2150°C (500X).

Figure 7 - Micrograph of B₄C pressed at 2000 psi and 2150°C (500X).

8a (500X)

8b (727X)

Figure 8 - Micrograph of B_4C nressed at 3000 psi and $2150^{\circ}C$.

Figure 9 - Micrograph of B₄C pressed at 3000 psi and 2200⁰c.
(225X).

10a (500X)

10b (500X)

Figure 10 - Micrographs of B_4C pressed at 3000 psi and $2100^{\circ}C$.

11a (500X)

11b (727X)

Figure 11 - Micrographs of U_4C pressed at 3000 psi and 2050°C .

Figure 12 - Micrograph of $B_4C + 10\% AlF_3$ pressed at 3000 psi and $1950^{\circ}C$ (250X).

Figure 13 - Micrograph of $B_4C + 10\% AlF_3$ pressed at 3000 psi and $1900^{\circ}C$ (250X).

Figure 14 - Micrograph of $B_4C + 10\%MgF_2$ pressed at 3000 psi and $1900^{\circ}C$ (500X).

Figure 15 - Micrograph of $B_4C + 10\%Ni$ pressed at 3000 psi and $1900^{\circ}C$ (445X).

TABLE 4: Grain Size, Twin Density, and Microhardness of the Specimens Investigated.

Material	Pressing Parameters		Hardness (kg/mm ²)	Twins/cm ²	Grain Size (μ m)
	T(°C)	p(psi)			
B ₄ C	2150	1000	4894	7x10 ⁶	8.3
"	2150	2000	4666	4x10 ⁶	8.5
"	2150	3000	4283	2x10 ⁶	22.0
"	"	"	4575	1x10 ⁷	6.3
"	2200	3000	4437	8x10 ⁶	6.1
"	2100	"	4219	2x10 ⁶	16.9
"	"	"	4699	6x10 ⁶	6.5
"	2050	"	4836	3x10 ⁶	17.6
"	"	"	4861	-----	2.5
B ₄ C + 10%AlF ₃	1950	"	4356	5x10 ⁵	36.0
B ₄ C + 10%AlF ₃	1900	"	4566	6x10 ⁵	30.0
B ₄ C + 10%MgF ₂	1900	"	4203	2x10 ⁶	20.7
B ₄ C + 10%Ni	1900	"	4236	-----	3.0
B ₄ C*	2150	"	4899	3x10 ⁶	18.6
"	"	"	-----	-----	2.0
B ₄ C + 10%AlF ₃ *	2000	"	4715	7x10 ⁶	8.0
B ₄ C + 1%AlF ₃ *	2000	"	4812	8x10 ⁶	5.6

*Specimens used for rupture testing and fracture analysis.

Figure 16 - Microhardness vs Grain Size at Constant Temperature and Pressure.

Figure 17 - Microhardness vs Temperature at Constant Pressure.

Figure 18 - Microhardness vs Pressure at Constant Temperature.

Figure 19 - Twin Density vs Temperature at Constant Pressure.

Figure 20 - Twin Density vs Pressure at Constant Temperature.

that, as one expects, a direct relationship exists between microhardness and grain size, as suggested by Figure 16. While the scatter in the data renders any useful interpretation of Figure 17 impossible, Figure 18 does indicate a secondary dependence of microhardness on pressure. Lastly, twin density, which is a direct reflection of the degree of internal strain energy in the lattice, appears to increase slightly as temperature increases (Figure 19), while pressure effects are unresolvable.

Microstructures of specimens used for fracture analysis are shown in Figures 21-23. Again, the high degree of grain size segregation in the pure B_4C specimen is apparent, while ball milled $B_4C + 1\%$ and $10\%AlF_3$ specimens exhibit a uniformly small grain size, which is in contrast to the large grain size shown in Figures 12 and 13 for similar specimens whose powders were not milled. SEM micrographs of fracture surfaces of the specimens of Figures 21-23 are shown in Figures 24-27. Their main purpose is to show what appears to be a mixed intergranular-transgranular fracture mode, with intergranular fracture predominating in the large-grained areas, while transgranular fracture assumes a larger role as grain size decreases.

Observed rupture strengths of the fracture specimens obtained from three tests on B_4C , $B_4C + 1\%AlF_3$, and $B_4C + 10\%AlF_3$, are listed in Table 5, and are in reasonable agreement with those obtained by Hamjian and Lidman.¹⁵ These results indicate a slight increase in fracture strength for the $B_4C + 1\%AlF_3$ over those for B_4C .

Scanning oscilloscope displays and backscatter micrographs of $B_4C + 10\%AlF_3$ and $B_4C + 10\%MgF_2$ using the electron microprobe are shown in Figures 28 and 29. Figure 28 indicates a significant degree of apparent solubility of Al in the boron carbide matrix coupled with the presence of residual Al precipitates. Figure 29 shows similar results for Mg, although Mg solubility appears to be slightly lower. Furthermore, the absence of any F in the matrix of either

21a (500X)

21b (727X)

Figure 21 - Microstructure of pure B_4C rupture specimen.

Figure 22 - Microstructure of 1%AlF₃ rupture specimen
(500X).

Figure 23 - Microstructure of 10%AlF₃ rupture specimen
(500X).

24a (110X)

24b (540X)

Figure 24 - Electron micrographs of the fracture surface of U_4C specimen showing intergranular fracture.

Figure 25 - Inclusion in pure B_4C specimen (650X).

Figure 26 - Fracture surface of B_4C specimen showing transgranular fracture (2600X).

27a (130X)

27b (620X)

Figure 27 - Electron micrographs of fracture surface of $B_4C + 1\%AlF_3$ showing predominantly transgranular fracture.

27c (2300X)

27d (6300X)

TABLE 5: Rupture Strengths of B_4C , $B_4C + 1\%AlF_3$, and $B_4C + 10\%AlF_3$.

Material	Average Bend Strength
B_4C	40,441 psi
$B_4C + 1\%AlF_3$	43,629 psi
$B_4C + 10\%AlF_3$	40,909 psi

BSE

28a

Figure 28 - Scanning oscilloscope display of $B_4C + 10\%AlF_3$ specimen (1000X).

A1
28b

F
28c

Mg

28d

Fe

28e

BSE

29a

Fe

29b

Figure 29 - Scanning oscilloscope display of $B_4C + 10\%MgF_2$ specimen (1000X).

Mg
29c

F
29d

specimen is most interesting, and suggests complete dissociation of Al and F during pressing. Lastly, the apparent Fe-rich inclusions are worth noting.

Figures 30, 31 and 32 are scanning oscilloscope displays of B_4C + 10%AlF₃, B_4C + 1%AlF₃, and B_4C fracture specimens. Again, the high degree of Al solubility is to be noted, which appears somewhat enhanced due to ball milling of the mixed blends before pressing, while no Al precipitates are present. The absence of F is again apparent, and the Fe-rich areas seen in the previous specimens are again present in all three instances. It should be noted that what appears to be Mg and F in solution in Figures 31 and 32 is actually the result of multiple exposures of these micrographs.

The results of comparative diffractometer scans of B_4C and B_4C + 10%AlF₃, which were performed in an attempt to define the means by which Al was incorporated into the boron carbide structure, are presented in Figures 33 and 34, and indicate an expansion of the lattice due to the presence of Al. This suggests the formation of a $B_xC_yAl_z$ type compound with a crystal structure similar to that of B_4C .

RSE

30a

Figure 30 - Scanning oscilloscope display of $B_4C + 10\%AlF_3$ fracture specimen (1000X).

A1
30b

F
30c

Hq

30d

Fe

30e

BSE

31a

Figure 31 - Scanning oscilloscope display of $B_4C + 1\%AlF_3$ fracture specimen (1000X).

A1
31b

F
31c

Mq

31d

Fe

31e

BSE

32a

Figure 32 - Scanning oscilloscope display of B_4C fracture specimen (1000X).

Fe
32b

Mg
32c

Figure 33 - Diffractometer scan of B_4C specimen.

Figure 33 cont.

Figure 34 - Diffractometer scan of $B_4C + 10\%AlF_3$ specimen.

Figure 34 cont.

Discussion

As evidenced by the micrographs of Figures 6-11, temperature and pressure tend to exert a significant influence on the final grain size of hot-pressed B_4C compacts. Under isothermal conditions, the incidence of "exaggerated" grain growth is reduced at lower pressures within the range investigated. A possible rationalization of this phenomenon is pointed out by Spriggs and Atteraa, ²⁸ who assert that final stage densification of hot-pressed compacts is due mainly to diffusion enhanced by the influence of the applied stress (e.g., Nabarro-Herring diffusional creep), so that the rate of pore shrinkage will increase with increased pressure. As Burke ²⁹ points out, grain growth in ceramics is limited by pores via the relation

$$dD/dt = AM\sigma(1/D - 1/D_1) \quad (2)$$

where D is the mean grain diameter, t is time, A is a geometrical constant, M is the grain boundary mobility, σ is the grain boundary energy, and $D_1 = d/f$, with d the pore diameter and f the volume fraction of pores. Thus, assuming grain boundary mobility M is high enough, grain growth will always be controlled by the rate of pore disappearance, with exaggerated growth promoted at higher rates of pore removal, i.e., at higher pressures.

The temperature dependence previously noted would appear somewhat puzzling, since grain growth per se is a rate process, and as such should be governed by a rate equation similar to that described by Burke, ²⁹

$$D^2 = A'M\exp(-Q/RT) \quad (3)$$

where Q is the activation energy for grain growth. However, in this instance, finer and more uniform grain sizes were attained at the highest temperature investigated, 2200°C. This observation of a critical temperature is supported by the work of Prochazka and Smith with SiC , ²⁶ who, as previously mentioned, noted that in order to obtain fine-grained, dense

bodies, temperature had to be maintained at 1900-1950°C, with a slight deviation from this range resulting in a coarsening of the grain structure by a factor of 50. It would appear that a similar critical temperature range occurs with B_4C , so that exact temperature control is required for the production of pure, fine-grained bodies.

The effect of additives on grain size (Figures 12-15 and 22-23) is informative. While a uniformly large grain size was obtained from compacts with 10% AlF_3 or MgF_2 whose powders were not milled prior to pressing, a uniformly small grain size, along with improved density, was encountered for 1% and 10% AlF_3 compacts whose powders were milled. Since the purpose of activators is to enhance sintering so as to produce fine-grained, dense compacts at reduced temperatures (usually by providing a thin layer between particles in which diffusion coefficients are greatly enhanced over those which would be present for the pure substance),³⁰ the abnormally large grain size obtained in the first case is most interesting. It would appear that the intimate contact between powder and activator provided by milling is an essential requirement in the production of fine-grained compacts with AlF_3 or MgF_2 additives. However, the uniformly small grain size of the $B_4C + 10\%Ni$ specimen, which also wasn't milled prior to pressing, provides a perplexing anomaly to the previous observations, and suggests that Ni contributed little to the sintering process other than possibly to provide localized "inclusions" which would serve to retard grain growth, by acting in the same manner as pores.

The results of the second of the microstructural variables investigated (i.e., microhardness), are not totally unambiguous, due to the error (± 200 kg/mm^2) associated with the data. Nevertheless, a definite dependence of hardness on grain size and a weaker correlation with pressure (at constant grain size) are suggested by Figures 16 and 18. Any possible temperature dependence of Figure 17 is masked by the scatter of data.

That microhardness should vary directly with grain size is intuitively apparent. Larger grain size is usually associated with decreased deformation of the matrix (e.g., annealing). Since decreased deformation will lower the resistance to penetration, a decrease in microhardness with increased grain size is logical. However, the secondary decrease of microhardness with increased pressure is not intuitively apparent. The two variables which would significantly affect microhardness, namely grain size and twin density, appear to have no influence on the observed trend. Grain size varied only from 6.3 to 8.6 μm in the small grain areas tested in each specimen, so that their effect (via annealing) should be negligible. Also, twin density demonstrated no significant shift with pressure, so that the strain energy of the lattice associated with twins should not be significantly affected, thus providing a negligible effect on resistance to penetration. Thus, no explanation is immediately apparent for this phenomenon, and further investigation would be appropriate to determine both the validity and cause behind this observed trend. It should be noted at this time that AlF_3 and MgF_2 additives had very little direct influence on microhardness other than that associated with grain size control, in that microhardness readings for activated specimens corresponded closely to those obtained for unactivated B_4C hot-pressed specimens of comparable grain size. Boron carbide with 10%Ni demonstrated reduced hardness at a small grain size, most likely the result of excess Ni left in the matrix (Table 4).

Within the limits of uncertainties in the present data, pressure had little effect on twin density; however, elevated temperatures seem to promote increased twin density at constant pressure and grain size (Figure 19).

The effect of additives on twin density varied, depending on the final grain size obtained (Table 4). For the powders which were not milled prior to pressing, twin density was significantly lowered, most likely a direct consequence of the excessive grain growth exhibited by these specimens.

Likewise, twin density increased for milled specimens which exhibited retarded grain growth to values associated with pure compacts, so that the additives investigated seem to have no effect on twin density, and only an indirect effect via grain growth.

As previously mentioned, the fracture analysis conducted in this investigation pointed to a mixed intergranular-transgranular fracture. This observation is in agreement with the work of Acquaviv and Chait,³¹ who observed similar fracture characteristics. Furthermore, the SEM micrographs of Figures 24-27 indicate enhanced transgranular fracture at smaller grain sizes. The importance of these observations is substantial. Provided fracture energy is higher for transgranular than intergranular fracture, ultimate strengths can be increased to a greater extent than normally expected by maintaining a small grain size. Furthermore, by decreasing lattice strain energy, fracture strengths could be increased even further. Thus, the importance of twin density concentrations as a measure of internal stress is apparent.

The observed increase in rupture strength of the $B_4C + 1\%AlF_3$ specimen over that noted for B_4C is likely due primarily to differences in twin density, and to a lesser degree to grain size differences, and again demonstrates the importance of these variables on mechanical properties.

The elemental scanning conducted with the electron microprobe, and the diffractometer scans of $B_4C + 10\%AlF_3$ and pure B_4C specimens, provide a most interesting insight into the method by which sintering is enhanced with these additives. As originally conceived, AlF_3 and MgF_2 were added to provide a thin layer on the B_4C particles with enhanced diffusivity to promote the sintering rate and lower the required temperature. It was also thought that, with this accomplished, the additive would molecularly sublime and outgas, leaving behind a pure, dense, fine-grained compact. Although a fine grain size was achieved for the milled specimens, it is quite evident from Figures 28-31 that the proposed mechanism was not accurate. It would appear

that a considerable amount of Al was incorporated into the matrix in all the samples, while no detectable F is present. Similarly, a detectable amount of Mg is present in the $B_4C + 10\%MgF_2$, while no F is present in the matrix (although F is present in nodules of, presumably MgF_2). Furthermore, the diffractometer scans of Figures 33 and 34 indicate, as previously noted, a consistent downward shift in peak location in the presence of $10\%AlF_3$, with a splitting of the peaks occurring in most instances. While the peak splitting may possibly be attributed to poor surface conditions, the peak shifts, however, seem to provide conclusive evidence that Al was incorporated substitutionally into the lattice, producing a slight expansion of the unit cell. As previously noted, the 1b position in the C chain (Figure 2) appears to be a preferred location for substitution of this type. It thus appears likely that a limited formation of a $B_{12}C_2Al$ type structure is occurring, with Al substituting for the 1b carbon. In support of this conclusion, it is interesting to further note that, in the shift of the strongest B_4C peaks to lower 2θ values, their new location corresponds closely to the strongest peaks of $B_{12}C_2Al$ reported by Lipp and Röder,³² who conducted X-ray analysis on $50\%B_4C$ - $50\%Al$ compacts pressed at 5700 psi and $1800^\circ C$, confirming the creation of an expanded B_4C lattice. It further appears that, on the basis of electron microprobe results, a similar substitution occurs with the MgF_2 . Further X-ray work would be required to confirm this conclusion.

It would also be appropriate to conduct X-ray analysis on milled $B_4C + 10\%AlF_3$ specimens, in which pitting is absent, to obtain exact information of the nature of the peak splitting associated with the possible formation of a new compound.

Finally, it is interesting to note that the liberation of free carbon provides a convenient means for the observed loss of F via the formation of a CF_x gas, most likely CF_3 or CF_4 (or a mixture of the two), thus providing

added credibility to the previous observations. Thus, it is proposed that B_4C interacts with AlF_3 in the following manner

The absence of thermodynamic data for the compound $B_{12}C_2Al$ makes it impossible to assess the energetics of the proposed reaction.

Conclusions

As with the work of Prochazka and Smith on SiC,²⁶ a critical temperature dependence was observed in the pressing of pure B_4C compacts, with exaggerated grain growth enhanced below 2200°C. Further, the pressure used also had a considerable effect in that exaggerated growth was retarded at lower pressures within the range tested (1000-3000 psi). Lastly, it was noted that ball milling considerably enhanced the effectiveness of AlF_3 activators in retarding grain growth and increasing density.

A definite dependence of microhardness on grain size was observed, along with a weaker dependence on pressure. The reason for the pressure dependence is still not clear, with further work required in this area.

It was noted that temperature and grain size were the main factors influencing twin density, with density decreasing as T decreased and as grain size increased. Since errors of as much as 25% are possible, the temperature dependence is not absolute, and further work would be appropriate. The observed grain size effects are most likely the result of annealing which occurs as grain growth proceeds.

Fracture mode analysis indicated a mixed intergranular-transgranular fracture, which emphasizes the influence of lattice strain energy (as represented by twin density determinations) on ultimate fracture strengths.

Bend strengths determined by 3-point testing of B_4C , $B_4C + 1\%AlF_3$, and $B_4C + 10\%AlF_3$, were in reasonable agreement with published values. Further, an increase in strength of the $B_4C + 1\%AlF_3$ over that for B_4C was noted, and was related to microstructural differences.

Elemental mapping and X-ray analysis of $B_4C + AlF_3$ specimens indicate an incorporation of Al into the B_4C lattice, most likely via the direct substitution of Al with a carbon atom in the 1b position. A similar substitution seems to be occurring in $B_4C + MgF_2$ compacts, with further X-ray analysis required for the confirmation of this conclusion for the latter case.

References

1. M. Moissan, *Compt. rend.*, 118, 556 (1899).
2. A. Lipp, *Boron Carbide: Production, Properties, Application*, from *Technische Rundschau*, Nos. 14, 28, 33 (1965), No. 7 (1966).
3. J. F. Lynch, C. G. Ruderer, and W. H. Duckworth eds., *Engineering Properties of Selected Ceramic Materials*, The American Ceramic Society, Columbus, Ohio, p. 5.2.2-1, 1966.
4. R. R. Ridgway, *Trans. Electrochem. Soc.*, 66, 17 (1934).
5. G. V. Samsonov, H. N. Schuravlev, and I. G. Annuel, *Fiz. Met. i Metal.*, 3, 309 (1956).
6. R. D. Allen, *J. Am. Chem. Soc.*, 75, 3582 (1953).
7. F. W. Glaser, D. Moskowitz, and B. Post, *J. Appl. Phys.*, 24(6), 731 (1953).
8. R. P. Elliott, Armour Research Foundation of I.T.T., ARF 2200-12, Final Rep. USAEC Contract AT(11-1)-578, Project Agreement No. 4, (1961).
9. R. Kieffer, G. Leimer, P. Ettmayer, and E. Gugel, *Berichte der Duet. Keram. Gessell.*, 48(9), 385 (1971).
10. G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend.*, 32, 432 (1941).
11. H. K. Clark and J. L. Hoard, *J. Am. Chem. Soc.*, 65, 2115 (1943).
12. G. S. Zhdanov, N. N. Zhuravlev, and L. S. Zevin cited in *Boron, its Compounds and Alloys*, by G. V. Samsonov et al. eds., Kiev, (1960) p. 163.
13. G. V. Samsonov in Reference 12, p. 163.
14. S. M. Lang, *Properties of High Temperature Ceramics and Cermets: Elasticity and Density at Room Temperature*, National Bureau of Standards Monograph 6 (March 1, 1960).
15. H. F. Hamjian and W. G. Lidman, *J. Am. Ceram. Soc.*, 35, 44 (1952).
16. Norton Co., *A Handbook on Boron Carbide, Elemental Boron, and Other Stable, Boron-Rich Materials* (1955).
17. R. S. Liebling, *Mat. Res. Bull.*, 2, 1035 (1967).
18. V. S. Neshpor in *Tugoplavkie Karbidy*, G. V. Samsonov ed., Kiev, (1970) p. 132.
19. H. C. Dunegan, *Notes on Hardness Measurements of Polycrystalline Materials*, Mechanical Properties of Engineering Ceramics, Proc. of Conf. of North Carolina State College, Interscience Publishers, (1961).
20. S. C. Carniglia, *J. Am. Ceram. Soc.*, 44, 419 (1961).
21. R. J. Stokes in *Fracture*, H. Liebowitz ed., Academic Press, New York, Vol. VII, (1972) pp. 157-241.

22. F. F. Lange in *Fracture Mechanics of Ceramics*, R. C. Bradt et al. eds., Plenum Press, New York, Vol. 2, (1974) pp. 599-609.
23. D. Stibbs, C. Brown, and R. Thompson, U.S. Patent 3,749,571, July 31, 1973.
24. V. V. Dzhanelinskii, M. S. Koval'chenko, and G. N. Makarenko, *Porosh. Met.*, 2(122), 97 (1973).
25. S. K. Dutta and T. Vasilos, *J. Am. Ceram. Soc.*, 53(5), 453 (1974).
26. S. Prochazka and P. C. Smith, Final Report No. SRD-74-040, General Electric Co., Schenectady, New York, April 1974.
27. R. W. Wittkopp, *Minerals Sci. Eng.* January 1971, p. 17.
28. R. M. Spriggs and L. Atteraaas in *Ceramic Microstructures*, R. M. Fulrath and J. A. Pask, eds., Wiley, New York (1968), p. 701.
29. J. E. Burke, *ibid*, p. 681.
30. R. L. Coble in *Fundamental Phenomena in the Material Sciences*, L. J. Bonis, and H. H. Hausner eds., Plenum Press, New York, (1964) p. 11.
31. S. J. Acquaviva and R. C. Chait, CA 77-117484s, 1972.
32. V. A. Lipp and M. Röder, *Z. anorg. allgem. Chem.*, 343(1 and 2), 1-5 (1966).

Appendix A
Thermal Histories of
Specimens Investigated

6	6	6	6
5	5	5	5
4	4	4	4
3	3	3	3
2	2	2	2
1	1	1	1

DATE—

THREE INCH INDUCTION HOT PRESS

Operator — Unknown

11/1/80

Pressing No. — 161

DESCRIPTION - 3" ATJ Die - Green, raised sand p. 1 - Length after green pressing 2.500"

[illegible]

START	74	48	36	-6	20	16	0	0
0700	74	48	36	-6	20	16	0	0

[illegible]

1020	102	57	57	1-3	70	✓	1520	1535	0	0	Even Wings
------	-----	----	----	-----	----	---	------	------	---	---	------------

1125	$\frac{1}{52}$	$\frac{1}{55}$	$\frac{1}{51}$	$\frac{1}{55}$	✓	3105	31.50	0	0	0000
------	----------------	----------------	----------------	----------------	---	------	-------	---	---	------

[illegible]

1136	✓	✓	✓	✓	✓	2105	2150	1700	3000	1000
------	---	---	---	---	---	------	------	------	------	------

DATE	DESCRIPTION	AMOUNT	BALANCE
11/46			
	1000	1000	1000
	1000	2000	2000
	1000	3000	3000
	1000	4000	4000
	1000	5000	5000
	1000	6000	6000
	1000	7000	7000
	1000	8000	8000
	1000	9000	9000
	1000	10000	10000

off-set pressure release - with temp constant

[illegible][illegible][illegible]

1000

123456
123456
123456

Date — SEPT 5 '74

TIME FROM FUNCTION 1st Press

COMPRESSOR — Kuhl

PRESSING No.	69	MATERIAL —	BY 2	KBI	Blend	44 45 46	
DESCRIPTION —	3" ATJ dia set	2 100°C	Kenetic	3000 PSI	at Temp	7.4628	
TIME	915	48	36	7	20	16.404	
950	75	47	55	25	20	16.404	
1030	91	54	53	31	29	16.404	
1045	"	58	58	33	"	"	Range 2
1100	"	"	"	"	"	"	
1150	11	58	58	58	200	200	
1150-30	11	58	58	58	200	200	
1151	11	51	51	51	3000	3000	
1152	11	52	52	52	3000	3000	
1153-30	11	53	53	53	3000	3000	
1155	11	55	55	55	3000	3000	
1157-30	11	57	57	57	3000	3000	
1201	12	01	01	01	3000	3000	
1205	12	05	05	05	3000	3000	
1221	12	21	21	21	3000	3000	
1225	12	25	25	25	3000	3000	

7.4628

7.4628

7.4628

7.4628

7.4628

7.4628

7.4628

7.4628

7.4628

1733746
1733756
1733766

DATE--9-11-74

TITRE INCH INJECTION HOT PRESS

K-7

2010

C4

OPERATOR--Holtz

PRESSURE NO.	KINETIC POSITION	- 2050°C	PRESSURE	APPLIED IN PUMP	OPERATOR
DESCRIPTION	3" HET Die Green Injection	MATERIAL	But. HBT - Blue	14.45 H	145 green charge
TIME	08:25	START	38	34	
	08:30		78	55	
	08:50		100	60	
	09:00		102	59	
	09:15				
	09:25				
	10:05				
	10:25				
	11:01				
	11:17				
	11:30				
	11:45				
	12:00				
	13:25				

11111

123456
123456
123456

DATE

THREE INCH INJECTION HOT PRESS

Operator Anthony

Pressure No.	98-A	Material	98-401	Pressure	10%	Operator
Description	3"	ATT De	Set			
TIME	90	51	45	7	1700	2000
0920	100	48	47	4	1700	2000
0930	100	48	47	4	1700	2000
1020	100	48	47	4	1700	2000
1040	100	48	47	4	1700	2000
1100	107	52	56	43	1700	2000
1145	102	50	53	43	1700	2000
1155	102	50	53	43	1700	2000
1225	102	50	53	43	1700	2000
1300	102	50	53	43	1700	2000
1315	102	50	53	43	1700	2000
1330	102	50	53	43	1700	2000
1345	102	50	53	43	1700	2000
1400	101	51	52	43	1700	2000
1410	101	51	52	43	1700	2000
1500	101	51	52	43	1700	2000
1510	101	51	52	43	1700	2000

Termination

123456
 123456
 123456

THREE INCH INDUCTION HOT PRESS										Operator — Kuhl	
DATE —											
PRESSURE NO. —	62									125.0 g. as changed	
DESCRIPTION —	3" ATI Diesel one preheated									Green passed 3000	
TIME											
0830	start										
835	14										
840	"										
845	"										
855	"										
930	"										
1000	"										
1025	"										
1035	"										
1045	"										
" 55	"										
1205	"										
1230	"										
1335	"										
1400	"										
1445	"										

123456
123456
123456

Date: 3-20-73

THREE INCH INDUCTION HOT PRESS

Operator: *W. J. W.*

Pressure No.	1-1	1-2	1-3	1-4	1-5	1-6	1-7	1-8	1-9	1-10	1-11	1-12	1-13	1-14	1-15	1-16	1-17	1-18	1-19	1-20	1-21	1-22	1-23	1-24	1-25	1-26	1-27	1-28	1-29	1-30	1-31	1-32	1-33	1-34	1-35	1-36	1-37	1-38	1-39	1-40	1-41	1-42	1-43	1-44	1-45	1-46	1-47	1-48	1-49	1-50	1-51	1-52	1-53	1-54	1-55	1-56	1-57	1-58	1-59	1-60	1-61	1-62	1-63	1-64	1-65	1-66	1-67	1-68	1-69	1-70	1-71	1-72	1-73	1-74	1-75	1-76	1-77	1-78	1-79	1-80	1-81	1-82	1-83	1-84	1-85	1-86	1-87	1-88	1-89	1-90	1-91	1-92	1-93	1-94	1-95	1-96	1-97	1-98	1-99	1-100	1-101	1-102	1-103	1-104	1-105	1-106	1-107	1-108	1-109	1-110	1-111	1-112	1-113	1-114	1-115	1-116	1-117	1-118	1-119	1-120	1-121	1-122	1-123	1-124	1-125	1-126	1-127	1-128	1-129	1-130	1-131	1-132	1-133	1-134	1-135	1-136	1-137	1-138	1-139	1-140	1-141	1-142	1-143	1-144	1-145	1-146	1-147	1-148	1-149	1-150	1-151	1-152	1-153	1-154	1-155	1-156	1-157	1-158	1-159	1-160	1-161	1-162	1-163	1-164	1-165	1-166	1-167	1-168	1-169	1-170	1-171	1-172	1-173	1-174	1-175	1-176	1-177	1-178	1-179	1-180	1-181	1-182	1-183	1-184	1-185	1-186	1-187	1-188	1-189	1-190	1-191	1-192	1-193	1-194	1-195	1-196	1-197	1-198	1-199	1-200	1-201	1-202	1-203	1-204	1-205	1-206	1-207	1-208	1-209	1-210	1-211	1-212	1-213	1-214	1-215	1-216	1-217	1-218	1-219	1-220	1-221	1-222	1-223	1-224	1-225	1-226	1-227	1-228	1-229	1-230	1-231	1-232	1-233	1-234	1-235	1-236	1-237	1-238	1-239	1-240	1-241	1-242	1-243	1-244	1-245	1-246	1-247	1-248	1-249	1-250	1-251	1-252	1-253	1-254	1-255	1-256	1-257	1-258	1-259	1-260	1-261	1-262	1-263	1-264	1-265	1-266	1-267	1-268	1-269	1-270	1-271	1-272	1-273	1-274	1-275	1-276	1-277	1-278	1-279	1-280	1-281	1-282	1-283	1-284	1-285	1-286	1-287	1-288	1-289	1-290	1-291	1-292	1-293	1-294	1-295	1-296	1-297	1-298	1-299	1-300	1-301	1-302	1-303	1-304	1-305	1-306	1-307	1-308	1-309	1-310	1-311	1-312	1-313	1-314	1-315	1-316	1-317	1-318	1-319	1-320	1-321	1-322	1-323	1-324	1-325	1-326	1-327	1-328	1-329	1-330	1-331	1-332	1-333	1-334	1-335	1-336	1-337	1-338	1-339	1-340	1-341	1-342	1-343	1-344	1-345	1-346	1-347	1-348	1-349	1-350	1-351	1-352	1-353	1-354	1-355	1-356	1-357	1-358	1-359	1-360	1-361	1-362	1-363	1-364	1-365	1-366	1-367	1-368	1-369	1-370	1-371	1-372	1-373	1-374	1-375	1-376	1-377	1-378	1-379	1-380	1-381	1-382	1-383	1-384	1-385	1-386	1-387	1-388	1-389	1-390	1-391	1-392	1-393	1-394	1-395	1-396	1-397	1-398	1-399	1-400	1-401	1-402	1-403	1-404	1-405	1-406	1-407	1-408	1-409	1-410	1-411	1-412	1-413	1-414	1-415	1-416	1-417	1-418	1-419	1-420	1-421	1-422	1-423	1-424	1-425	1-426	1-427	1-428	1-429	1-430	1-431	1-432	1-433	1-434	1-435	1-436	1-437	1-438	1-439	1-440	1-441	1-442	1-443	1-444	1-445	1-446	1-447	1-448	1-449	1-450	1-451	1-452	1-453	1-454	1-455	1-456	1-457	1-458	1-459	1-460	1-461	1-462	1-463	1-464	1-465	1-466	1-467	1-468	1-469	1-470	1-471	1-472	1-473	1-474	1-475	1-476	1-477	1-478	1-479	1-480	1-481	1-482	1-483	1-484	1-485	1-486	1-487	1-488	1-489	1-490	1-491	1-492	1-493	1-494	1-495	1-496	1-497	1-498	1-499	1-500	1-501	1-502	1-503	1-504	1-505	1-506	1-507	1-508	1-509	1-510	1-511	1-512	1-513	1-514	1-515	1-516	1-517	1-518	1-519	1-520	1-521	1-522	1-523	1-524	1-525	1-526	1-527	1-528	1-529	1-530	1-531	1-532	1-533	1-534	1-535	1-536	1-537	1-538	1-539	1-540	1-541	1-542	1-543	1-544	1-545	1-546	1-547	1-548	1-549	1-550	1-551	1-552	1-553	1-554	1-555	1-556	1-557	1-558	1-559	1-560	1-561	1-562	1-563	1-564	1-565	1-566	1-567	1-568	1-569	1-570	1-571	1-572	1-573	1-574	1-575	1-576	1-577	1-578	1-579	1-580	1-581	1-582	1-583	1-584	1-585	1-586	1-587	1-588	1-589	1-590	1-591	1-592	1-593	1-594	1-595	1-596	1-597	1-598	1-599	1-600	1-601	1-602	1-603	1-604	1-605	1-606	1-607	1-608	1-609	1-610	1-611	1-612	1-613	1-614	1-615	1-616	1-617	1-618	1-619	1-620	1-621	1-622	1-623	1-624	1-625	1-626	1-627	1-628	1-629	1-630	1-631	1-632	1-633	1-634	1-635	1-636	1-637	1-638	1-639	1-640	1-641	1-642	1-643	1-644	1-645	1-646	1-647	1-648	1-649	1-650	1-651	1-652	1-653	1-654	1-655	1-656	1-657	1-658	1-659	1-660	1-661	1-662	1-663	1-664	1-665	1-666	1-667	1-668	1-669	1-670	1-671	1-672	1-673	1-674	1-675	1-676	1-677	1-678	1-679	1-680	1-681	1-682	1-683	1-684	1-685	1-686	1-687	1-688	1-689	1-690	1-691	1-692	1-693	1-694	1-695	1-696	1-697	1-698	1-699	1-700	1-701	1-702	1-703	1-704	1-705	1-706	1-707	1-708	1-709	1-710	1-711	1-712	1-713	1-714	1-715	1-716	1-717	1-718	1-719	1-720	1-721	1-722	1-723	1-724	1-725	1-726	1-727	1-728	1-729	1-730	1-731	1-732	1-733	1-734	1-735	1-736	1-737	1-738	1-739	1-740	1-741	1-742	1-743	1-744	1-745	1-746	1-747	1-748	1-749	1-750	1-751	1-752	1-753	1-754	1-755	1-756	1-757	1-758	1-759	1-760	1-761	1-762	1-763	1-764	1-765	1-766	1-767	1-768	1-769	1-770	1-771	1-772	1-773	1-774	1-775	1-776	1-777	1-778	1-779	1-780	1-781	1-782	1-783	1-784	1-785	1-786	1-787	1-788	1-789	1-790	1-791	1-792	1-793	1-794	1-795	1-796	1-797	1-798	1-799	1-800	1-801	1-802	1-803	1-804	1-805	1-806	1-807	1-808	1-809	1-810	1-811	1-812	1-813	1-814	1-815	1-816	1-817	1-818	1-819	1-820	1-821	1-822	1-823	1-824	1-825	1-826	1-827	1-828	1-829	1-830	1-831	1-832	1-833	1-834	1-835	1-836	1-837	1-838	1-839	1-840	1-841	1-842	1-843	1-844	1-845	1-846	1-847	1-848	1-849	1-850	1-851	1-852	1-853	1-854	1-855	1-856	1-857	1-858	1-859	1-860	1-861	1-862	1-863	1-864	1-865	1-866	1-867	1-868	1-869	1-870	1-871	1-872	1-873	1-874	1-875	1-876	1-877	1-878	1-879	1-880	1-881	1-882	1-883	1-884	1-885	1-886	1-887	1-888	1-889	1-890	1-891	1-892	1-893	1-894	1-895	1-896	1-897	1-898	1-899	1-900	1-901	1-902	1-903	1-904	1-905	1-906	1-907	1-908	1-909	1-910	1-911	1-912	1-913	1-914	1-915	1-916	1-917	1-918	1-919	1-920	1-921	1-922	1-923	1-924	1-925	1-926	1-927	1-928	1-929	1-930	1-931	1-932	1-933	1-934	1-935	1-936	1-937	1-938	1-939	1-940	1-941	1-942	1-943	1-944	1-945	1-946	1-947	1-948	1-949	1-950	1-951	1-952	1-953	1-954	1-955	1-956	1-957	1-958	1-959	1-960	1-961	1-962	1-963	1-964	1-965	1-966	1-967	1-968	1-969	1-970	1-971	1-972	1-973	1-974	1-975	1-976	1-977	1-978	1-979	1-980	1-981	1-982	1-983	1-984	1-985	1-986	1-987	1-988	1-989	1-990	1-991	1-992	1-993	1-994	1-995	1-996	1-997	1-998	1-999	1-1000	1-1001	1-1002	1-1003	1-1004	1-1005	1-1006	1-1007	1-1008	1-1009	1-1010	1-1011	1-1012	1-1013	1-1014	1-1015	1-1016	1-1017	1-1018	1-1019	1-1020	1-1021	1-1022	1-1023	1-1024	1-1025	1-1026	1-1027	1-1028	1-1029	1-1030	1-1031	1-1032	1-1033	1-1034	1-1035	1-1036	1-1037	1-1038	1-1039	1-1040	1-1041	1-1042	1-1043	1-1044	1-1045	1-1046	1-1047	1-1048	1-1049	1-1050	1-1051	1-1052	1-1053	1-1054	1-1055	1-1056	1-1057	1-1058	1-1059	1-1060	1-1061	1-1062	1-1063	1-1064	1-1065	1-1066	1-1067	1-1068	1-1069	1-1070	1-1071	1-1072	1-1073	1-1074	1-1075	1-1076	1-1077	1-1078	1-1079	1-1080	1-1081	1-1082	1-1083	1-1084	1-1085	1-1086	1-1087	1-1088	1-1089	1-1090	1-1091	1-1092	1-1093	1-1094	1-1095	1-1096	1-1097	1-1098	1-1099	1-1100	1-1101	1-1102	1-1103	1-1104	1-1105	1-1106	1-1107	1-1108	1-1109	1-1110	1-1111	1-1112	1-1113	1-1114	1-1115	1-1116	1-1117	1-1118	1-1119	1-1120	1-1121	1-1122	1-1123	1-1124	1-1125	1-1126	1-1127	1-1128	1-1129	1-1130	1-1131	1-1132	1-1133	1-1134	1-1135	1-1136	1-1137	1-1138	1-1139	1-1140	1-1141	1-1142	1-1143	1-1144	1-1145	1-1146	1-1147	1-1148	1-1149	1-1150	1-1151	1-1152	1-1153	1-1154	1-1155	1-1156	1-1157	1-1158	1-1159	1-1160	1-1161	1-1162	1-1163	1-1164	1-1165	1-1166	1-1167	1-1168	1-1169	1-1170	1-1171	1-1172	1-1173	1-1174	1-1175	1-1176	1-1177	1-1178	1-1179	1-1180	1-1181	1-1182	1-1183	1-1184	1-1185	1-1186	1-1187	1-1188	1-1189	1-1190	1-1191	1-1192	1-1193	1-1194	1-1195	1-1196	1-1197	1-1198	1-1199	1-1200	1-1201
--------------	-----	-----	-----	-----	-----	-----	-----	-----	-----	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------

Appendix B

Detail Drawings of Tool and
Die Used for Fracturing Specimens

Bottom Bearing Edges (2 Req'd)

Note: Faces of Block Parallel

Bottom Block

Top Bearing Edge

Note: All parts fabricated from 1040 steel.

Appendix C

Texttronix 4010 Programs
Used to Plot Data

```

*SET AUTOBIND
*BIND = FROM ADVTKSUBS, TKSUBS
*USE /TKTRNX/ FOR TKCOMMON
*USE /BPPCOM/ FOR ADVTKCOMMON
*SET SUPRS
DIMENSION XDATA(5), YDATA(5), TITLE(7), T(4)
DATA XDATA/4.,2.5,6.3,16.9,22.0/
DATA YDATA/4.,4861.,4575.,4219.,4283./
DATA TITLE/39HMICROHARDNESS VS G.S. AT CONSTANT T & P/
DATA T/20HGRAIN SIZE (MICRONS)/
CALL INITT(0,0)
CALL BINITT
CALL SPBEGN(9.,6.)
CALL SYMBL(1)
CALL SIZES(0.5)
CALL XFRM(4)
CALL YFRM(4)
CALL XHFRM(3)
CALL YHFRM(3)
CALL MOVABS(50,640)
CALL VLABEL(2,HMICROHARDNESS KG/SQ MM,22)
CALL NOTITE(300,740,TITLE,39)
CALL NOTITE(400,50,T,20)
CALL BLIND(0,0,25,0)
CALL CHECKCNDA(XDATA,YDATA)
CALL DISPLAYCNDA(XDATA,YDATA)
CALL ROOMIN
CALL PAPER(112)
CALL SETHD(1)
CALL FINITT(0,700)
STOP
END

```



```

1SET AUTOBIND
1BIND = FROM ADVTKSUBS, TKSUBS
1USE ATETRMZ FOR TCOMMON
1USE PERPCOMZ FOR ADVTKCOMMON
1SET SUPPS
DIMENSION XDATA(4), YDATA(4), TITLE(7), T(2)
DATA XDATA/3., 1000., 2000., 3000./
DATA YDATA/3., 4894., 4666., 4575./
DATA TITLE/39MHICPOHAPINESS VS PRESSURE AT CONSTANT T/
DATA T CHP (PSI)
CALL INIT(0,0)
CALL DINIT
CALL DBEG(9., 6.)
CALL CEND(1)
CALL SICES(0, 5)
CALL XFRM(4)
CALL YFRM(4)
CALL XFRM(3)
CALL YFRM(3)
CALL DYNHDS(50, 640)
CALL WIND(39MHICPOHAPINESS KG/SQ MM, 22)
CALL DATIE(0, 0, 740, TITLE, 39)
CALL DATIE(0, 0, 50, T, 7)
CALL RUTIE(500., 1000)
CALL CNDI(0, 0, 0, YDATA)
CALL DEND(0, 0, 0, YDATA)
CALL DEND
CALL END(0, 1, 2)
CALL TEND(1)
CALL FTHIE(0, 0, 0)
1TOP
END

```

```

*SET AUTOBIND
*BIND = FROM ADVTKSUBS, TKSUBS
*USE /TPTPNC/ FOR TKCOMMON
*USE /BPFCOM/ FOR ADVTKCOMMON
*SET SUPRS
DIMENSION XDATA(5), YDATA(5), TITLE(7), T(2)
DATA XDATA/4., 2050., 2100., 2150., 2200./
DATA YDATA/4., 3000000., 6000000., 10000000., 8000000./
DATA TITLE/41HTMIN DENSITY VS TEMP AT CONSTANT PRESSURE/
DATA T/5HT (C)/
CALL INIT(0,0)
CALL BINITT
CALL SPBEGN(9., 6.)
CALL SYMCL(1)
CALL SIZES(0.5)
CALL XFRM(4)
CALL YFRM(4)
CALL XNFRM(3)
CALL YNFRM(3)
CALL MOVHES(50, 540)
CALL VLABEL(11HTMINS/50 CM, 11)
CALL NOTIT(300, 740, TITLE, 41)
CALL NOTATE(475, 50, T, 5)
CALL BLIND(2000., 2250.)
CALL BLIND(2000000., 12000000.)
CALL CHEF(4DATA, YDATA)
CALL DEFLAY(4DATA, YDATA)
CALL BROWTH
CALL PAFTH(112)
CALL SPEND(1)
CALL FINITT(0, 700)
STOP
END

```

```

*SET AUTO2IND
IBIND = FROM ADVTKSUBS, TKSUBS
FUSE /TKTANH/ FOR TKCOMMON
FUSE /BPPCOM/ FOR ADVTKCOMMON
TSET SUPRS
DIMENSION XDATA(4), YDATA(4), TITLE(7), T(2)
DATA XDATA/3., 1000., 2000., 3000./
DATA YDATA/3., 7000000., 4000000., 10000000./
DATA TITLE/38HTMIN DENSITY VS PRESSURE AT CONSTANT T/
DATA T/THP (PSI)/
CALL INITT(0.0)
CALL BINITT
CALL SPSEGN(9., 6.)
CALL SYMGL(1)
CALL SIZES(0.5)
CALL XFRM(4)
CALL YFRM(4)
CALL XNFRM(3)
CALL YNFRM(3)
CALL NOVHES(50, 340)
CALL VLABEL(11HTMIN/50 CM, 11)
CALL NOTATE(300, 740, TITLE, 38)
CALL NOTATE(425, 50, T, 7)
CALL DLIN(500., 7500.)
CALL DLIN(7000000., 12000000.)
CALL CTEXT(0.001, YDATA)
CALL DISPLAY(0DATA, YDATA)
CALL BROWTH
CALL ENDTH(10)
CALL SPEND(1)
CALL FINIT(0.0, 700)
STOP
END

```

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractor's subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."