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NOVEL HARD METAL COMPOSITIONS AND PROPERTIES

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ABSTRACT

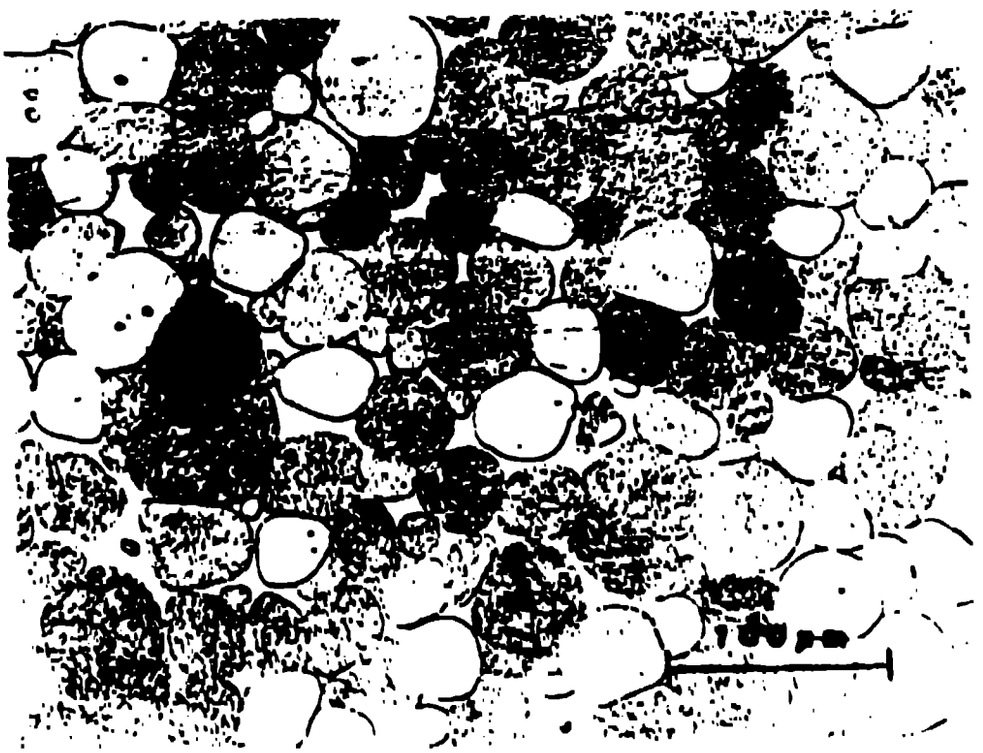
A new family of hard metal compositions consisting primarily of borides, borocarbides and carbides of nickel, iron and tungsten or molybdenum is made by reaction hot pressing and/or liquid phase sintering mixtures of elemental powders with small quantities of boron carbide. The hardness of these compositions is in the range of the hardest conventional tungsten carbide-cobalt compositions. Density of this family of materials can be varied from about 8 to 17 Mg/m^3 with only slight variations in hardness. Preliminary data on hot hardness, hardness, fracture toughness, and abrasion resistance are encouraging.

INTRODUCTION

Tungsten carbide-cobalt is the conventional material used worldwide for tool bits, rock drill bits, armor piercing projectiles and other applications where high hardness and abrasion resistance are important. Hard metal compositions which contain no cobalt are increasingly important because of United States dependence on unstable sources of supply of this strategic material. Because the United States also imports a large portion of the tungsten it consumes, substitutes for strategic tungsten also are of considerable interest. With a metal-boron carbon system (M-B-C), hardness in the range of the hardest conventional tungsten carbide-cobalt has been achieved and superiority over the conventional material for ultra high pressure anvil applications has been demonstrated.[a] The well known tungsten-nickel-iron "heavy metal" was principally used as the metal and boron carbide was the source of boron and carbon. Additionally it was demonstrated that non-strategic molybdenum could be substituted in part or totally for the tungsten in the M-B-C system with no change in hardness, or (in the limited number of samples tested) in abrasion resistance or compressive strength.

In Figure 1, the [illegible] of the readily machineable 95.0 wt. W-3.5 [illegible] "heavy metal" is [illegible] with the same alloy to which [illegible] carbide (B_4C) has been added; both materials were [illegible] the same conditions. Hardness of structures containing boron [illegible] R_A. In [illegible] electron [illegible] that the hardness [illegible] primarily to formation

2.0 B_4C-98.0 [95 Wt. % W-3.5 Ni-1.5 Fe]



[95 Wt. % W-3.5 Ni-1.5 Fe]

Fig. 1 "Heavy Metal" And "Heavy Metal" – Boron Carbide

of borides, carbides and borocarbides, but the paper concluded that further definition of the nature and extent of reactions involved was required.

In more recent work, the compositional and density range of this nonconventional hard metal system has been dramatically extended. Tungsten content was reduced from the previous minimum of 90 wt% (balance nickel and iron) to 70 wt%; in the molybdenum series of alloys, the molybdenum was similarly reduced with appropriate increases in boron carbide concentration. In an effort to reduce the complexity of this material system and gain an understanding of reactions involved, iron was eliminated from several pressings and separately, boron was substituted for boron carbide. Both hot pressing and cold pressing/sintering were employed in this study.

RAW MATERIALS

The powders used in this study were obtained from commercial sources. Powder characteristics are compiled in Table I; chemical analysis and size distribution of powders are included in the previously cited publication. Average particle size was determined with a calibrated Fisher Sub-Sieve Sizer.[b] Values of mean and mode particle size were calculated from sedimentation data obtained with a Model 5000-D) Sedigraph[c] or with a sedimentation balance. Surface area was determined with a Numec Model APA-3 absorption flow apparatus[d] that uses a modified Brunauer-Emmett-Teller (BET) technique.

The molybdenum powder was freshly reduced in hydrogen at 650°C and screened -325 prior to use. The previous work indicated the necessity for removing the boric oxide impurity in the boron carbide powder. The powder was boiled in water for 3h with stirring, alcohol washed, vacuum dried and screened prior to blending with elemental powders.

Airco-Speer Carbon Co. grade 560.S graphite[e] was used to make the hot pressing die and punch assemblies.

Table I

Powder Characteristics

Powder Lot	Bulk Density % theoretical	Tap Density % theoretical	Surface Area m^2/g	Average Particle Size FSSS, µm	Sedimentation Particle Size Mean, µm	Mode, µm
[illegible]	33.7	44.0	0.2	4.7	9.7	5.5
[illegible]	26.8	37.6	4.5	0.6	11.3	17.5
[illegible]	24.1	39.5	0.7	8.0	11.1	6.5
[illegible]	[illegible]	17.3	4.3	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	37.6	4.1	[illegible]	[illegible]	[illegible]
[illegible]	28.1	41.1	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

PROCEDURES AND EQUIPMENT

Blending

Nickel and iron powders were preblended for 4h in bottles equipped with aluminum agitator wires; this mixture was similarly blended with the tungsten or reduced molybdenum powder for an additional 4h prior to a final 4h blending with boron or boron carbide powder.

Hot-Pressing

A weighed charge of the blended constituents was leveled in the cavity of a 76.2-mm-o.d. by 31.8-mm-i.d. by 101.60-mm-long graphite die, and the upper punch was inserted into the die. Thermal insulation was a single layer of 6.3-mm-thick carbon felt, cut and sewn to enclose the die completely. After the charge was cold-pressed at 10.3 MPa, the assembly length was measured and the necessary ram movement for complete densification was determined. The insulated die was centered accurately in a 101.6-mm-i.d. by 152.4-mm-long current-concentrator induction coil coupled to a 10,000-Hz, 50-kW motor generator. The hot-press arrangement is shown in Fig. 2. A typical time-temperature-pressure cycle for pressing a 31.8-mm-diam by 25.4-mm-long cylinder is shown in Fig. 3; hot-pressing was performed in an argon atmosphere.

Cold-Pressing and Sintering

Powder blends were loaded into polyvinyl alcohol pressing sacks, lids were inserted and sealed to the sacks which were then evacuated. The evacuated sacks were isostatically pressed at 345 MPa and the pressings were sintered in hydrogen at temperatures ranging from 1450 to 1470°C in a tungsten resistance furnace or in a silicon carbide heated aluminum oxide tube furnace. Time at temperature ranged from 0.25 to 1.0h.

Density measurement

Theoretical density in this M-B-C system was calculated using the rule of simple mixtures; formation of compounds will increase true theoretical density. Densities of hot-pressed cylinders were determined by mensuration with frequent correlation with immersion techniques. Densities of all cold-pressed, sintered cylinders were determined by immersion.

Hardness

Values of hardness were measured in accordance with American Society of Testing Materials (ASTM) Test No. E294-7[illegible] using a Rockwell Hardness Tester, Model [illegible].[4] Hardness was measured at five positions located radially and substantially equidistant from the center to the circumference. Ends of the hot pressed cylinders were ground flat and parallel prior to measurement of hardness by an additional 0.5 mm of stock was ground from end prior to [illegible] measurement.

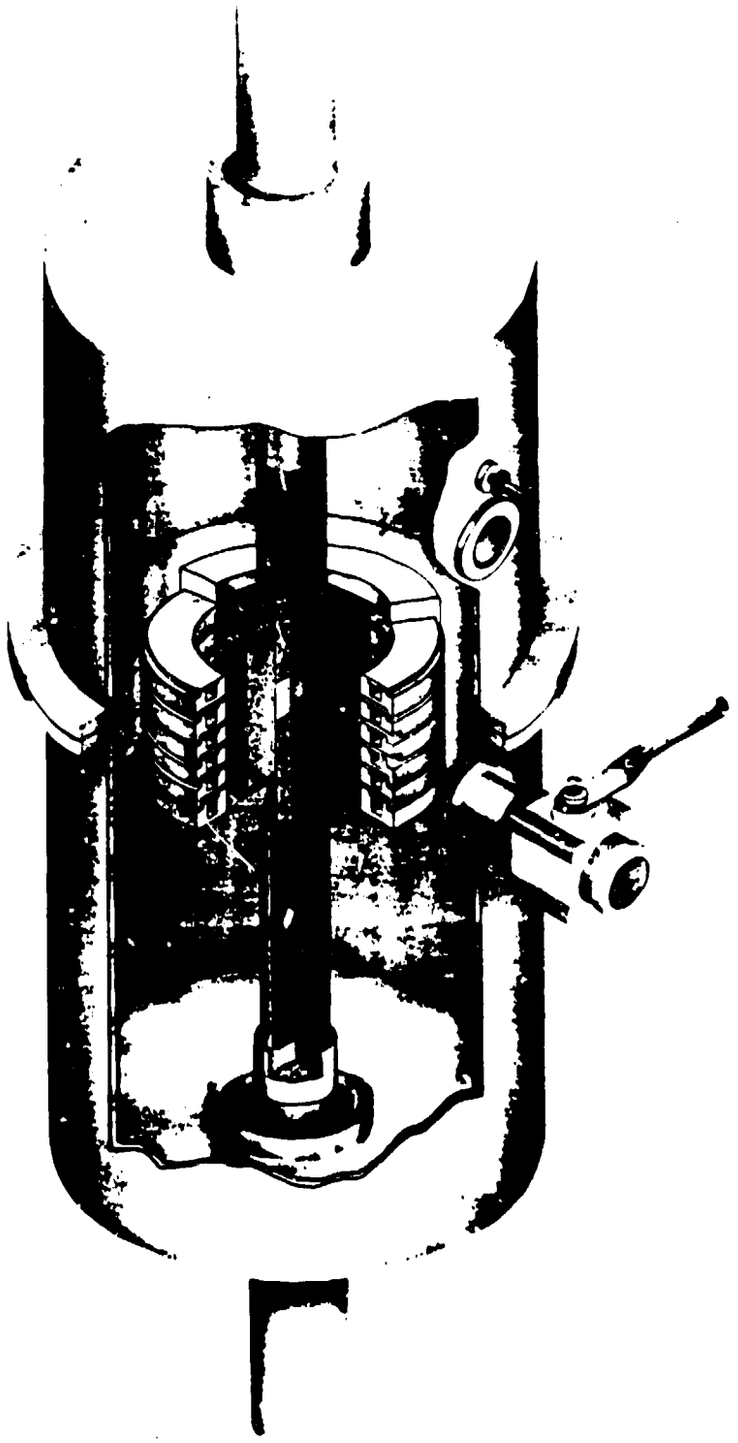


Fig. 2 Schematic Of Hot Pressing Arrangement

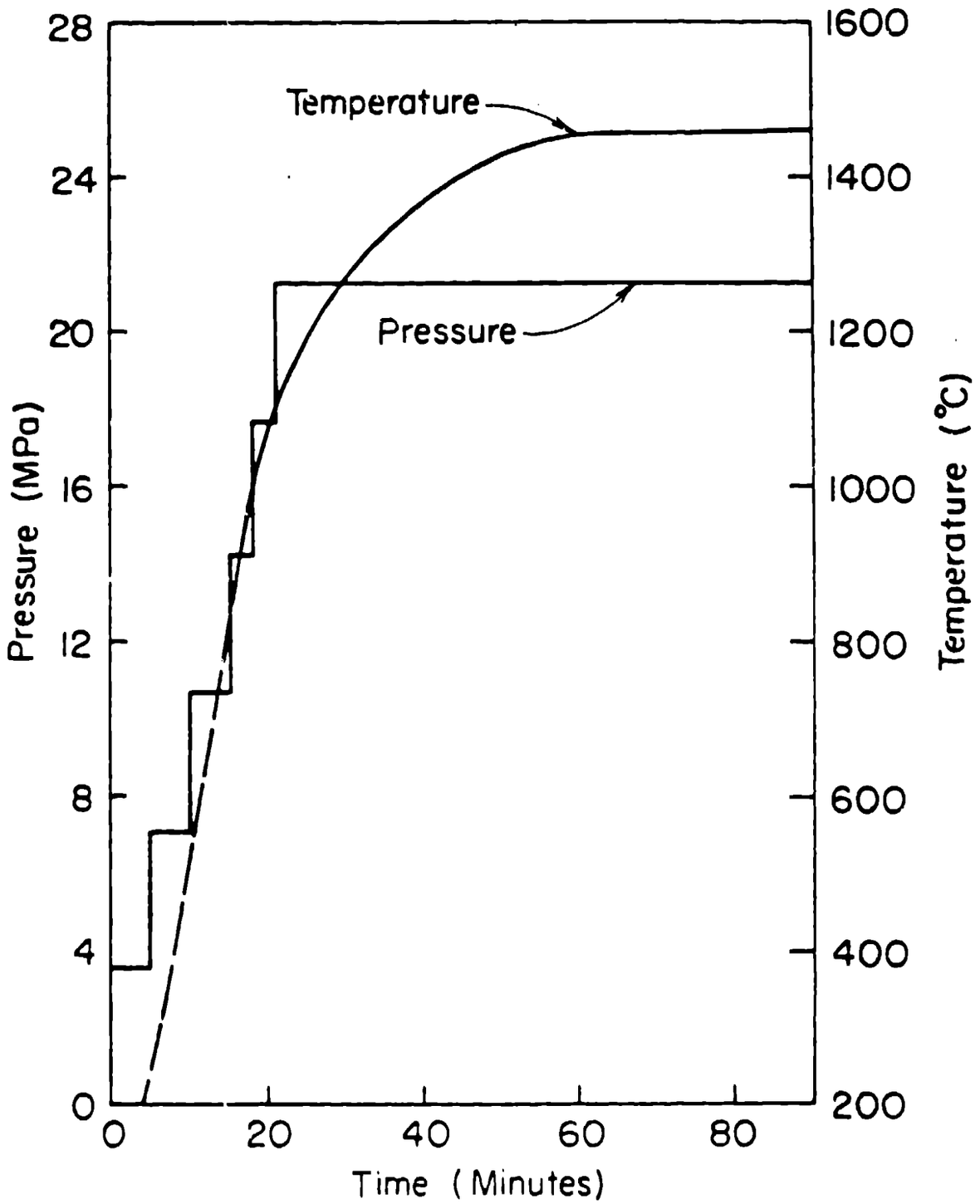


Fig. 3 Typical Time-Temperature-Pressure Cycle

Fracture Toughness

Values of fracture toughness, K_{ICSR}, were determined with a Fractometer I system by using a 13-mm-diam by 19-mm-long slotted specimen as described by Barker[g]. In addition fracture toughness was measured on some specimens by indentation hardness in a manner described by Anstis, et. al.[h]

Abrasion Resistance

Abrasion resistance was determined by Hughes Tool Co. Hughes MPD, Houston, TX in accordance to ASTM B-611-76 Standard. Abrasion resistance was measured on samples as hot-pressed and after a post hot-press HIP treatment at 1300°C, 103 MPa for 2h.

Hot Micro-hardness

Hot hardness of six specimens was determined by the Philip McKenna Laboratories of Kennamental Inc. using a Nikon Hot Micro Hardness Instrument. Testing parameters were as follows: eight Vickers indentations were made at each test temperature from room temperature to 800°C with a 1000 gram load and 10 second dwell time. The mean hardness value and standard deviation were recorded for each test temperature.

Electron Microprobe

The electron microprobe uses a finely focused electron beam (0.2 μm diam) with a 1 to 50 KeV energy to excite ~ 1 cubic micrometer of the specimen. Signals emitted from the specimen include secondary, back scattered and absorbed electrons and characteristic x-rays. Electron signals provide information on average atomic number differences and chemical composition on a microscale is obtained from the x-ray signals. Energy dispersive and wave length spectrometers were employed to chemically characterize metallographically polished specimens.

EXPERIMENTAL RESULTS AND DISCUSSION

Extension of Composition Range

In order to extend the compositional range and density of this family of hard materials, the tungsten content was reduced from the previous minimum of 90 wt (balance nickel and iron) to 70 wt%. In the molybdenum series of alloys, the molybdenum was reduced from the previous minimum of 90.3 wt (balance nickel and iron) to 72.0 wt%. Boron carbide concentration in the new series of tungsten alloys was increased to a maximum of 5.0 wt and in the new series of molybdenum alloys to 9.1 wt. In two pressings, the iron was eliminated in an effort to simplify this complex material system. Ten 31.8-mm-diam. by 16-mm-long cylinders were hot pressed at 1460°C and 21 MPa; density of all cylinders was > 100 of theoretical based on the rule of mixtures of blended constituent powders. Ends of the hot pressed

cylinders were ground flat and parallel and an additional 0.5-mm stock was removed from one end prior to hardness testing. Hardness and composition are shown in Table II. For comparison, maximum hardness of the 90 and 95% tungsten compositions were 90.0 and 93.4 R_A respectively and 90.9 R_A for the 90.9 wt% molybdenum.

The same new extended range of alloy compositions was fabricated by conventional isostatic pressing and sintering in hydrogen in the 1460-1470°C range. These specimens were sintered with a 250°C/h heating rate in an attempt to reduce solid state reactions. Composition of specimens which exceeded 100% of theoretical density were 7.45 B_4C-92.55 [80.48 Mo-13.66 Ni-5.86 Fe] and 3.5 B_4C-96.5 [85.0 W-15.0 Ni]; hardness of the latter was 88.6 R_A.

Hot Micro Hardness

Metallography on early hot pressed specimens indicated somewhat larger grains of borides (or carbides/borocarbides) than in most grades of tungsten carbide-cobalt. Parameters which probably markedly affect final grain size are size of starting powders and rate of rise of temperature (both of which affect solid state reactions), and time at maximum temperature during which liquid phase sintering and activated reaction and sintering occur. Size of the tungsten and nickel was varied in two blends designated A and B in which the finer size powders were used in blend B. Time at maximum temperature and pressure was reduced from the original 30 min. to 15 or 0 minutes. Rate of rise of temperature was maintained essentially constant. The hot microhardness of six hot pressed specimens was determined by the Philip McKenna Laboratory of Kennametal, Inc.. Results of these measurements are shown in Fig. 4. Two of the values at 800°C are 10-20% higher than conventional tungsten carbide-cobalt at the same temperature, according to Kennametal. Composition and average hardness at 800°C of specimens are presented in Table III. However, standard deviation of hardness values as shown in Table IV was considerably higher than conventional materials primarily because of porosity as revealed by post test metallographic examination of cylinders from which the specimens were machined. Another factor which might have contributed to high standard deviation in hot hardness values is the microcompositional variability which was observed metallographically and determined by electron microprobe on similar specimens. The measured specimens will be HIPED at 1455°C and remeasured. The limited data suggests increased hot hardness with the shortest time at temperature with finer powder, and with higher boron carbide content. The markedly lower standard deviation for the molybdenum base compositions is not understood.

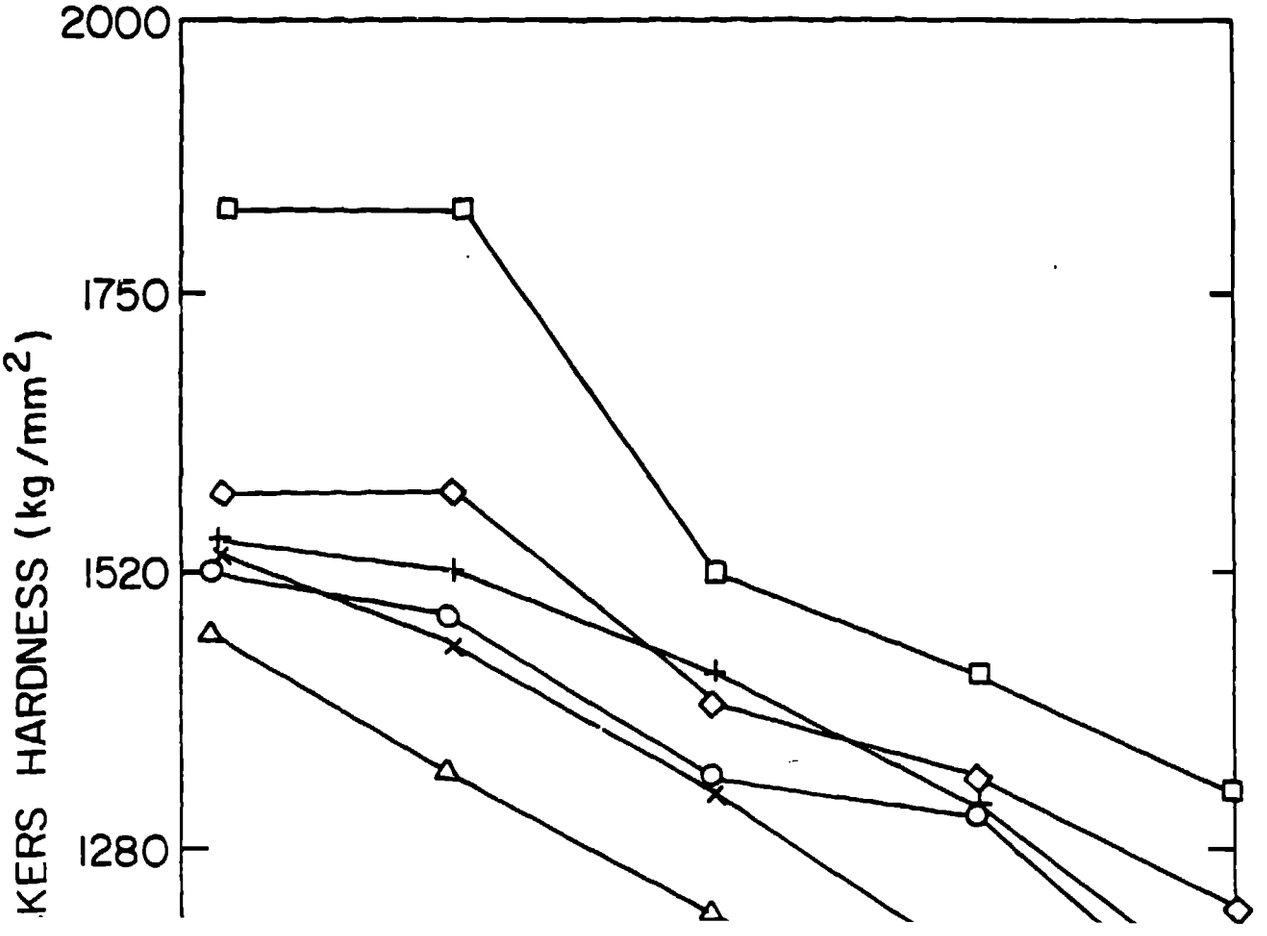

2000
1750
1520
1280
KERS HARDNESS (kg/mm²)

Table II

Composition and Hardness of Extended Composition Range of Materials

Run No.	Composition, Wt%	Av. Hardness, R_A Stock Removal End	Opposite End
PA-1	3.50 B_4C -96.50 [85.0 W-10.5 Ni-4.5 Fe]	89.2	89.8
PA-2	4.00 B_4C -96.00 [80.0 W-14.0 Ni-6.0 Fe]	89.2	89.5
PA-3	6.54 B_4C -93.46 [87.1 Mo-9.02 Ni-3.87 Fe]	91.0	90.8
PA-4	7.45 B_4C -92.55 [80.5 Mo-13.6 Ni Ni-5.9 Fe]	89.4	89.9
PA-5	4.50 B_4C -95.50 [75.00 W-17.5 Ni-7.50 Fe]	87.3	87.0
PA-6	5.00 B_4C -95.00 [70.00 W-21.0 Ni-9.00 Fe]	89.4	90.2
PA-7	8.20 B_4C -91.80 [77.00 Mo-16.10 Ni-6.90 Fe]	91.0	89.1
PA-8	9.10 B_4C -90.90 [72.00 Mo-19.60 Ni-8.40 Fe]	88.6	89.1
PA-9	3.50 B_4C -96.50 [85.00 W-15.00 Ni]	89.7	87.0
PA-10	6.54 B_4C -93.46 [87.11 Mo-12.89 Ni]	86.9	90.9

Table III

Hot Hardness Specimen Composition

Run No.	Composition wt%	Blend*	Time at Temperature min	Hardness at 800°C Kg/mm^2
9	2.50 B_4C-97.50 [95 W-3.5Ni-1.5 Fe]	B	0	1333
10	2.25 B_4C-97.75 [95 W-3.5Ni-1.5 Fe]	A	0	1123
14	2.25 B_4C-97.75 [95 W-3.5Ni-1.5 Fe]	B	15	1061
15	2.50 B_4C-97.50 [95 W-3.5 Ni-1.5 Fe]	B	15	1232
20	5.03 B_4C-94.97 [90.9 Mo-6.4 Ni-2.7 Fe]	-	15	1074
21	5.03 B_4C-94.97 [90.9 Mo-6.4 Ni-2.7 Fe]	-	0	1152

*Blend A: medium size elemental powders
Blend B: fine size elemental powders

Table IV

Vickers Hardness (Kg/mm^2) and Standard Deviations

Temperature (°C)	Specimen # R-9	R-10	R-14	R-15	R-20	R-21
RT25	1840±103	1523±142	1470±161	1588±191	1533±84	1546±49
200	1839±98	1481±284	1346±122	1590±188	1457±61	1520±70
400	1525±193	1346±162	1232±127	1413±108	1331±155	1433±46
600	1437±182	1315±157	1091±129	1343±142	1177±93	1321±18
800	1333±100	1123±146	1061±131	1232±145	1074±19	1152±24

Fracture Toughness

Short rod fracture toughness data is reported in Table V. Apparently because of the combination of high hardness and abrasion resistance (and probable micro variability in grain composition) difficulties are encountered in slotting the short rod specimens to the specified tolerance for testing with the Fractometer II instrument. Some specimens required up to 3h for the chevron slotting. Reed Rock Bit Company (Houston, TX), a major manufacturer of conventional tungsten carbide-cobalt, slots that conventional material in ~ 10 minutes and without difficulty in meeting specimen tolerance. They found that it required up to 1.5 h to slot some of our compositions, and it was difficult to maintain tolerances.

Fracture toughness determination by indentation hardness does not require the expensive grinding to form the 13-mm-diam by 19-mm-long cylinder with flat and parallel ends or the expensive precision slotting operation for testing with the Fractometer, but it does require many accurate measurements and a known value of modulus of elasticity for calculation of fracture toughness. For values of fracture toughness obtained by this technique, an average of modulus for tungsten carbide-cobalt materials (400 GPa) was assumed. Values of toughness for four pressings as determined by the indentation technique are also recorded in the Table V. Although the values obtained by the two methods do not closely agree and the number of specimens tested is small, they do show the same general trend of improved toughness with use of finer elemental powders and with decreased boron carbide concentration.

Table V

Fracture Toughness Data

Run No.	Composition wt%	K_{ICSR}* MPa $m^{1/2}$	K_{IC} Indentation MPa $m^{1/2}$
RA	1.52 B_4C-98.48 [95W-3.5Ni-1.5 Fe]	12.2	
R83	2.25 B_4C-97.75 [95W-3.5Ni-1.5 Fe]	8.2	10.5
R12	2.25 B_4C-97.74 [95W-3.5Ni-1.5 Fe]	8.0	
R13	2.25 B_4C-97.75 [95W-3.5Ni-1.5 Fe]	8.2	
R73	2.50 B_4C-97.50 [95W-3.5Ni-1.5 Fe]	8.1	9.8
R16	2.50 B_4C-97.50 [95W-3.5Ni-1.5 Fe]	8.7	
R47	2.66 B_4C-97.33 [95W-3.5Ni-1.5 Fe]	5.8	
R49	2.83 B_4C-97.13 [95W-3.5Ni-1.5 Fe]	2.8	
PA-2	4.00 B_4C-96.0 [80 W-14Ni-6.0 Fe]	15.9	
PA-5	4.50 B_4C-95.5 [75W-17.5 Ni-7.5 Fe]	17.1	
R48	5.03 B_4C-94.97 [90.9 Mo-6.4 Ni-2.7 Fe]	7.9	
R77	5.03 B_4C-94.97 [90.9 Mo-6.4 Ni-2.7 Fe]	7.3	5.8
R76	5.92 B_4C-94.08 [90.9 Mo-6.4 Ni-2.7 Fe]	4.5	5.7
PA-4	7.45 B_4C-92.65 [80.5 Mo-13.6Ni-5.9 Fe]	9.75	
PA-7	8.20 B_4C-91.8 [77.0 Mo-16.0 Ni-6.9 Fe]	7.5	
X	WC-12 Co calibration specimen	13.2	
RB	WC-4.5 Co hot pressed, unannealed	7.8	
RC	B_4C hot pressed unannealed	3.4	

*Values are the average of three or four measurements

Reaction During Sintering

In preliminary experiments with cold pressing and sintering of the original blends using 90 and 95 wt% tungsten, the specimens were heated at 100 to 150°C/h and did not densify to greater than 92% of theoretical. It was postulated that substential reactions occurred in the solid state which inhibited sintering at the liquid state sintering temperature. This suggests increased heating rates to the liquid state temperature.

A set of five blends of fine and medium size powders were prepared to study reactions and rates of reaction during sintering. All powders were screened for this series of mixtures which had the same nominal composition of 97.5 [91.0W-3.5Ni-1.5Fe] -2.5 B_4C or B. The powder lots and screen size are shown in Table VI.

Table VI

Powder Blends and Screen Size

Blend	V	W (fine)	X medium	Y fine	Z medium
W	W-140 (-400)	W-107 (-325)	W-200 (-400)	W-200 (-400)	W-107 (-325)
Ni	Ni-[illegible] (-500)	Ni-[illegible] (-500)	Ni-38 (-500)	Ni-38 (-500)	Ni-[illegible] (-500)
Fe	Fe-[illegible] (-500)	Fe-46 (-500)	Fe-46 (-500)	Fe-46 (-500)	Fe-46 (-500)
B_4C	B_4C (-400)	B_4C-[illegible] (-10μ)	B_4C-[illegible] (-10μ)	B_4C-[illegible] (-400)	B_4C-[illegible] (-400)

Boron was used in blends W and X in an effort to reduce the complexity of this material system. Powder blends were loaded in polyvinyl pressing sacks which were evacuated and isostatically pressed at 345 MPa. Portions of each pressing were separately heated at a rate of 250°C/h to temperatures of 800°, 1100, 1400, and 1460°C in hydrogen and will be examined metallographically and by x-ray diffraction. A 7-mm-diam by 38-mm-long specimen of each blend was isostatically pressed and machined for dilatometry studies. Correlation of the results from dilatometry, x-ray diffraction, metallography and electron microprobe (which will be appended) are expected to elucidate nature and extent of reactions as a function of particle size of reactants, temperature, and time at temperature.

Hot Isostatic Pressing (HIP)

Samples of the three compositions listed below were HIPPED by Argonne National Laboratory for 1h at 207 MPa and alternately at 1370°C and at 1400°C and re-examined metallographically.

R9 2.50 B_4C -97.50 [95.0 W-3.5 Ni-1.5 Fe]

R14 2.25 B_4C -92.75 [95.0 W-3.5 Ni-1.4 Fe]

R21 5.03 B_4C -94.77 [90.9 Mo-6.4 Ni-2.7 Fe]

There was no significant change in microstructure; other samples cut from the same hot pressed cylinders were recently HIPPED at 1455°C and reexamined metallographically. HIPPING at the 1455°C temperature reduced porosity and this procedure will be employed as a post hot pressing or cold press/sinter densification operation. Many commercial grades of conventional tungsten carbide-cobalt are HIPPED after sintering.

Electron Microprobe Examination

The structure of the hot pressed composition, 6.54 B_4C - 93.46 [87.11 Mo-11.89 Ni] shown in fig. 5 was examined by electron microprobe; its electron back scatter image is shown in fig. 6. Secondary electron image and two dimensional distributions for molybdenum, nickel, boron and carbon are shown in fig. 7. In addition, point count scans for the elements were made along different type grains in the electron back scatter image. Although the two dimensional scans indicate relatively uniform distributions of each element in the structure with some nickel and boron poor areas, wide compositional variations exist in different type phases as shown by the point count data recorded in Table VII. Concentration of elements for similar phases agree reasonably well.

The structure of the hot pressed composition, 4.5 B_4C-95.5 [75.0 W-17.5 Ni-7.5 Fe] was similarly examined; Structure and electron back scatter image are shown in fig. 8. Carbon and boron appear relatively uniform throughout in the two dimensional scan and there are tungsten rich and nickel/iron rich areas shown in Fig. 9 and 10. Again wide compositional variations exist for different type grains as determined by point count scans along grains in the electron back scatter image; point count scans recorded in Table VIII indicate relatively uniform element concentrations for similar phase grains.

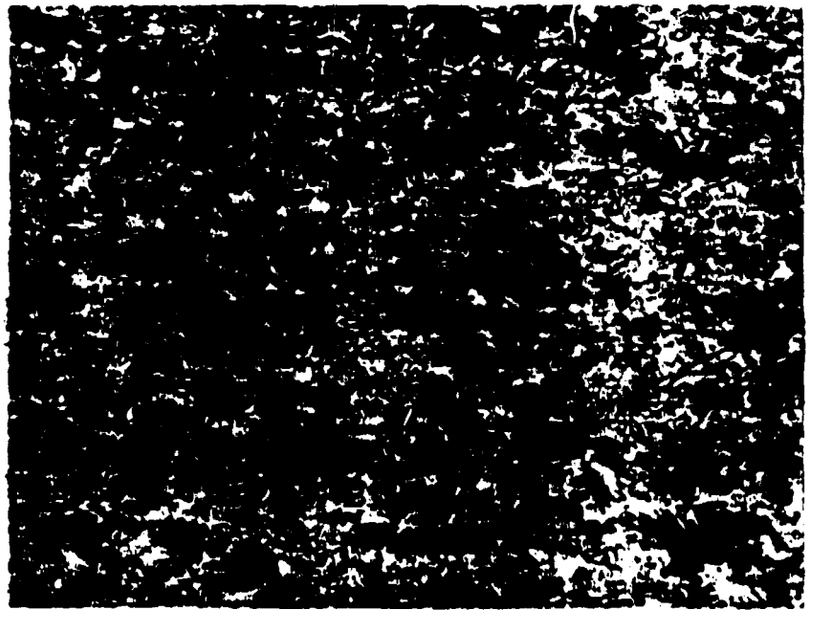


Fig. 5 Structure of 6.54 B_4C - 93.46 [87.11 Mo-12.89 Ni] 250X

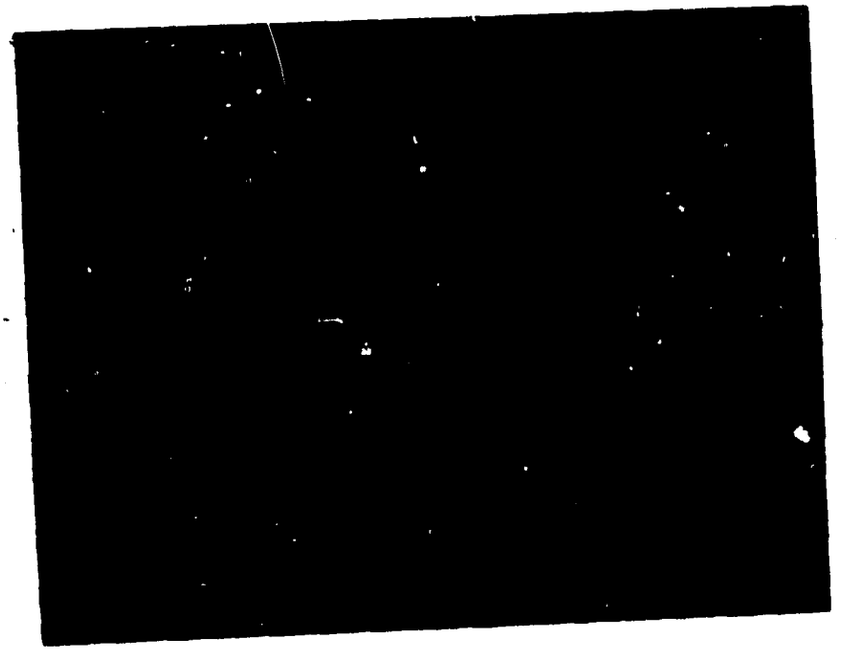
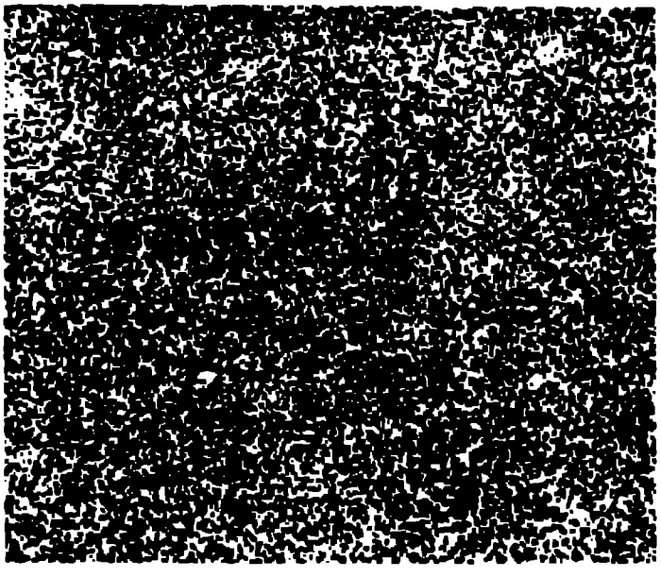
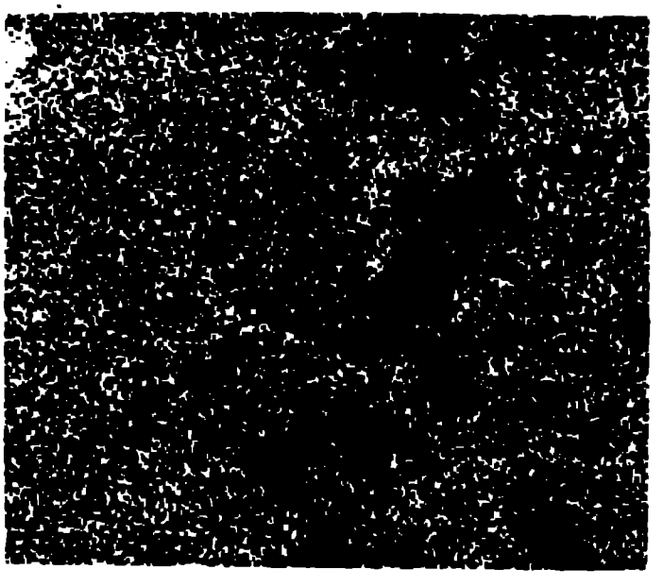


Fig. 6 Electron Back Scatter Image, 2000X

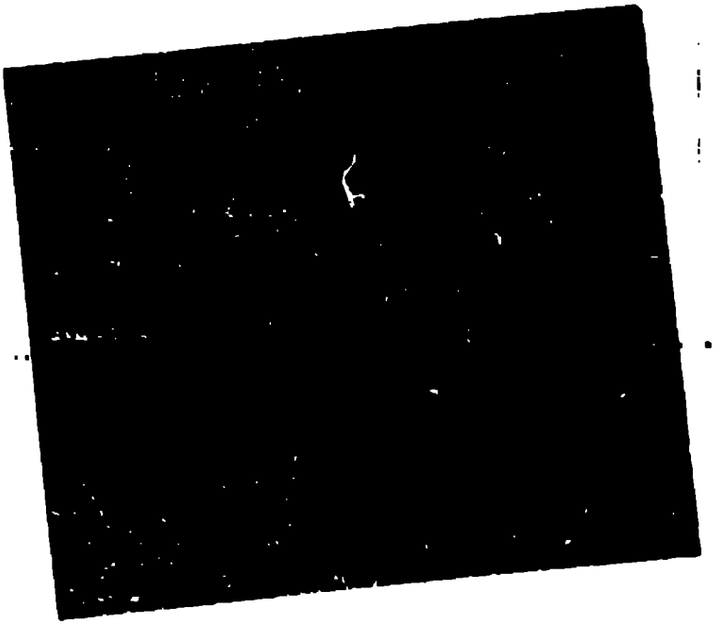


Molybdenum



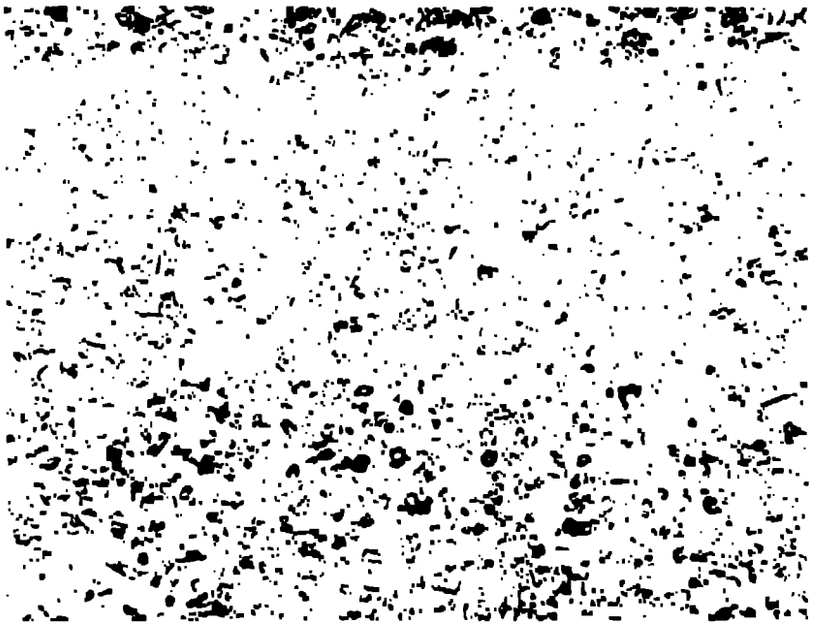
Nickel

Boron



Carbon

Fig. 7 Two dimen ional distribution for elements



Microstructure, 250X

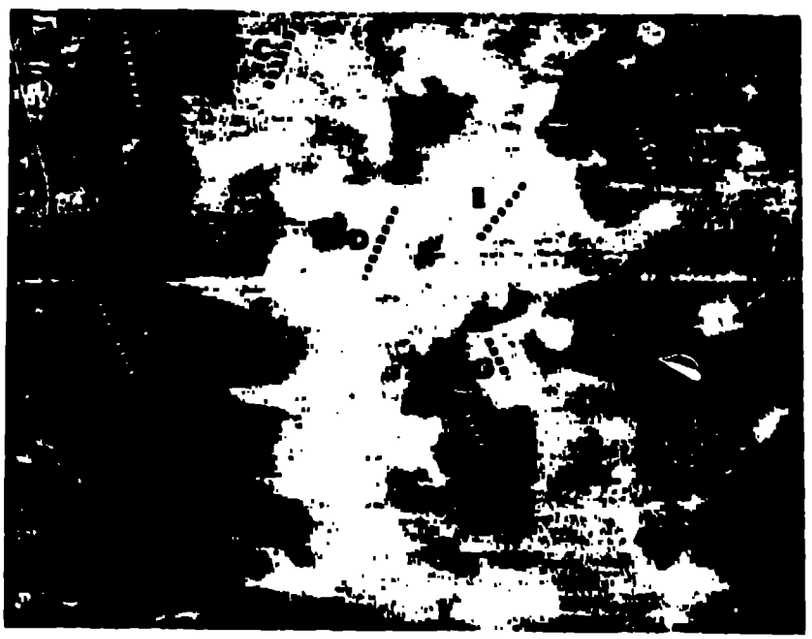
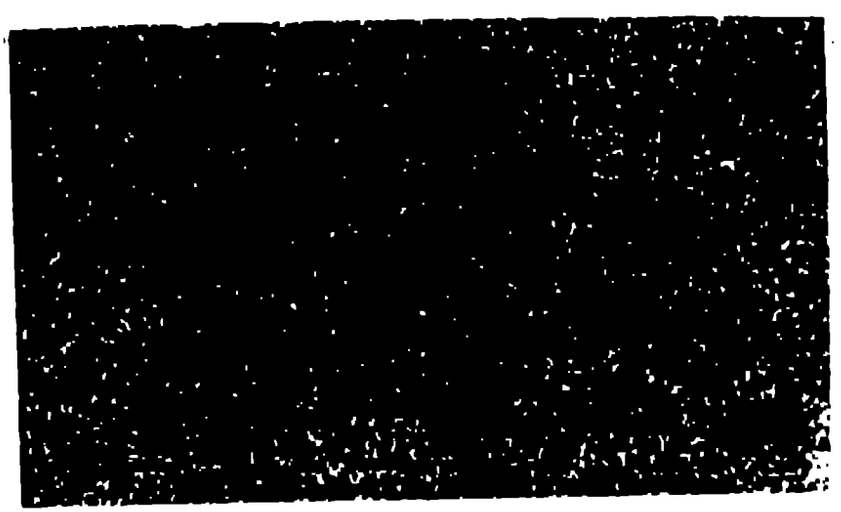


Fig. 8 Structure and Electron Image of 4.5 B_4C - 95.5 [75W-17.5 Ni-7.5Fe]

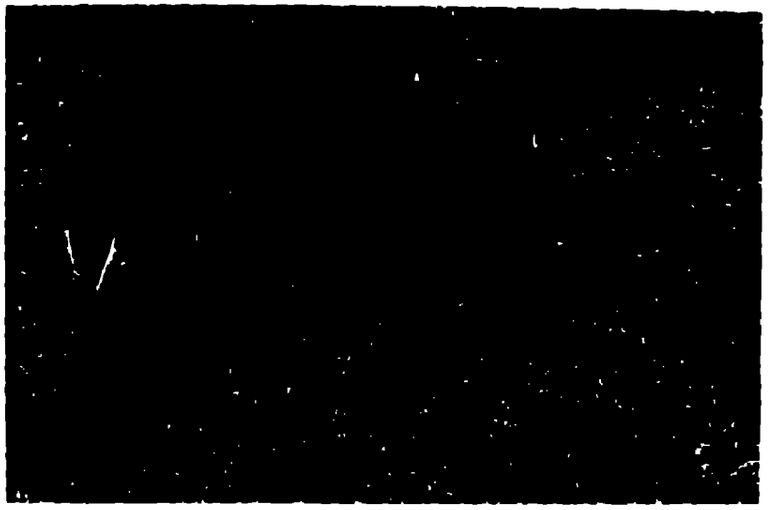
Iron

Nickel



Tungsten

Fig. 9 Two dimensional distribution of elements



Carbon

Boron

Fig. 16 Two dimensional distribution of elements

Table VII

Point Count Scan on 6.4=54 B_4C - 93.46 [87.11 Mo-12.89Ni]

	Intensity Ratio		Wt.%			
No.	S	C	Mo	Ni	Phase Description	Area
1	.046	.004	71.1	21.5	Dark Grey	A
2	.048	.002	71.5	21.4	Dark Grey	A
3	.038	.004	71.0	21.1	Dark Grey	A
4	.040	ND	71.0	21.0	Dark Grey	B
5	.047	.004	71.4	20.6	Dark Grey	B
6	.033	.002	70.6	20.9	Dark Grey	B
17	.056	.007	70.8	21.0	Dark Grey	F
18	.063	ND	70.6	20.8	Dark Grey	F
23	.043	.004	70.5	20.9	Dark Grey	H
24	.052	.006	70.1	21.0	Dark Grey	H
7	ND	.015	80.2	16.6	Med. Light Grey	C
8	ND	.015	78.7	16.9	Med. Light Grey	C
9	ND	.014	80.0	16.8	Med. Light Grey	C
10	ND	.015	79.6	16.8	Med. Light Grey	D
11	ND	.017	79.4	17.2	Med. Light Grey	D
12	ND	.014	79.1	16.9	Med. Light Grey	D
13	.071	.010	96.2	1.6	Light Light	
14	.097	.008	94.1	2.0	Med. Light Grey	E
15	.096	.010	94.0	1.8	Med. Light Grey	E
16	.087	.007	93.7	1.6	Med. Light Grey	E
19	ND	.030	93.3	1.3	Light Grey	
20	ND	.006	96.9	2.3	Light Grey	G
21	.081	.011	93.5	1.8	Light Grey	G
22	.062	.009	84.0	8.2	Light Grey	G
25	ND	.028	93.6	1.2	Light Grey	
26	ND	.028	92.2	1.9	Light Grey	
27	.068	.014	93.9	2.1	Light Grey	
28	.065	.006	73.8	16.8	Med. Dark Grey	
29	.048	.009	75.8	15.2	Med. Dark Grey	
30	ND	.017	79.1	16.8	Med. Dark Grey	

L.L.* .010 L.L. = .0020 L.L. = .07 L.L. = .06

$\cdot 10$ $\cdot 10$ $\cdot 1$ $\cdot$

*Lower limit of detection.

Table VIII

Point Count Scan of 4.5 B_4C-95.5 [75W-17.5Ni-7.5 Fe]

Point	Intensity Ratio		Wt.%				
No.	B	C	Fe	Ni	W	Phase Identification	
1	ND	.021	3.94	7.39	86.7	Light Grey	
2	ND	.024	4.06	7.12	85.4	Light Grey	A
3	ND	.021	3.19	7.02	87.1	Light Grey	
4	ND	.040	0.12	0.38	91.5	Light Grey (Ni W+C)	
7	ND	.020	3.79	7.94	85.4	"	
8	.006	.021	3.62	7.92	86.6	"	B
9	ND	.018	3.23	7.31	88.0	"	
14	ND	.028	3.45	7.16	85.3	"	
15	ND	.028	3.51	6.93	85.8	"	C
16	ND	.028	3.40	6.92	85.9	"	
17	ND	.025	3.48	7.06	86.9	"	
18	.005	.033	3.66	7.05	86.2	"	
19	ND	.024	3.37	6.90	86.4	"	D
20	ND	.027	3.17	7.18	87.0	"	
30	ND	.046	1.24	1.94	90.6	Light Grey - Edge	
32	.006	.030	4.24	9.00	84.1	"	
33	ND	.028	3.73	8.20	85.9	"	
34	ND	.030	3.85	6.15	84.2	"	
10	.020	.016	3.24	9.10	81.4	Med. Grey	
11	.024	.015	3.15	8.97	82.0	"	E
12	.010	.016	3.04	9.16	81.9	"	
13	.007	.014	3.31	9.22	81.4	"	
21	.013	.017	3.21	9.02	80.9	"	
22	.016	.022	3.16	9.41	80.6	"	
23	.012	.017	3.14	9.05	81.4	"	F
24	ND	.022	3.26	9.15	80.6	"	
25	.015	.017	3.21	9.15	80.6	"	
26	.016	.021	3.23	9.43	81.9	"	
31	ND	.015	23.0	46.4	23.3	Dark Grey	
35	ND	.018	21.0	44.8	30.0	"	G
27	ND	.013	25.8	41.4	19.2	"	
36	ND	.015	26.8	57.9	9.2	"	
37	ND	.004	26.4	57.6	10.0	"	
[illegible]	ND	.011	27.1	57.[illegible]	[illegible]	"	
[illegible]	ND	.011	24.7	54.9	[illegible]	"	H

42	ND	.015	24.0	51.1	20.2	"	
43	ND	.013	25.0	53.8	15.5	"	
5	ND	.023	3.49	7.47	85.8	Light Grey	H
6	.017	.016	3.16	9.16	81.0	Med. Grey	
27	.014	.019	3.30	9.24	81.8	"	
28	.008	.019	3.06	9.55	81.7	"	I
29	ND	.018	3.35	9.25	81.7	"	
31	ND	.016					

Abrasion Resistance

Abrasive wear resistance was determined in accordance to the ASTM standard in which abrasion resistance, A, is defined as the specimen's loss in volume per revolution of the steel wheel carrying the aluminum oxide abrasive; the wear number, W, is the reciprocal of the specimen's total volume loss in cm^3. The wear number, W, for the specimens in the as-pressed and after the 2h HIP treatment at 1300°C is recorded in Table IX. The limited data suggests an adverse effect of the HIP treatment on wear resistance, not unlike the effect with HIP of conventional tungsten carbide-cobalt which frequently causes grain coarsening and low wear number. The higher values of the wear numbers are in the range of numbers for wear resistance grades of conventional material.

Table I.

Abrasion Test Wear Number, W

Run	Composition Blend	Blend*	Wear Number, W, $(cm^3)^{-1}$	
			As pressed	After HIP
6	2.5 B_4C-97.5 [95W-3.5Ni-1.5Fe]	A	38.9	30.3
7	2.5 B_4C-97.5 [95W-3.5Ni-1.5Fe]	B	—	24.7
14	2.0 B_4C-98.0 [95W-3.5Ni-1.5Fe]	A	20.9	16.9
15	2.0 B_4C-98.0 [95W-3.5Ni-1.5Fe]	B	24.3	22.9

*Blend A medium size powder

Blend B fine size powder

Conclusions

With this cobalt-free, non-conventional family of hard materials, still in its embryonic stage of development, hardness in the range of the hardest conventional tungsten carbide-cobalt material has been achieved and superiority over the conventional material for ultra high pressure anvil application has been demonstrated.

The compositional range of this Metal-Boron-Carbon system has been dramatically extended both in the tungsten and molybdenum series to permit tailoring the density from 7.8 to 17.1 Mg/m^3 while maintaining essentially the same high hardness. Fracture toughness of the earlier compositions of 90 to 95 wt% tungsten or 91% molybdenum were in the 7 to 10 MPa$\sqrt{m}$ range, but fracture toughness of ~16 and 17 MPa $\sqrt{m}$ were obtained with materials containing only 80 and 75% tungsten successively, indicating achievement of the necessary high toughness for tool and rock bit applications and a fertile field of study of toughness as a function of tungsten content (and probably molybdenum).

High hot microhardness is another important property for machine tool bit and rock drilling bit applications, and the achievement of 10-20% higher values of hardness at 1,000°C than that attainable with conventional tungsten carbide-cobalt materials is also extremely encouraging for these applications.

Electron microprobe examination confirmed relatively uniform distribution of elements in the hot pressed specimens, and microcompositional variation in grains which suggests use of finer powders. Results of x-ray diffraction, metallographic examination and electron microprobe analysis of specimens (of the five powder blends of medium and fine powders) sintered at varying temperatures are expected to elucidate effect of powder size on microcompositional variation.

Progress has been made in achieving relatively high density in specimens made by the economically favored cold press/sinter process, but hot isostatic pressing of these materials prior to testing probably will prove necessary.

It is believed that the principal contribution to hardness is primarily due to formation of tungsten or molybdenum borides, borocarbides and carbides, but considerable effort is necessary to define the nature and extent of reactions involved. Optimizing the composition, raw material properties and fabrication parameters to achieve microstructure uniformity, refined grain size and an improved combination of toughness, compressive strength, high hardness and abrasion resistance is necessary for commercial application of this new material system.

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REFERENCES

[a] H. Sheinberg, Nonconventional Tungsten Base Hard Metal, Int. J. of Refractory and Hard Metals, Vol 2 No 1 March 1983 pg. 17-26.
[b] Fisher Scientific Co., Boston MA
[c] Micromeritics Instrument Co., Norcross, GA
[d] Nuclear Materials and Instrument Co., Apollo, PA
[e] Division of Air Reduction Co., St. Mary's, PA
[f] Wilson Mechanical Instrument, Division of American Chain and Cable Co.
[g] L. M. Barker, "A Simplified Method for Measuring Plain Strain Fracture Toughness", Eng. Fract. Mech. 9, 361-369 (1977)
[h] R. Anstis, P. Chantakul, B. R. Lawn, D. B. Marshall A Critical Review of Indentation Techniques for Measuring Fracture Toughness: I Direct Crack Methods. J. Am. Cer. Soc. Vol 64 No 9 pgs. 533-538.