LA-UR -82-1140

Conf- 821102--1

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LA-UR--82-1140

DE82 014051

TITLE: NONCONVENTIONAL HARD-METAL COMPOSITIONS

AUTHOR(S): HASKELL SHEINBERG

SUBMITTED TO: SIXTH INTERNATIONAL CONFERENCE ON POWDER METALLURGY, BRNO, CZECHOSLOVAKIA, NOVEMBER 10-12, 1982

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Los Alamos National Laboratory
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FORM NO 836 R4
ST NO 2629 5/81

NONCONVENTIONAL HARD-METAL COMPOSITIONS

by

Haskell Sheinberg

U.S.A.

ABSTRACT

A novel hard-metal composition comprising borides and carbides of tungsten, nickel, and iron is made by reaction hot-pressing mixtures of elemental tungsten, nickel, and iron powders with small quantities of boron carbide. The hardness of these compositions is in the range of the hardest conventional tungsten carbide-cobalt compositions. It was subsequently determined that molybdenum can be substituted in part or totally for the tungsten in the composition with a minimum reduction in hardness. This new composition can be used in high-pressure anvils; it sustains higher pressures than commercial carbides without plastic deformation.

Introduction

Hard metal compositions that contain no cobalt are of considerable interest because of dependence on relatively unstable sources of supply for this strategic material. The presentation describes preliminary powder metallurgy work with a metal-boron-carbon system (M-B-C), wherein the metal was principally the well known tungsten-nickel-iron "heavy metal", and boron carbide was used as the source of boron and carbon. Nonstrategic molybdenum was substituted in part or totally for the tungsten in some of the work.

Procedures and Equipment

A weighed charge of the blended constituents was leveled in the cavity of a graphite die. The die was positioned in a 102-mm-I.D. induction coil coupled to a 50 kW, 10 kHz power supply. A typical time-temperature-pressure cycle for hot pressing a 3?.-mm-diam by 25.-mm-long cylinder is shown in Fig. 1; hot pressing was performed in an argon atmosphere.

Metallography

The structure of conventional 95 wt% W-3.5 Ni-1.5 Fe "heavy metal" alloy is shown in Fig. 2a; hardness of this alloy is 60 to 65 Rockwell A (R_A). The structure is drastically altered by small amounts of boron carbide. Figure 2b shows the relatively uniform, finer angular grain structure obtained when 2 wt% or more boron carbide is added to the "heavy metal".

DATA

Hardness

Results of the hardness tests on selected M-B-C compositions are shown in Table I. This data shows that maximum and average hardness values are in the range of the highest hardness tungsten carbide-cobalt compositions.

TABLE I HARDNESS OF SELECTED W-B-C PRESSING

RUN NO.	B_4C CONC.	W	Ni	Fe	Mo	MAX	AV
		ALLOY COMPOSITION				HARDNESS	
	WT%	WT%				R_A	
5	1.52	95	3.5	1.5		87.5	85.5
6	2.50	95	3.5	1.5		93.0	92.6
7	2.75	95	3.5	1.5		94.0	93.2
11	2.58	95	3.5	1.5		92.9	92.5
12	2.67	95	3.5	1.5		93.4	92.1
25	2.67	95	3.5	1.5		92.9	89.8
26	3.00	90	7.0	3.0		92.8	92.1
38	5.03		6.4	2.7	90.9	91.9	91.5
39	5.92		6.4	2.7	90.9	91.8	90.7
41	2.76	76	3.5	1.5	19.0	90.1	89.3

Microprobe Analysis

A specimen of hot-pressed 1.5 wt% B_4C-98.5 wt% tungsten alloy was examined by electron microprobe. The area examined consisted of large grains and essentially featureless matrix areas between areas of the grains. The carbon appeared to be relatively constant across matrix and grains; the grain regions containing high concentrations of tungsten and boron but almost no nickel or iron are probably tungsten boride containing some carbon. The other regions contained no detectable boron, high nickel and iron, and somewhat variable tungsten concentrations with the tungsten concentration being considerably lower than in regions containing boron. The hardness of the grains averaged ~2500 DPH, whereas the hardness in the matrix material was ~500 DPH.

High Pressure Anvil Test

Two Bridgman anvils, made with a 2.7 wt% B_4C-97.3 wt% tungsten alloy, were tested with a Jamieson high-pressure x-ray diffraction apparatus to determine the ability of the anvil material to sustain high pressure without deformation. Additionally, sets of premium-grade commercial tungsten carbide-cobalt were tested. Pressure was applied to each set of anvils, the pressure was measured, and after the pressure was released, the deformation across the 2.54-mm flat bearing the peak load was measured. The results are summarized in Table II. It should be noted that none of the anvils failed.

TABLE II RESULTS OF HIGH PRESSURE ANVIL TESTS

MATERIAL COMPOSITION WT%	PEAK PRESSURE GPA	PEAK PRESSURE KBAR	AVERAGE DEFORMATION MICRONS
2.67 B_4C-97 TUNGSTEN ALLOY (95% W)	14.0	145	1
91.0 WC-90 Co, GE-779	12.0	124	14
94.2 WC-5.8 Co, KENNAMETAL K68	10.8	112	11
94.0 WC-6.0 Co, GE-883	11.1	115	11
94.0 WC-6.0 Co, GE-883 (HIPPED)	13.5	140	11

Fracture Toughness

Slotted short rod fracture-toughness specimens, were tested with a Fractometer I instrument. The test results and the values determined by the instrument manufacturer on commercial tungsten carbide-cobalt materials are shown in Table III. For comparison, reported K_{ICSR} values for unspecified grades and compositions of WC-Co range from 6.17 to 16.80 $MPa\sqrt{m}$. It is possible that a post hot pressing heat treatment will increase the fracture toughness values. The B_4C-alloy fracture-toughness and compression specimens were cored from larger diameter hot pressings by electrical discharge machining (EDM), a method that causes microcracks in tungsten carbide-cobalt compositions. Effects of EDM on the B_4C W-alloy or B_4C-Mo alloy have not been explored.

TABLE III

FRACTURE TOUGHNESS DATA

RUN NO.	COMPOSITION	K_{ICSR} (MPa $\sqrt{m}$)
RA	1.52 wt% B_4C-98.48 wt% (95W-3.5Ni-1.5Fe)	12.20
R47-1	2.66 wt% B_4C-97.33 wt% (95W-3.5Ni-1.5Fe)	6.60
R47-2	2.66 wt% B_4C-97.33 wt% (95W-3.5Ni-1.5Fe)	5.00
R48-1	5.03 wt% B_4C-94.97 wt% (90.9Mo-6.4Ni-2.7Fe)	7.90
R48-2	5.03 wt% B_4C-94.97 wt% (90.9Mo-6.4Ni-2.7Fe)	7.60
R48-3	5.03 wt% B_4C-94.97 wt% (90.9Mo-6.4NI-2.7Fe)	8.10
R49-1	2.83 wt% B_4C-97.13 wt% (95W-3.5Ni-1.5Fe)	2.90
R49-2	2.83 wt% B_4C-97.13 wt% (95W-3.5Ni-1.5Fe)	2.80
R49-3	2.83 wt% B_4C-97.13 wt% (95W-3.5Ni-1.5Fe)	2.60
X	WC-12 wt% Co CALIBRATION SPECIMEN	13.20
RB	WC-4.5% Co (HOT PRESSED, UNANNEALED)	7.81
RC	B_4C (HOT PRESSED, UNANNEALED)	3.35

Compressive Strength

Compression test results of two compositions and of a commercial-grade tungsten carbide-cobalt tested with the same equipment are presented in Table IV. The values obtained for WC-Co were considerably lower than those reported by the manufacturer, possibly because surface finish on tested specimens may not have been as smooth as the finish on specimens tested by the manufacturer.

Abrasion Resistance

Abrasion resistance determined in accordance with proposed standard ASTM-B9-06.11 and hardness of hot pressed B_4C-content materials are shown in Table V together with published values of those properties of conventional hard metals. Test data from the limited number of materials containing boron carbide indicate abrasion resistance in the range of high cobalt content tungsten carbide but a factor of ~3 less than premium-grade low cobalt content hard metals.

TABLE IV COMPRESSIVE STRENGTH OF M-B-C ALLOYS AND WC-Co

SPECIMEN NO.	COMPOSITION	COMPRESSIVE (GPa)	STRENGTH (Kpsi)
R56-1	2.67 wt% B_4C-97.33 wt% (95 W-3.5Ni-1.5Fe)	3.75	545
R56-2		3.58	520
R56-3		3.93	570
R57-1	5.03 wt% B_4C-94.87 wt% (90.9Mo-6.4Ni-2.7Fe)	3.05	442
R57-2		2.99	434
R57-3		2.93	426
K-68-1	94.2 wt% WC-5.8 wt% Co	5.43	790
K-68-2		5.04	732
K-58-3		4.07	590

TABLE V ABRASION RESISTANCE TEST DATA

RUN NO. OR GRADE	B_4C WT%	ALLOY OR CARBIDE COMPOSITION WT% W	Mo	Ni	Fe	WC	Co	ABRASION RESISTANCE 1/VOLUME REMOVED	HARDNESS RANGE R_A
R-41	2.67	76.0	19.0	3.5	1.5			2.9	88.9-89.4
R-44	2.50	95.0		3.5	1.5			10.7	92.6-92-8
R-46	5.03	90.9	6.4	2.7				6.3	91.5-91.8
GE-55B						84.0	16.0	2.8	86.0-87.1
GE-779						91.0	9.0	10.0	89.0-89.7
GE-241						90.0	10.0	6.0	88.1-88-8
GE-248						89.0	11.0	7.0	89.4-90.1
GE-883						94.0	6.0	35.0	91.7-92.2

Observations

The hardness and structure of conventional "heavy metal" alloys are altered drastically by the addition of small amounts of boron carbide to yield relatively uniform and relatively fine grained structures.

Within the limited range of tested compositions, the maximum hardness was achieved when 2.50 to 2.75 wt% boron carbide was added to the 95 wt% tungsten alloy and when 3.00 to 3.25 wt% boron carbide was added to the 90 wt% tungsten alloy. Average hardness values ranged from 91.5 to 93.5 R_A. Within the limited range of boron carbide additions made to the molybdenum alloy, the 5.0 to 5.9 wt% range yielded average hardness values of 90.7 to 91.5 R_A.

Substituting a prealloyed W-Ni-Fe powder for elemental powder blend of the same composition did not appear to affect structure or hardness. Maximum density achieved by cold pressing and sintering these compositions was only 96% of theoretical and maximum hardness was only 87 R_A.

The structures of all these compositions appear considerably coarser than the structures of most commercial "hard metals". It is likely that reduction in time at temperature during the liquid phase hot pressing and use of a finer tungsten powder would reduce grain growth drastically. It should be pointed out the density of this family of hard materials can be varied for ~10 to 17 mg/m^3.

Conclusions

This new type of hard metal, still in its embryonic state of development, had demonstrated superiority for ultra high pressure anvil application. High hardness values comparable to values of the hardest commercial tungsten carbide-cobalt compositions, indicate a potential utility for tool bit, munitions, and abrasion resistance applications. Substitution of molybdenum for tungsten with only slightly reduced hardness indicated a potential for reduction in use of strategic tungsten powder.

Although it is almost certain that the principal contribution to hardness is the formation primarily of tungsten boride, considerable effor will be necessary to define the nature and extent of the reactions involved and to optimize the compositions, raw material properties, and fabrication parameters to achieve structure uniformity, finer grain size, and an improved combination of toughness, compressive strength, high hardness, and abrasion resistance.

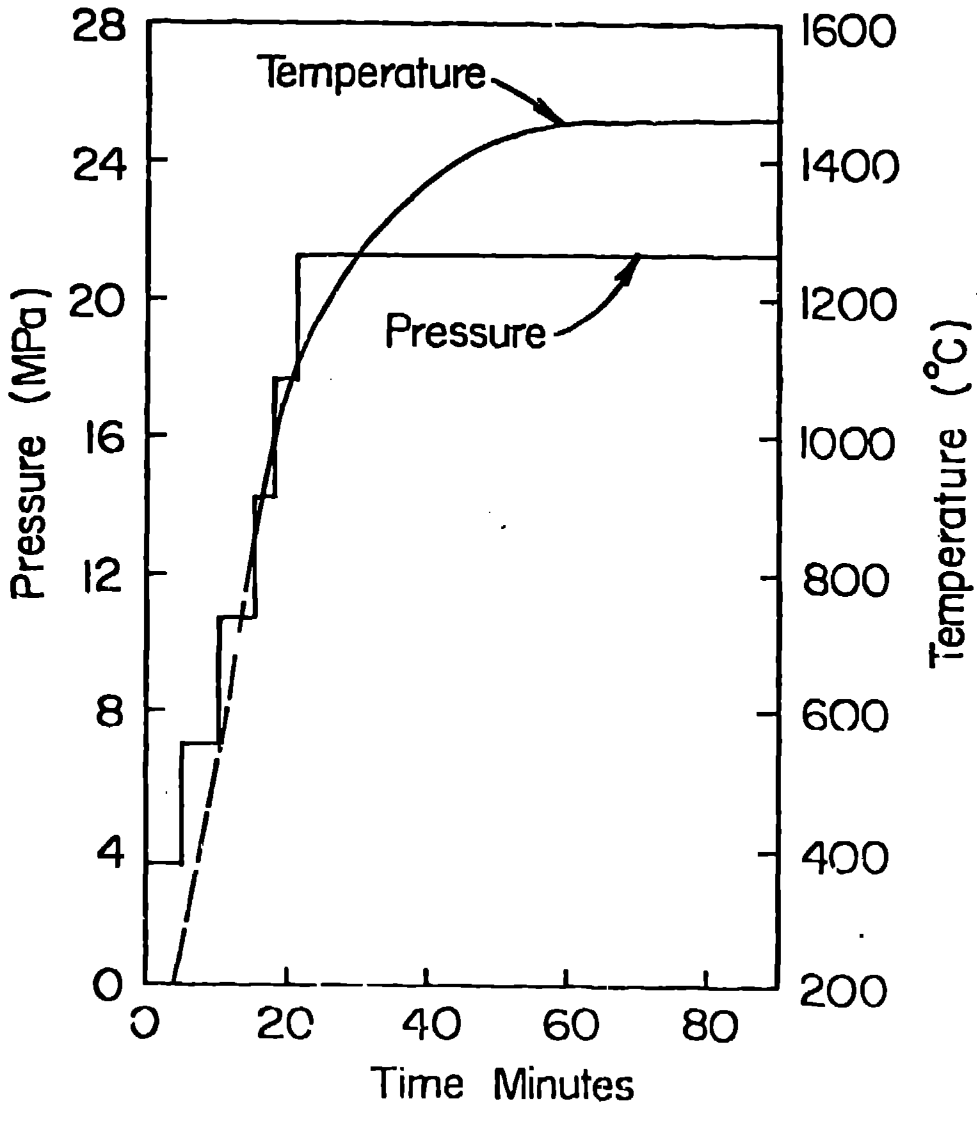

Fig. 1 Time-Temperature-Pressure Cycle

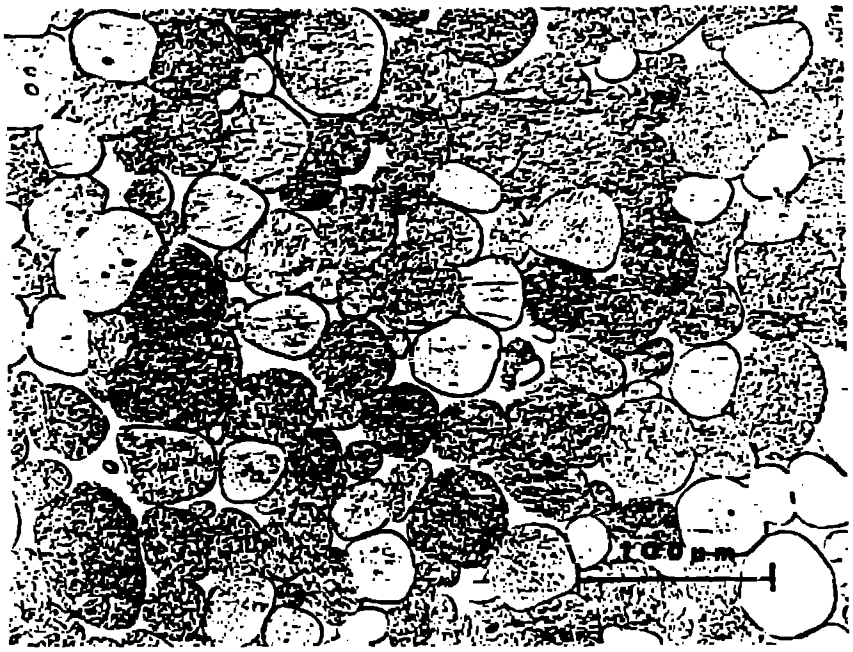

Fig. 2a. Structure of 95 W-3.5 Ni-1.5 Fe "Heavy Metal"

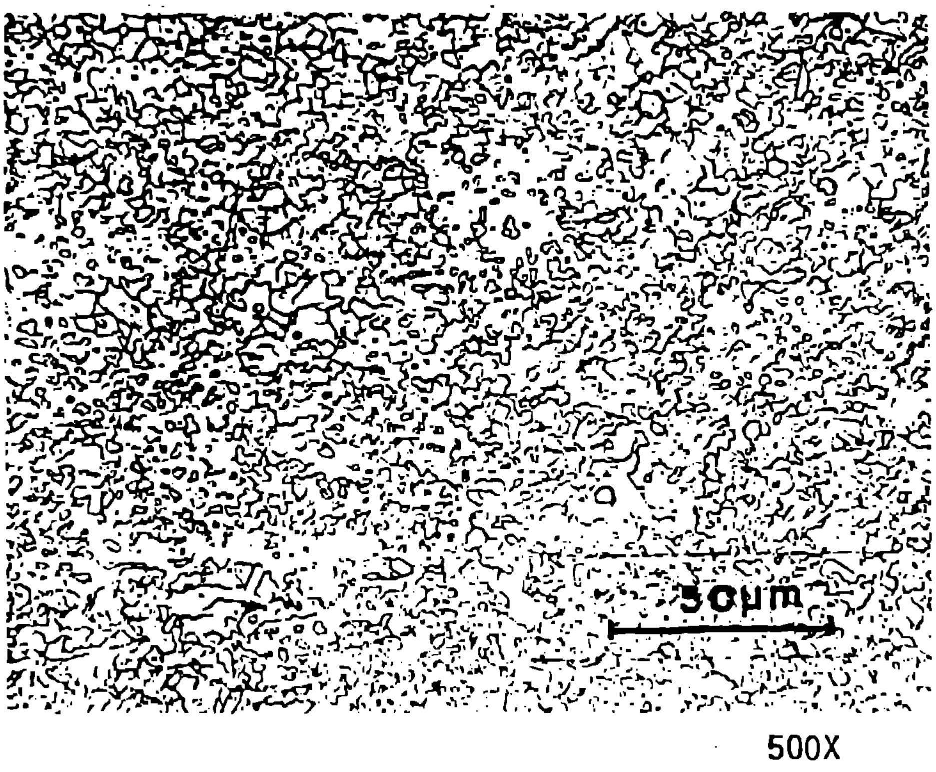

Fig. 2b. Structure of 95 W-3.5 Ni-Fe with 2.0 wt% B_4C