Quarterly Report No. 3

INVESTIGATION OF THE FRACTURE MECHANICS OF BORIDE COMPOSITES

Contract No. NASW-2088

Submitted to:

NASA Headquarters
Washington, D.C. 20548

Attention: Mr. James Gangler

June 1971

MATERIALS RESEARCH AND DEVELOPMENT

MANLABS, INC.
21 ERIE STREET
CAMBRIDGE 39
MASSACHUSETTS

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I. INTRODUCTION AND SUMMARY

A. Introduction

The present study of the fracture mechanics of diboride composites has progressed during the past quarter with principal emphasis on the generation of impact and slow bend fracture energies in order to establish the characteristics of the base composites and cobalt bonded tungsten carbide. Fabrication studies of boride composites containing additive materials is continuing and some success has been achieved in lowering the hot pressing temperature by means of metallic additives. This advantage will provide extended flexibility in adding and maintaining the strength of graphite and alumina fibers in future fabricating experiments. Nevertheless, the main emphasis during the past quarter was measurement of the fracture strength for a large number of samples in order to establish meaningful baseline data. As a consequence, this report is principally concerning with presenting the results of the fracture energy tests and reporting of fabrication experiments will appear in the final report which will be prepared during the next six weeks.

A. Summary

Approximately fifty measurements of the energy required to fracture notched bars of boride composites and cobalt bonded tungsten carbide were carried out during the present reporting period. The results of these tests as well as those reported earlier (1,2)* are presented below. These data provide a description of the fracture energies of current boride composites and allow a direct comparison to be made with cobalt bonded tungsten carbide. The latter is chosen as a base for comparison since it is a brittle ceramic type material which has been improved markedly by addition of

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* Underscored numbers in parentheses denote references

the cobalt binder. The temperature and oxidation resistance of WC and/ or WC-6Co is substantially less than that of the present boride composites. The latter however do not exhibit the fracture energies which characterize WC-6Co. Hence the goal of this study is to provide a means for raising the fracture energy of the boride composites to the level of WC-6Co.

The present measurements indicate that fracture energies of 2.69 in-lbs/in^2 and 73.9 in-lbs/in^2 are characteristic of standard size charpy bars of WC-6Co broken in slow bend and impact tests respectively. As indicated earlier (2) the large difference (of a factor of 27) is quite surprising since strain rate factors should not be important for a brittle material. Similar tests conducted on high strength tool steels like H-11 never show a disparity exceeding 60% for these energies. Slow bend tests on WC-6Co samples having a thickness of 0.200 inches rather than the standard 0.394 inches yielded an average fracture energy of 2.51 in-lbs/in^2 as compared with the 2.69 in-lbs/in^2 result cited above. Thus, no substantial effect of size is noted in this range (t = 0.200 and 0.394 inches).

By comparison, Boride V ($80^v/o ZrB_2 + 20^v/o SiC$) yielded fracture energies of 0.65 and 24.3 in-lbs/in^2 in the slow bend and impact tests, while Boride VIII ($56^v/o ZrB_2 + 14^v/o SiC + 30^v/o C$) exhibited fracture energies of 1.16 and 17.7 in lbs/in^2 in the slow bend and impact tests. Modification of the carbon distribution in Boride VIII in order to obtain better machinability results in a composite designated Boride VIII-M2 of the same composition ($56^v/o ZrB_2 + 14^v/o SiC + 30^v/o C$). The measured fracture energies for this material are 1.30 and 17.3 in lbs/in^2. Thus in all of the cases studied, the impact fracture energy is much larger (13 to 37 times larger) than the slow bend fracture energy. Moreover, the fracture energies which characterize the current boride composites are 33% to 50% of the values observed for cobalt-bonded tungsten carbide.

II. RESULTS OF FRACTURE TESTS

The results of the slow bend and impact tests conducted on the boride composites and cobalt bonded tungsten carbide are presented in Tables 1 through 5. Table 6 contains a summary of the average values of fracture energy for each material and sample size. The details concerning test procedures and sample configuration were presented earlier (1,2). Briefly, sample bars are 2.175 inches long and 0.394 inches high. A 45° notch with a 0.001" radius at the root is machined to a depth of 0.073 inches in the height dimension. The thickness, t, of standard charpy bars is 0.394 inches. In the present series of tests thickness of t = 0.125, 0.200 and 0.394 have been employed. The impact tests are conducted on a ManLabs Model CIM-1 (24 ft-lb) impact tester with a read-out accuracy of 0.01 in-lbs. The slow bend tests are conducted in three point bending using a span length, l, of 1.75 inches at a loading rate of 100 lbs/minute so that failure is observed in one or two minutes. Metallographic and electron fractographic results for the boride composites and cobalt bonded tungsten carbide have been presented earlier (1,2).

Tables 1-5 present data on the height under the notch, l, and the thickness of the test bars. In addition, the slow bend tests are characterized by the maximum load, P, and the energy, W, under the load-deflection curve (1). The fracture energy values for both slow bend and impact tests in units of in-lbs/in^2 is presented for each of the materials tested.

The slow bend fracture energies for Boride V are shown in Table 1 for a range of thicknesses. Reference to the mean values for these tests in Table 6 shows values of 0.65, 0.61 and 0.72 in-lbs/in^2 for bars which

TABLE I

SUMMARY OF NOTCHED BAR SLOW BEND AND IMPACT TESTS OF BORIDE V ($80^{v}/oZrB_2-20^{v}/oSiC$)

SLOW BEND TESTS

l = span length = 1.75 inches

Number	h (in)	t (in)	P(max) (lbs)	W (in-lbs)	A (in^2)	Slow Bend Fracture Energy (W/A) ($in-lbs/in^2$)
3-13-4	0.319	0.390	225	0.0844	0.1243	0.679
5-28-1	0.317	0.394	221	0.0774	0.1249	0.620
5-28-2	0.317	0.394	231	0.0832	0.1249	0.666
5-28-3	0.315	0.394	230	0.0771	0.1241	0.621
3-13-5	0.313	0.202	99	0.0386	0.0632	0.611
3-13-6	0.313	0.201	106	0.0445	0.0629	0.707
5-28-4	0.315	0.200	114	0.0345	0.0630	0.548
5-28-5	0.318	0.200	116	0.0394	0.0636	0.619
5-28-6	0.317	0.200	116	0.0348	0.0634	0.549
3-13-7	0.314	0.127	68	0.0275	0.0397	0.693
5-28-7	0.317	0.125	70	0.0311	0.0396	0.785
5-28-8	0.316	0.125	68	0.0278	0.0395	0.704
5-28-9	0.317	0.125	68	0.0269	0.0396	0.679
Boride V + Nickel ($70^{v}/oZrB_2-20^{v}/oSiC-10^{v}/oNi$)						
8-6-1	0.322	0.201	85	0.0298	0.0647	0.461
8-6-2	0.324	0.201	74	0.0377	0.0651	0.579
8-6-3	0.324	0.201	69	0.0417	0.0651	0.641
8-6-4	0.319	0.201	78	0.0384	0.0641	0.599
Boride V + Graphite Cloth -1/8" Spacing						
HP80-4	0.314	0.394	206	0.0847	0.124	0.683
Boride V + Graphite Cloth -1/16" Spacing						
HP82-3	0.314	0.394	164	0.0822	0.124	0.663
HP82-4	0.314	0.394	164	0.0644	0.124	0.519

IMPACT TESTS

Number	h (in)	t (in)	ft-lbs	Impact Energy = ($in-lbs/in^2$)
HP-28-1	0.315	0.393	0.222	21.5
HP-28-2	0.317	0.393	0.225	21.7
31-LIC	0.317	0.394	0.203	19.6
31-L2C	0.311	0.393	0.382	37.5
31-L3C	0.317	0.394	0.241	23.2
31-L4C	0.316	0.394	0.223	21.5
31-L5C	0.315	0.394	0.277	26.8
31-L6C	0.315	0.394	0.229	22.2
Boride V + Graphite Cloth - 1/8" Spacing				
HP80-1	0.316	0.393	0.272	26.3
HP80-2	0.314	0.393	0.294	28.6
Boride V + Graphite -1/16" Spacing				
HP82-1	0.312	0.393	0.255	25.0
HP82-2	0.312	0.393	0.262	25.6

TABLE 2

SUMMARY OF NOTCHED BAR SLOW BEND AND IMPACT TESTS OF TUNGSTEN CARBIDE - $6^{w}/oCo$ ($90^{v}/oWC-10^{v}/oCo$)

SLOW BEND TESTS

l = span length = 1.75 inches

Number	h (in)	t (in)	P(max) (lbs)	W (in-lbs)	A (in^2)	Slow Bend Fracture Energy (W/A) (in-lbs/ in^2)
10-6-5	0.316	0.203	270	0.1431	0.0641	2.23
10-6-6	0.317	0.202	268	0.1675	0.0640	2.62
10-6-7	0.317	0.202	282	0.1720	0.0643	2.68
10-6-8	0.317	0.202	254	0.1600	0.0640	2.50
4S	0.309	0.394	482	0.2076	0.1217	1.71
9S	0.322	0.395	562	0.3934	0.1272	3.09
10S	0.316	0.394	530	0.3551	0.1243	2.86
11S	0.317	0.395	535	0.3478	0.1252	2.78
12S	0.319	0.395	558	0.3794	0.1260	3.01

IMPACT TESTS

Number	h (in)	t (in)	ft-lbs	Impact Energy = (in-lbs/in^2)
1C	0.318	0.394	0.608	58.2
2C	0.313	0.394	0.700	68.1
6C	0.314	0.395	0.916	88.9
7C	0.311	0.395	0.754	73.8
8C	0.312	0.395	0.778	76.0
13C	0.316	0.395	0.878	85.5
14C	0.320	0.395	0.706	67.1

TABLE 3

SUMMARY OF NOTCHED BAR SLOW BEND AND IMPACT TESTS OF BORIDE VIII ($56^{v}/o ZrB_2 - 14^{v}/o SiC - 30^{v}/o C$)

SLOW BEND TESTS

l = span length = 1.75 inches

Number	h (in)	t (in)	P(max) (lbs)	W (in-lbs)	A (in^2)	Slow Bend Fracture Energy (W/A) ($in-lbs/in^2$)
D198						
10-6-1	0.318	0.202	112	0.0689	0.0641	1.08
10-6-2	0.317	0.201	111	0.0705	0.0636	1.11
10-6-3	0.321	0.200	115	0.0661	0.0642	1.03
D201M						
3S	0.314	0.394	190	0.1101	0.1240	0.89
4S	0.314	0.394	180	0.1074	0.1240	0.87
11S	0.321	0.393	212	0.1717	0.1260	1.36
12S	0.318	0.393	203	0.1543	0.1248	1.24
13S	0.313	0.393	206	0.1751	0.1230	1.42
14S	0.314	0.393	205	0.1579	0.1234	1.28
15S	0.317	0.393	201	0.1387	0.1244	1.12
16S	0.315	0.393	206	0.1318	0.1238	1.07

IMPACT TESTS

Number	h (in)	t (in)	ft-lbs	Impact Energy = ($in-lbs/in^2$)
D201M				
5C	0.318	0.393	0.169	16.3
6C	0.314	0.393	0.173	16.8
7C	0.316	0.393	0.196	19.0
8C	0.318	0.394	0.200	19.2
9C	0.316	0.394	0.193	18.7
10C	0.319	0.393	0.172	16.5
1C	0.310	0.394	0.181	17.8
2C	0.311	0.394	0.172	17.5

TABLE 4

SUMMARY OF NOTCHED BAR SLOW BEND AND IMPACT TESTS

OF BORIDE VIII ($56^{v}/oZrB_2$-$14^{v}/oSiC$-$30^{v}/oC$) M2

SLOW BEND TESTS

l = span length = 1.75 inches

Number	h (in)	t (in)	P(max) (lbs)	W (in-lbs)	A (in^2)	Slow Bend Fracture Energy (W/A) (in-lbs/in^2)
HP45						
8-31-1	0.316	0.200	120	0.1140	0.0632	1.80
8-31-2	0.321	0.200	123	0.0836	0.0642	1.30
8-31-3	0.317	0.200	122	0.0970	0.0632	1.53
8-31-4	0.318	0.200	147	0.1169	0.0635	1.84
NP2						
3S	0.314	0.394	224	0.1668	0.1240	1.36
4S	0.314	0.394	179	0.1250	0.1240	1.01
11S	0.317	0.394	208	0.1726	0.1249	1.38
12S	0.317	0.394	176	0.1584	0.1249	1.27
13S	0.315	0.394	198	0.1841	0.1241	1.48
14S	0.314	0.394	181	0.1620	0.1237	1.31
15S	0.315	0.394	178	0.1566	0.1241	1.26
16S	0.313	0.394	179	0.1593	0.1233	1.29

IMPACT TESTS

Number	h (in)	t (in)	ft-lbs	Impact Energy = (in-lbs/in^2)
NP2				
1C	0.318	0.393	0.168	16.1
2C	0.314	0.393	0.186	18.1
5C	0.315	0.394	0.183	17.7
6C	0.317	0.394	0.170	16.3
7C	0.314	0.394	0.169	16.4
8C	0.318	0.394	0.172	16.5
9C	0.315	0.394	0.213	20.6
10C	0.310	0.394	0.173	17.0

TABLE 5

SUMMARY OF NOTCHED BAR IMPACT TESTS

OF $80^{w}/o ZrB_2-20^{w}/o$ NICKEL

Number	h (in)	t (in)	ft-lbs = Impact Energy =	(in-lbs/in^2)
HP901C	0.317	0.394	0.266	25.6
HP902C	0.316	0.394	0.286	27.6
HP911C	0.317	0.394	0.239	23.0
HP912C	0.318	0.394	0.252	24.2

TABLE 6

SUMMARY OF NOTCHED BAR SLOW BEND

AND IMPACT TEST DATA

(height under notch, h = 0.312-0.324 inches)

Material	Bar Thickness t (in)	Average Slow Bend Fracture Energy (in-lbs/in^2)	Average Impact Fracture Energy (in-lbs/in^2)
Boride V	0.394	0.65	24.3
Boride V	0.200	0.61	-
Boride V	0.125	0.72	-
Boride V+ Nickel	0.201	0.57	-
Boride V+ Graphite Cloth (1/8" Spacing)	0.394	0.68	27.5
Boride V+ Graphite Cloth (1/16" Spacing)	0.394	0.59	25.3
90^v/oWC-10^v/oCo	0.202	2.51	-
90^v/oWC-10^v/oCo	0.394	2.69	73.9
Boride VIII	0.202	1.07	-
Boride VIII	0.394	1.16	17.7
Boride VIII M2	0.200	1.62	-
Boride VIII M2	0.394	1.30	17.3
ZrB_2+ Nickel	0.394	-	25.1

are 0.394, 0.200 and 0.125 inches thick. This variation does not indicate any strong dependence on thickness. Addition of nickel to Boride V did not produce any increase in the fracture energy due to the reaction of the nickel with the silicon carbide. This reaction precluded achievement of full density (2) and the resulting value of (W/A) = 0.57 in-lbs/in^2 shown in Table 6 is below the value obtained with Boride V bars of comparable size. The impact energy of this composite is shown in Tables 1 and 6. The average impact value is 24.3 in-lbs/in^2.

Exploratory additions of graphite cloth at 1/8" and 1/16" spacings have been made (2). These additions have not led to any large changes in the fracture energies, although a slight increase in the impact energy has been noted as seen in Table 6. Current fabrication tests have been successfully carried out at 1/32" spacing. Measurements of the impact strength of this composite are in progress.

The fracture energies of 0.200 and 0.394 inch thick bars of WC-6Co are reported in Tables 2 and 6. Reference to the average values shown in Table 6 indicate little size effect on the slow bend energy. Values of 2.51 in-lbs/in^2 and 2.69 in-lbs/in^2 are noted for the 0.200 and 0.394 sizes respectively. The impact tests conducted on 0.394 inch bars yield an average value of 73.9 in-lbs/in^2 for WC-6Co.

Tables 3,4 and 6 present the results obtained for Boride VIII and Boride VIII-M2. These composites contain graphite as well as SiC additions to ZrB_2. As a consequence, they exhibit lower moduli and higher resistance to thermal stress than Boride V (1,2). In addition, the specific graphite addition to Boride VIII-M2 provides enhanced machinebility along with a greater degree of anisotropy in strength and modulus (1,2). Reference to Table 6 shows that these composites exhibit higher fracture energies in slow bend tests that Boride V, but lower impact fracture energies than Boride V.

A number of billets of ZrB_2 plus nickel have been hot pressed in order to avoid the reaction between SiC and nickel which has been observed in the Boride V plus nickel pressings (2). The purpose of these experiments is to lower the hot pressing temperatures (normally near 4000°F) to a level where fibrous additives can be added without degradation. Preliminary results of these experiments are described in Section III. Tables 5 and 6 show the results of impact tests performed on samples of ZrB_2 plus nickel which exhibited an impact fracture energy comparable to Boride V. Significantly, this composite was hot pressed at 2400°F rather than 4000°F.

III. RESULTS OF FABRICATION EXPERIMENTS

The results of previously reported fabrication experiments designed to provide a nickel metalloid or cermet structure with a ZrB_2+SiC matrix showed that reaction of SiC and Ni interferred with densification. Processing temperatures of 3000° to 3200°F produced extensive reaction; processing temperatures of less than 2800°F produced low density billets. In order to further examine the potential of nickel for formation of an intergranular metallic reinforcement, fabrication experiments were performed with metallic nickel and ZrB_2 as the matrix phase. In the first experiment the processing cycle was planned and performed at a maximum temperature of 3020°F, HP88. The resulting billet density was 6.14 g/cc compared to a calculated density of 6.90 g/cc for the mixture of 20 weight percent nickel and 80 weight percent ZrB_2. Metallographic examination of HP88 shows a typical dense ZrB_2 microstructure, Figure 1. X-Ray fluorescence revealed that a small amount of Ni was retained in the billet; X-ray diffraction data provided identification of ZrB_2. The final density of 6.14 g/cc and the microstructure, Figure 1, are consistent with the formation of dense ZrB_2 containing minor amounts of impurity phases and the loss in processing of the added nickel. Examination of the densification data for HP88 obtained from measurements of piston travel showed that considerable densification took place abruptly at 2400°F. Accordingly, a second fabrication experiment was planned and carried out at maximum processing temperature of 2420°F, HP90. The resulting billet was approximately of the same weight as the starting powders, 80.5 grams; the overall density was 5.97 g/cc relative a calculated full density of 6.90 g/cc. Examination of cut and ground surfaces revealed that considerable densification had taken place in the center

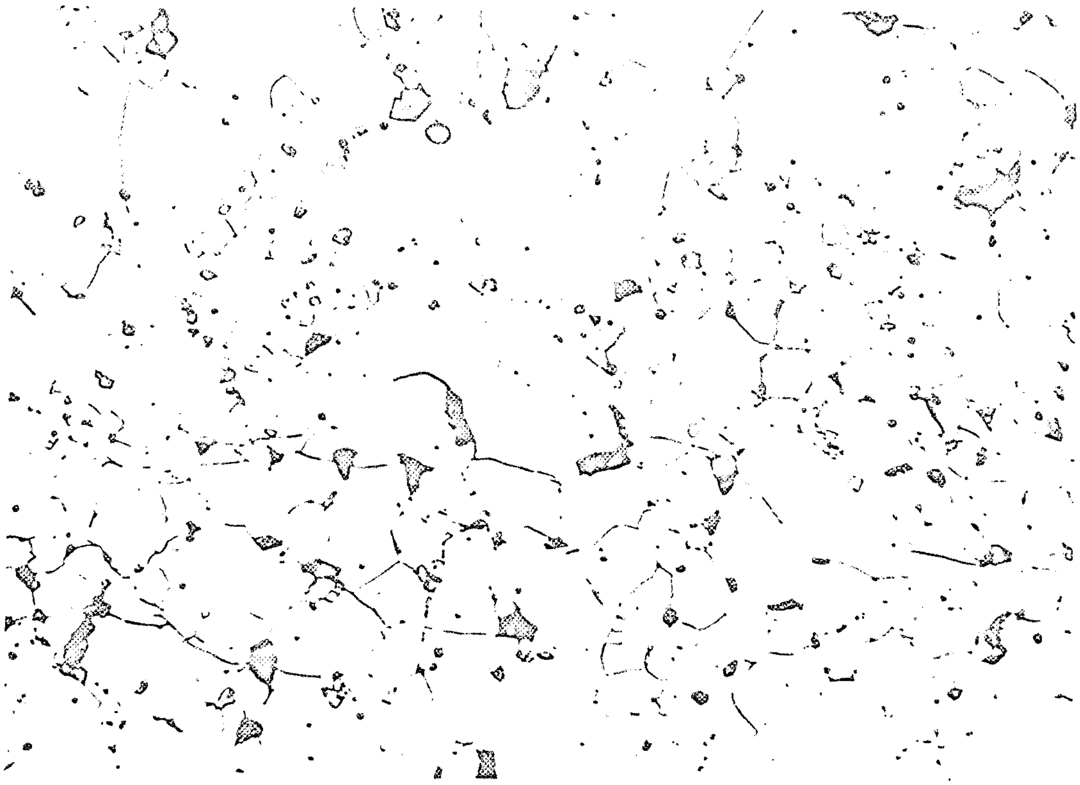

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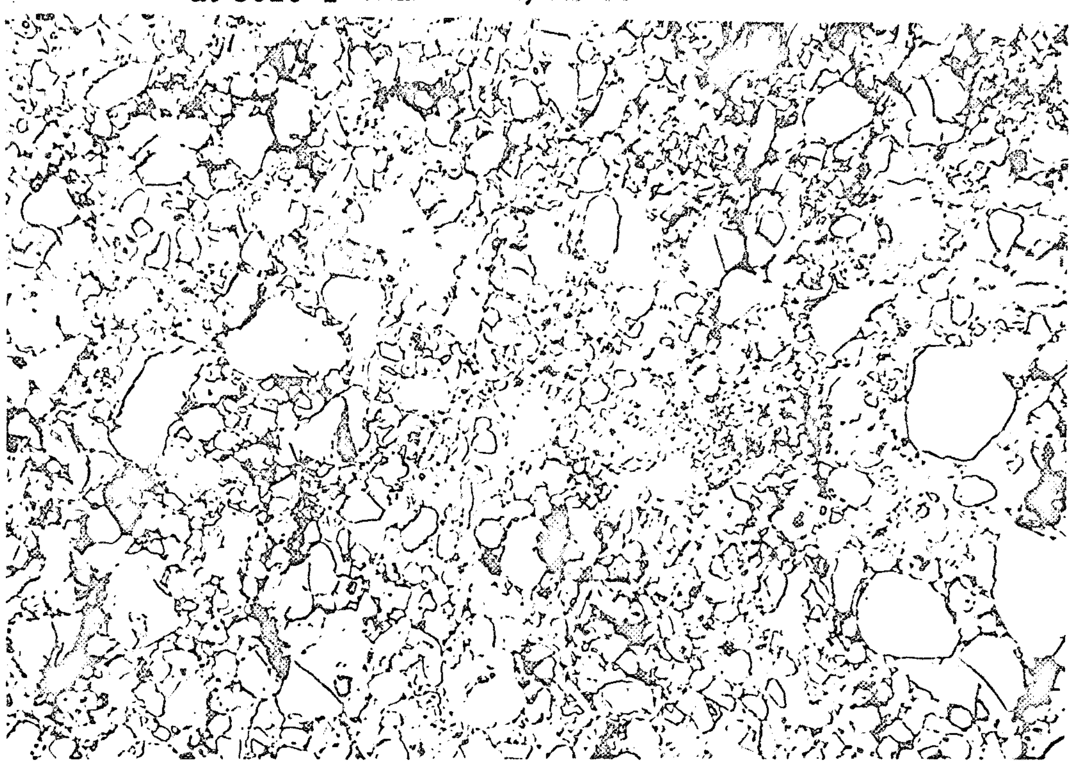
Figure 1. Microstructural Features of ZrB_2-Ni Composition Processed at 3020°F Maximum, HP88



ManLabs Plate No. 6221

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Figure 2. Microstructural Features of ZrB_2-Ni Composition Processed at 2420°F Maximum, HP90

of the billet but that the top, the bottom, and to some extent the edges of the billet were quite porous. The variation of density within the billet is believed to be caused by side wall friction in the hot pressing operation. The density of the center section is 6.46 g/cc and the microstructure is provided in Figure 2. X-ray diffraction data provide identification of ZrB_2 and monoclinic Ni_4B_3; and d-spacings for elemented Ni were observed. Examination of the microstructure of the dense center from HP90 does not show the features of a typical cermet material, however, some evidence for liquid phase assisted sintering was observed. Impact test data for samples cut from this billet are shown in Table 5.

IV. PLANS FOR FUTURE WORK

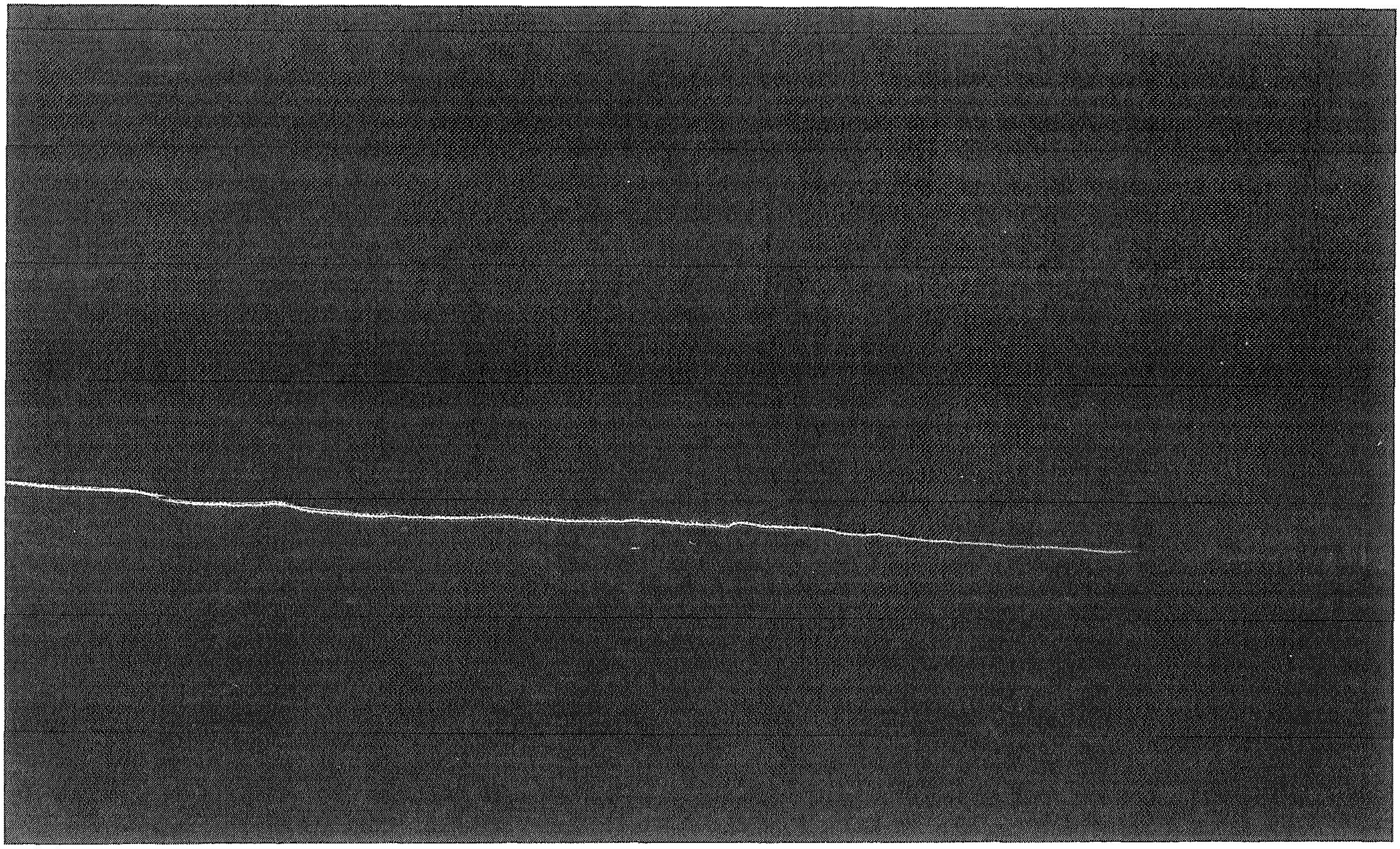
During the next report period, the effects of additional metallic ingrediants on the processing conditions and fracture energy of boride composites will be evaluated. These include iron, chromium and tantalum. Moreover the level of graphite cloth loading will also be increased from the present 1/16" spacing to 1/32 and 1/64" spacings.

A summary technical report detailing the first year effort will be prepared for submission to NASA during the second week in July.

REFERENCES

1. "Investigation of Fracture Mechanics of Boride Composites" Contract No. NASW-2088, Quarterly Report No. 1, November 1970

2. "Investigation of Fracture Mechanics of Boride Composites" Contract No. NASW-2088, Quarterly Report No. 2 March 1970



MATERIALS RESEARCH AND DEVELOPMENT

MANLABS, INC.
21 ERIE STREET
CAMBRIDGE
MASS. 02139