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**FINAL REPORT OF THE
LIGHT ARMOR MATERIALS PROGRAM**

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Foreword

This report covers the work performed on the August 1970 extension of the Advanced Research Projects Agency (ARPA) order 980. This effort was directed toward the development of light armor materials. The initial concepts behind the development of these materials are described in previous LLL reports.¹⁻⁵

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FINAL REPORT OF THE LIGHT ARMOR MATERIALS PROGRAM

Abstract

Beryllium boride compounds have been evaluated as potential materials for use in light armor applications. Target specimens have been prepared by hot-pressing and casting techniques and subjected to ballistic testing. In each case, ballistic performance was found to be strongly related to composition and to the microstructure of the target material. One important microstructural feature has been found to be the grain size of the target material. The mechanism of fracture is described and the relationship of the type of fracture to grain size

discussed. It has been shown that grain size can in some cases be controlled by process variables. Toxicity investigations have also been carried out. As a part of these toxicity studies the amount and size distribution of ballistic debris has been determined. Environmental studies have shown the beryllium borides to be resistant to high temperature oxidation and thermal shock, but adversely affected by salt water. A working Be-B phase diagram is also provided. The ballistic performance of beryllium borides was improved when they were incorporated in metal-graded targets.

Introduction

Studies conducted at these laboratories¹⁻⁵ have led to a better understanding of penetration mechanics. Knowledge of the important material parameters that operate during the penetration process has helped reveal the path to be taken in the development of materials for use as light armor. In general, the ideal material should exhibit the proper balance between low density, high incompressibility (high yield strength and impedance) and the ability to dissipate tensile stresses without fracturing (ductility). A detailed evaluation of these material parameters has been previously described.^{3,4}

Several ceramics (i. e. B_4C , Al_2O_3 , SiC , AlB_{12}) possess the qualities of low density and high incompressibility, but even at high hydrostatic confining pressures, only a few low-density ceramics (BeO , Be_2B , Be_4B , and MgO) show ductility. However, ductility can be incorporated in some ceramics by addition of the proper metal to form a cermet. An improvement in ballistic performance by the addition of metal, and the existence of an optimum in metal concentration have been previously demonstrated with the $TiC-Ni-Mo$ system.⁵ Unfortunately, no cermets having both low density (<3.0 g/cc) and high incompressibility have been heretofore developed.

Beryllium borides have the above properties plus the capability of forming low density cermet. Indeed, combining beryllium metal with beryllium boride

actually reduces the density of the ceramic. Increasing the beryllium metal content leads to a more ductile cermet. The ductile behavior of beryllium has been

Table 1. Ballistic limits for various ceramics bonded to 0.25-in. 6061-T6 aluminum.³

Ceramic	Density ρ_0 (g/cc)	Δ^a (in.)	V_{BL}^b (ft/sec)	$\Delta 2700^c$ (in.)	$\rho_0 \Delta 2700^d$ (g/cm ²)	ϕ^e
B ₄ C	2.50	0.290	2700 ± 50	0.29	1.84	1.00
BeO	2.84	0.250	2500 ± 50	0.27	1.95	0.94
BeO + B	2.50	0.250	2320 ± 80	0.29	1.84	1.00
Coors AD85 alumina	3.43	0.340	2850 ± 50	0.32	2.79	0.66
Coors AD999 alumina	3.96	0.250	2660 ± 80	0.25	2.51	0.73
WESG [®] 995 alumina	3.85	0.303	2870 ± 50	0.285	2.79	0.66
Diamonite alumina	3.72	0.340	3170 ± 50	0.29	2.74	0.67
Carborundum hot-pressed alumina	3.92	0.250	2550 ± 50	0.26	2.59	0.71
Sapphire	3.98	0.250	2470 ± 80	0.27	2.73	0.67
Si	2.33	0.250	1200 ± 50	0.56	3.31	0.56
SiC	3.09	0.250	2175 ± 75	0.31	2.43	0.76
Si ₃ N ₄	2.815	0.355	1450 ± 50	0.66	4.72	0.39
Quartzite	2.58	0.250	1250 ± 100	0.54	3.54	0.52
B	2.36	0.246	2100 ± 80	0.29	1.74	1.06
AlB ₁₂	2.53	0.250	2250 ± 80	0.30	1.93	0.95
Be ₂ B	2.03	0.250	2150 ± 50	0.31	1.60	1.15
TiB ₂	4.46	0.236	2270 ± 50	0.28	3.17	0.56
TiBe ₁₂	2.25	0.250	2250 ± 100	0.30	1.74	1.06
Pure TiC	4.88	0.25	2500 ± 80	0.27	3.25	0.55
TiC + (Ni, Mo) cermet	5.63	0.25	3050 ± 80	0.22	3.15	0.58
WC-(K-a)	15.24	0.25	3300 ± 200	0.20	7.7	0.24

^a Δ = ceramic thickness.

^b V_{BL} = experimental ballistic limit.

^c $\Delta 2700$ = extrapolated ceramic thickness for $V_{BL} = 2700$ ft/sec.

^d $\rho_0 \Delta$ = ceramic areal density.

^e $\phi = B_4C$ areal density/ceramic areal density.

demonstrated under hydrostatic confining pressures of 6 to 63 kb.r at relatively low strain rates ($3 \times 10^{-1} \text{ sec}^{-1}$).⁶ In view of the above facts, we undertook to explore the possibility of using beryllium boride systems in light armor applications.

Extensive evaluation of the promising Be-B compounds (Be_4B and Be_2B) was initiated after exceptionally high ballistic performances^{4, 5} had been obtained on many preliminary test specimens. Ballistic performances of several materials are compared in Table 1 and Figs. 1 and 2. A detailed description of the Be-B system is given in Appendix A. Efforts to prepare

Be-B armor for specific applications were considered unrealistic during early stages of the program. Evaluation studies were directed instead toward more general areas in the expectation that such results would be useful in selecting and designing specific applications in the future. The general areas studied were the relationship of composition and microstructure to ballistic performance, the effect of fabrication processes on microstructure, the ballistic performance of metal-graded or reinforced beryllium boride armor, beryllium boride toxicity, and environmental effects on beryllium borides.

Fig. 1. Ballistic limit versus ceramic areal density for aluminum backed ceramic targets.⁵

Fig. 2. Ballistic limit of targets with various ceramic impact surfaces compared to targets with B_4C impact surfaces.⁵

The Effect of Composition and Microstructure on Ballistic Performance of Be_2B and Be_4B

HOT-PRESSED TARGETS

Hot-pressing

Hot-pressing was the primary fabrication process used in preparing $Be-B$ samples for investigations into the effects of variations in composition and microstructure on ballistic performance. Hot-pressing allowed easy control of fabrication parameters since relatively low

temperatures ($\leq 1100^\circ C$) and pressures (≤ 4500 psi) were sufficient to achieve fully dense targets.

The Be_4B and Be_2B powders were hot-pressed into target disks (3 in. diam). The following experimental procedure was used in the fabrication of these disks:

- The powder was uniformly loaded into the lined (graphite paper) graphite die and cold pressed at ~ 1000 psi.

- The die was next heated to the desired temperature under minimum pressure (<500 psi).
- The desired pressure was applied at temperature and the powder allowed to consolidate.
- The pressure was released and the disk removed from the die at $\leq 400^\circ\text{C}$.

Since no ballistic degradation was found to occur when the targets were extracted hot ($\leq 800^\circ\text{C}$) from the dies and cooled, degradation by thermal shocking was not considered to be a problem under the above conditions. Heating of the hot-press dies was accomplished by one of the following methods: induction heating of the graphite die in an argon atmosphere, resistance heating of elements around the graphite die in an argon atmosphere, or resistance heating of the graphite die in an air atmosphere. Typical experimental conditions for the fabrication of Be_4B and Be_2B targets are listed in Table 2. Slightly higher tem-

peratures were required to achieve dense (>98% of theoretical) disks if the BeO or higher boride contaminants (Be_2B , BeB_2 , etc) exceeded ~3 wt% in Be_4B or Be_2B .

Reaction Hot-Pressing

Reaction hot-pressing of stoichiometric blends of Be and B powder is an alternative approach to the fabrication of Be_4B and Be_2B targets by hot-pressing. This approach offers a substantial saving in cost since it eliminates synthesis of the starting materials.

The Be and B powders were blended together in batches of $\frac{1}{2}$ kg or less by either wet or dry ball milling in 2 quart Al_2O_3 or WC ball mills. A uniform blend of fine powders is essential in obtaining a uniform, predominantly one phase (>90%) microstructure. The general hot-pressing procedure just described was also used for reaction hot-pressing, with the exception that the blended powders were held at

Table 2. Summary table of hot-pressing and reaction hot-pressing parameters for Be_4B and Be_2B .

Desired composition	Powder charged	Type of heating ^a	Atmosphere	Heating time (min)	Consolidation			Cooling time (min)	Typical density	
					Temp ($^\circ\text{C}$)	Pressure (psi)	Time (min)		g/cc	%
Be_2B	Be_2B	1	Argon	20	1105 ^b	5000	10	180	2.06	109 ^d
Be_2B	Be_2B	2	Argon	30	1060 ^b	4000	4	180	2.03	107 ^d
Be_2B	Be_2B	3	Air	20	1095 ^c	4000	5	60	2.08	110 ^d
Be_2B	Be + B	3	Air	20	1065 ^c	4000	8	60	2.10	111 ^d
Be_4B	Be_4B	2	Argon	20	1010 ^b	5000	7	180	1.92	98.7
Be_4B	Be_4B	2	Argon	30	1075 ^b	4000	7	180	1.92	88.7 ^e
Be_4B	Be_4B	3	Air	20	1040 ^c	4000	5	60	1.94	99.7
Be_4B	Be + B	3	Air	20	1030 ^c	4000	8	60	1.94	89.7 ^e
4 vol% BeO- Be_4B	BeO + Be_4B	3	Air	20	1075 ^c	4000	5	60	1.98	100.5 ^e
4 vol% Al_2O_3 - Be_4B	Al_2O_3 - Be_4B	3	Air	20	1055 ^c	4000	5	60	2.03	100.0

^a1—Induction heating of graphite die.
2—Resistance heating of elements around graphite die.
3—Resistance heating of graphite die.

^bOptical pyrometer readings ($\pm 15^\circ\text{C}$).

^cPt-Rh thermocouple readings ($\pm 7^\circ\text{C}$).

^dContaminated with BeB_2 and BeO.

^eContaminated with 3 to 5 wt% BeO.

temperature for 3 to 5 min before the final pressure of 3000 to 4500 psi was applied. Disks were generally hot-pressed in the resistance heated graphite dies since this procedure was fastest. Typical reaction hot-pressing parameters are given in Table 2.

The fine particle size of amorphous boron powder ($<1\ \mu$ diam) is well suited to this process. On the other hand, incomplete reaction of larger Be particles ($>20\ \mu$ diam) was revealed by microhardness tests and metallography (Fig. 3). The microhardness of the Be (gray phase) grains was $<600\ \text{kg/mm}^2$ and the Be_4B matrix was $>1300\ \text{kg/mm}^2$. Beryllium powder lots with smaller particle sizes have since been used to improve the uniformity of the microstructure. Some typical beryllium particle-size distributions are shown in Fig. 4.

Grain Size

Various combinations of well dispersed minor phases (BeO , Be_2B , Be_4B and/or

Fig. 3. Reaction hot-pressed Be_4B . Note the large unreacted particles of Be (gray phase).

Be) were found to be present in early targets.³⁻⁵ When these minor phases were reduced ($<2\ \text{vol}\%$) in Be_4B targets, a corresponding reduction (33%) in ballistic performance was noted. However, 70% of this reduction could be restored by dispersing a minor phase (10 vol%, $<44\ \mu$ diam, Be_2B) in the high purity Be_4B powder prior to the hot-pressing operation. The early ballistic performance of Be_4B was completely restored by the similar dispersal of 4 vol% of BeO powder ($<2\ \mu$ diam) in the high purity Be_4B powder. Since these results indicate a dependence of ballistic performance on composition; the effect of composition on microstructure, and microstructure on ballistic performance was further investigated.

Several mechanisms can be postulated to explain the role of impurities in improving the ballistic performance of Be_4B . One possible explanation involves dispersion-strengthening of the matrix material. If dispersion-strengthening of Be_4B with BeO were operative, increased microhardness and improved ballistic performance should be expected with finer-grained dispersions of BeO . Such finer dispersions were prepared by oxidizing the surface of the Be_4B powder before

Fig. 4. Particle-size distribution of beryllium powder.

hot-pressing. The resulting targets (5.8 vol% BeO-Be₄B) had the same ballistic performance and microhardness as the 4 vol% BeO-Be₄B powder blended targets. The high-purity Be₄B had the same microhardness as both of the compositions containing BeO. Thus, dispersion-strengthening evidently does not explain the role of BeO in improving the ballistic performance of Be₄B targets.

Another mechanism involves the role of impurities in interfering with crack propagation. This effect will be discussed in the section on Fracture Mechanism.

Alteration of the target grain size by impurities is another possibility. The Heyn's intercept method⁷ was used to determine the average number of grains per unit area, or average grain density. It is important to keep in mind that an increase in the average number of grains or grain density represents a decrease in grain size. Even though the actual sizes of the grains are larger than the calculation indicates (see Appendix B), these relative values are useful for purposes of comparison.

A marked correlation between grain size and ballistic limit (V_{BL}) was found* (Figs. 5 and 6). An increase in the average number of grains per unit area (average grain density) from 0.022 grains/ μ^2 to 0.052 grains/ μ^2 (decrease in grain size)

resulted in a 50% rise in V_{BL} (Fig. 5). The existence of an optimum size was first suggested by the observation that a further increase in grain density to 0.12 grains/ μ^2 had little effect on V_{BL} (Fig. 5). This concept was verified by observing the effect of a further increase in grain density (Fig. 6). Additional confirmation that grain size exerts a strong influence on ballistic performance comes from further inspection of Fig. 6. It can be seen that targets 2 and 3, which had the highest ballistic limits, also had lower BeO contents (≤ 1.8 vol%) than targets 1 and 5 (≥ 3.5 vol% BeO). The influence of grain size was greater than that of composition.

The effect of BeO particles on the ballistic performance of Be₄B was compared with that of Al₂O₃ particles. A slight decrease in V_{BL} was observed when 4 vol% of Al₂O₃ powder (ultrafine polishing compound) was blended with high-purity Be₄B powder. Note the similarity in grain densities of targets 1 and 4 in Fig. 6. X-ray diffraction studies of these hot-pressed powder blends indicated that neither Al₂O₃ nor BeO were soluble in Be₄B. These minor phases appeared mainly as fine particles in the grain boundaries (Fig. 7).

Grain size has also been observed to affect the ballistic performance of Be₂B targets. Targets were hot-pressed from Be₂B powder after the powder lot had been separated into two size-fractions (20 μ to 37 μ and 5 to 20 μ). The grain density of the target hot-pressed from the powder of larger particle size was 0.1 grains/ μ^2 and its ballistic velocity 2500 ft/sec, while the values for the smaller sized fraction were 0.13 grains/ μ^2 and 2400 ft/sec.

* In tests using fiberglass reinforced plastic backup plates and .30 cal U. S. Army AP projectiles, a high degree of data scatter was noted (Fig. 5). We found that by using sharp point projectiles made of Allegheny 609 steel and Be₄B targets backed with 6061-T6 aluminum we were able to reduce data scatter and detect the effects of smaller changes in target materials (Fig. 6).

Fig. 5. Ballistic limits of Be_4B with various impurity levels versus average grain density. The thicknesses of the Be_4B and aluminum backup plates were constant.

Fig. 6. Ballistic limit versus average grain density for Be_4B targets with fiberglass backup plates.

a. 4 vol% BeO-Be₄B

b. 4 vol% Al₂O₃-Be₄B

Fig. 7. Typical microstructures of hot-pressed Be₄B prepared from blends of Be₄B powder (2-44 μ diam) and either 4 vol% of BeO (a) or Al₂O₃ powder (<2 μ diam) (b).

The BeO content in these two powder fractions and the resultant hot-pressed targets was relatively low (<3%) according to x-ray diffraction. Traces of Be₄B were detected in the powders but not in the hot-pressed targets. The presence of BeB₂ in the hot-pressed Be₂B was varified from microhardness tests and metallography. The lighter phase (BeB₂) in Fig. 8 had a Knoop microhardness of >2000 kg/mm² (100 g load), while the hardness of the matrix phase (Be₂B) was ~1300 kg/mm² (100 g load). Identification of amounts less than 40 vol% of BeB₂ in BeO contaminated Be₂B is difficult since the two compounds have overlapping x-ray diffraction patterns. More extensive efforts will be made to identify this minor phase in the course of determining the entire Be-B phase diagram.

Similar effects of grain size on the ballistic performance of other hot-pressed

or sintered ceramics have also been observed. A significant increase (12.2%)

Fig. 8. Typical microstructure of target hot-pressed from fine (<20 μ) Be₂B powder. The microcracks were induced during ballistic testing. The target was etched for 15 sec in HNO₃:HF:H₂O (10:2:88 by vol) to improve resolution.

in ballistic limit was obtained with an Al_2O_3 target of fine grain size. The ballistic limits of the typical high-purity Al_2O_3 targets prepared from starting powders furnished by three different vendors and fabricated by two different techniques fell on a linear slope when plotted against target thickness (Fig. 9). Targets with finer grain sizes had V_{BL} 's above this line. The material with the highest grain density (~ 0.099 grains/ μ^2) was prepared at LLL by hot pressing a blend of 1% $\text{MgO-Al}_2\text{O}_3$ powder at relatively low temperature (1475°C) (see Fig. 10). MgO inhibited grain growth in Al_2O_3 .

The effect of microstructure on ballistic performance was also observed in AD-85 alumina and B_4C .⁵ Large differences in microstructure have been observed in different lots of AD-85 armor plates. Variation in the microstructure of B_4C was noticed during dimension-scaling studies.⁵ Thick B_4C plates (>0.25 in.) had a larger grain size, more porosity, and poorer ballistic performance than thinner plates. Consistent scaling results could be obtained only by grinding all the B_4C plates from the thickest plates used in these studies.

Fracture Mechanism

Early indications from examinations of ballistically fractured surfaces with the scanning electron microscope were that foreign particles altered crack propagation. The smooth fractured surfaces of the high-purity Be_4B targets contrasted sharply with the rough fractured surfaces of the 4 vol% $\text{BeO-Be}_4\text{B}$ targets (see Fig. 11). The BeO particles were located predominantly in the grain boundaries. It can be

postulated, that where BeO is concentrated, the fracture does not traverse the boundary smoothly, but must instead be renucleated or bypass that site. In either case, a higher stress would be required for fracture. Independent evaluation of the scanning electron photomicrographs has favored this interpretation.⁸

A working hypothesis* for the observed correlation between ballistic performance and grain size can also be proposed from a consideration of fracture mechanism. This hypothesis assumes the existence of a critical grain-density range, which imparts to a material, a higher resistance to the propagation of a fracture. In addition, there are three modes of fracture to be considered; transgranular (across the grain), intergranular (along the grain boundaries), and a transitional mode. The transitional mode of fracture is characterized by the activation of multiple modes of fracture, in contrast to the predominantly singular modes of the other two types. It is proposed that the critical grain-density range is coincident with the transitional mode of fracture or within the transition zone defined in Figs. 5 and 6.

Support for this hypothesis comes from observations of the fracture mode of ballistically tested targets, and the general condition of the targets after ballistic tests. A transition in fracture mode seemed to occur when the grain density of the Be_4B targets approached 0.085 grains/ μ^2 .

* This hypothesis should not be confused with the one previously put forward to explain the fracture of graded armor.⁵ Experimental evidence to support the above hypothesis has been collected on the single-phase Be_4B targets while multiphase targets are used for the crack blunting in graded armor.

Fig. 9. Ballistic limit versus thickness for Al_2O_3 targets.

Fig. 10. Fine grained Al₂O₃ (~0.089 grains/ μ^2) prepared by low temperature (1475°C) hot pressing of a fine powder blend (1% MgO-Al₂O₃).

Metallographic examination of ballistically fractured pieces of Be₄B displayed predominantly transgranular fracture for average grain densities less than about 0.04 grains/ μ^2 and predominantly intergranular fracture for average grain densities greater than about 0.12 grains/ μ^2

(see Fig. 12). In the transition region between these two size limits (0.04 to 0.12 grains/ μ^2), the fracture bifurcates at grain boundaries and proceeds as multiple fractures (see Fig. 13a). The paths of these multiple fractures are not predominantly transgranular or intergranular. Their paths are influenced by crystal orientation and aligned grain boundaries, the propagation preferring the paths of least resistance (see Fig. 13b).

Electron microscope techniques were also used to examine debris from the targets used to obtain the V_{BL} of points 1, 2, and 5 in Fig. 6. Each point is in a different fracture zone. A general description of these techniques and the features of interest on the fractured surface of this debris are given in Appendix C. Detailed examination of these fractured surfaces indicated that a higher stress was required to sustain fracture in the transition zone (point No. 2 in Fig. 6) than in the other two zones. The fractured

a. High purity Be₄B

b. 4 vol% BeO-Be₄B

Fig. 11. The typical difference in ballistically fractured surfaces of high purity (a) and doped (BeO) Be₄B (b) as detected with the scanning electron microscope.

a. Transgranular fracture in a target of average grain density $< 0.04 \text{ grains}/\mu^2$

b. Intergranular fracture in a target of average grain density $> 0.12 \text{ grains}/\mu^2$

Fig. 12. The different modes of fracture in ballistically tested Be_4B targets with different grain sizes.

a. Fracture branches at grain boundary.

b. Multiple fractures.

Fig. 13. Multiple fractures in the transition region (~ 0.04 - $0.12 \text{ grains}/\mu^2$) of hot-pressed Be_4B powder ($< 20 \text{ diam}$).

surfaces from the transition zone contained large amounts ($> 10\%$ of surface) of hackle^{9,10} with nearly random orientation (see Fig. 14). Smoother fractured surfaces with little hackle were observed for the predominantly transgranular (see

Fig. 15) and intergranular (see Fig. 16) fracture zones.

The largest pieces recovered from the 3 in. diam targets with grain density in the transition zone (0.04 to $0.12 \text{ grains}/\mu^2$) are approximately $1/2$ in. square and only

a. Prepared on the scanning electron microscope.

b. Prepared by replica on an electron microscope.

Fig. 14. Typical fracture patterns in the transition region (Fig. 6, point 2) for ballistically impacted Be_4B targets.

a. Prepared on the scanning electron microscope.

b. Prepared by replica on an electron microscope.

Fig. 15. Typical fracture patterns in the transgranular region (Fig. 6, point 1) for ballistically impacted Be_4B targets.

come from the edge of the targets. The Be_4B with average grain densities outside these limits had larger (~1 in. diam) pieces recovered from areas near the point of impact. Similar trends between ballistic performance and size and amount of debris

generated from ballistic impact are described in the section on toxicity.

There are several reasons that explain why the effect of grain size on the ballistic performance of most ceramics is not always readily apparent. The mode of

a. Prepared on the scanning electron microscope.

b. Prepared by replica on an electron microscope.

Fig. 16. Typical fracture patterns in the intergranular region (Fig. 6, point 3) for ballistically impacted Be_4B targets.

a. Indentation at $> 10^\circ$ to slip plane

b. Indentation parallel to slip plane

Fig. 17. Effect of preferred orientation in Be_4B on the Knoop microhardness indentations.

fracture is not entirely governed by the grain size if the ceramic contains any of the following features: relatively small amounts (~ 1 to 5 vol%) of porosity; a significant amount (≥ 2 vol%) of finely dispersed impurities; small amounts (≤ 2 vol%) of relatively large (~ 4 times the average grain size) features such as large grains

or agglomerated impurities; and excessive amounts (≥ 10 vol%) of grain orientation (ratios $\geq 4:1$, length to width). Usually one or more of these features shows up in all of the commercially manufactured ceramics. This is especially true of most ceramics used for armor since tight specifications on high purity

and uniform microstructure are not maintained.

The last feature (preferred orientation) was also observed in taking microhardness readings on tetragonal Be_4B . Slightly lower microhardnesses were obtained when the longer dimension of the Knoop indenter was at an angle $>10^\circ$ to the most active slip plane (see Fig. 17a). No slip was evident when the longer dimension was parallel to the slip direction (see Fig. 17b). Similar slip in many grains was observed after ballistic impacting Be_4B targets (see Fig. 18).

Process Variables

The important property of grain size was found to be influenced by several process variables. Microstructure was controlled primarily by the particle-size distribution of the starting powders and the amount, nature and dispersion of impurities (Figs. 19 and 20). The particle-size distribution ranges offered by two vendors are shown in Figs. 21 and 22.

Two other fabrication parameters, temperature and time at temperature,

also affected the grain size of hot-pressed beryllium boride. The average grain density decreased with increasing temperature for each powder (Fig. 20). Repeating the hot-pressing procedure on the same target also decreased the grain density (Fig. 20). The decrease in grain density with increasing time at temperature and pressure is shown for 2 powders in Fig. 23. Insufficient pressure (<3000 psi) at processing temperature resulted in lower density and higher porosity. Porosity also inhibited grain growth.

Attempts to increase the grain size of hot-pressed targets of Be_4B and Be_2B with post-heat treatments at various temperatures (800 – 1000°C) and times (8–18 hours) were unsuccessful. Vacuum (10^{-6} mm Hg) heat treatments caused growth inhibiting pores to form along grain boundaries. No increase in grain growth or pore formation was observed during heat treatment in an inert atmosphere.

Improvements in the V_{BL} of reaction hot-pressed Be_4B were obtained by using process variables to manipulate the grain size of the targets (Fig. 6). The approaches

a. 30 cal projectile impact

b. 50 cal projectile impact

Fig. 18. Typical activation of slip planes by ballistic impact on Be_4B targets.

Fig. 19. Average grain density versus the particle size of the starting material for Be₄B targets.

Fig. 20. The effect of the hot-pressing temperature on the average grain density of Be_3B targets.

Fig. 21. Typical particle-size distribution curves of Be_4B powder from two vendors.

for increasing grain size were less successful on the reaction hot-pressed targets than they had been on the targets hot-pressed from the pre-synthesized powders (Figs. 19, 20, and 23).

An average fine grain microstructure of $<5\ \mu$ in diam could be obtained under the conditions listed in Table 2 if complete reaction between the Be and B powders was achieved. Under these conditions complete reaction was impossible if relatively large Be particles ($>20\ \mu$ diam) were present. This incomplete reaction is apparent in Fig. 3 and is the primary cause of decreasing grain density with increasing Be particle size (see upper curve of Fig. 19). While incomplete reaction results in the formation of a cermet microstructure, the desired fine distribution of the metal phase is difficult to control by this approach.

A small decrease in average grain density was obtained by either increasing the hot-pressing temperature or time at temperature during reaction hot-pressing (Figs. 20 and 23). Higher temperatures ($>1040^\circ\text{C}$) were impractical, requiring

Fig. 22. Typical particle-size distribution curves of Be_2B powder from two vendors.

very tight temperature control to avoid melting. Longer hot pressing times ($>30\ \text{min}$) seemed impractical in the light of the shape of the upper curve in Fig. 23. Complete reaction of relatively large particles ($\leq 44\ \mu$ diam) could be achieved within 30 min at temperature and pressure. Without the applied pressure ($\leq 3000\ \text{psi}$), no apparent grain growth was detected.

Attempts to increase the grain size of reaction hot-pressed Be_4B and Be_2B targets by vacuum or inert atmosphere heat treatments produced the same results obtained with hot-pressed targets. Voids were formed in vacuum and no increases in grain size were obtained with either heat treatment.

The apparent resistance to grain growth of reaction hot-pressed targets is in contrast to results obtained in hot-pressing. This behavior can be attributed to higher concentrations of fine BeO particles which

Fig. 23. The effect of the hot-pressing time on the average grain density of Be₄B targets.

Fig. 24. Non-uniform Be_4B grain growth resulting from long exposure at hot-pressing temperature and pressure.

inhibit grain growth during pressing. The main sources of this contamination are BeO present in the starting Be powder and oxidation of this powder during reaction hot-pressing. The total BeO content can vary from 1 to 6 vol%.

Long times (>30 min) at hot-pressing temperatures and pressures increased non-uniform grain growth as shown in Fig. 24 and caused excessive formation of carbides at the interface between the graphite die and the target. The non-uniform grain growth was reduced by wet ball milling which improved the blend mix. Interfacial reactions were reduced by the inexpensive method of lining the graphite dies and punches before hot pressing. A slurry made of fine powder (BN , B , or BeB_2) mixed with alcohol and a wax binder was painted or sprayed on the inside surfaces of the die and on the surface of the punches exposed to the Be-B blends. The wax binder and alcohol were baked out of

the loaded die during the initial stages of hot pressing (<400°C). The use of BN powder in the slurry prevented the carbonization reactions at the interfaces. The B or BeB_2 slurries improved the hardness and salt water corrosion resistance of the targets. Surfaces exposed to B or BeB_2 slurries during hot-pressing were proposed for use as impact surfaces, while those exposed to BN slurries were proposed for the surface to be bonded to the backup plates.

CAST TARGETS

Casting is generally an economical fabrication process for large-scale manufacturing. The relatively low liquidus temperature ($\geq 1165^\circ\text{C}$) of Be_4B (see Fig. A-1) prompted an investigation of the casting behavior of this compound and the ballistic performance of cast targets.

According to the Be-B phase diagram (Fig. A-1), the cooling of a melt with a composition of 20 at.% B-Be from $\geq 1350^\circ\text{C}$ will result in approximately 28% of the melt forming Be_2B between 1350 and 1165°C . The remaining melt should then form Be_4B at 1165°C . This peritectic behavior of Be_4B was not observed when melts were rapidly cooled ($\geq 10^\circ\text{C/sec}$) between 1350 and 1165°C . Only an insignificant amount of (<5 vol%) Be_2B was formed.

Attempts to prepare Be_4B targets by melting and furnace cooling resulted in targets containing shrinkage cracks, varying amounts of porosity, and large grains.⁵ Two commercial techniques, chill casting and hot topping, were used to get dense targets of two compositions, 12.5 and

20.0 at.% Be-B. The low ballistic performance (50% of hot-pressed 12.5 and 20.0 at.% B-Be) of these targets was attributed to their microstructures. These targets contained large columnar grains which were mostly oriented parallel to the path of the projectile.⁵ As expected, the mode of fracture was predominantly intergranular with this grain orientation.

Directional Solidification

Two alternate casting techniques were tried in the hope of improving microstructure and with it ballistic performance. Directional solidification to orient the columnar grains perpendicular to the path of the projectile was one of the approaches. Two methods of preparing directionally solidified targets were investigated. In the first instance, molten Be_4B was poured into hot BN molds and the melt cooled from the bottom. The BN molds reacted with the molten Be_4B (1400°C) when the molds were preheated to temperatures of 1180, 1150, or 1100°C. The reaction with BN occurred even though the BN molds had been vacuum degassed at temperatures above 1400°C. Plates with marginal densities ($\geq 97\%$) were obtained by grinding off the reacted layers (see Fig. 25a).

The second method consisted of cooling the bottom of a BeO crucible containing molten Be_4B . Bottom cooling was accomplished by use of a top loading vacuum furnace with a cylindrical tungsten mesh heating element. Be_4B fragments from previous ballistic tests were placed in the crucible (4 in. diam, 7 in. high) and suspended by a molybdenum wire into the heating element. The crucible was lined with a porous (80% porous) BeO layer ($\geq \frac{1}{4}$ in. thick) for the following reasons:

(1) molten Be_4B does not wet or infiltrate porous BeO surfaces, (2) porous BeO acts as an insulator and prevents cooling of the Be_4B from the side walls, and (3) the liner prevents cracking of the crucible, absorbing the pressure which results from the difference in expansion coefficients between the BeO crucible and the solidifying Be_4B . The liner was prepared by hand packing BeO powder ($< 5 \mu$ diam) in a graphite mold and sintering at 1300°C for $\frac{1}{2}$ hour.

The Be_4B fragments were heated in this apparatus to $\sim 800^\circ\text{C}$ in vacuum. The vacuum chamber was filled with argon and the Be_4B was melted and was held at 1300°C for $\frac{1}{2}$ hour. The crucible was then lowered about 2 in. onto a copper chill block. After another 10 min, the temperature of the heating element was gradually reduced to room temperature. In this manner directional solidification parallel to the liner surface was obtained. This technique also yielded a slightly finer, more uniform grain structure than obtained with BN molds (Fig. 25b).

The directionally solidified targets had relatively fine columnar grains that were perpendicular to the path of the projectile (Fig. 25). The ballistic performance of these targets was 35% higher than the first Be_4B castings but still $\sim 30\%$ below the performance of hot-pressed Be_4B . The mode of fracture of the cast targets was predominantly transgranular. These results suggested that finer grain size might improve ballistic performance. The practical problem of removing porosity while maintaining unidirectional orientation hampered any further reduction of the grain size by the above casting techniques.

Direction of Projectile

a. Molten Be_4B poured into hot BN molds and cooled from the bottom.

b. Be_4B melted in BeO crucible and cooled from the bottom.

Fig. 25. Typical fine columnar grain structure of Be_4B targets fabricated by unidirectional solidification from the melt. These targets have been ballistically tested.

Grain Nucleation

The second general approach involved increasing the number of nucleation sites and decreasing grain growth in order to obtain a fine, randomly oriented grain structure similar to that found for hot-pressed Be_4B . A casting with these properties was achieved by employing the following techniques: doping with BeO to provide grain nucleation sites; ultrasonic vibration to stimulate nucleation; vacuum casting to prevent gas bubble voids; and rapid cooling to prevent grain growth. Experimentally, Be_4B containing 4 vol% of small particle ($<1 \mu$ diam) BeO was heated by induction in vacuum to $\sim 800^\circ\text{C}$ before melting under a partial pressure of argon ($\sim 3/4$ atm). The Be_4B melt was agitated to keep the BeO particles suspended by coupling on the melt instead of using a

Fig. 26. Typical fine random grain structure obtained by ultrasonically vibrating the melt (4 vol% BeO - Be_4B) to stimulate grain nucleation during vacuum chill-casting.

susceptor. The melt was rapidly quenched by lowering the crucible three-fourths of the way into an ultrasonically vibrated bath. The ultrasonic agitation stimulated grain nucleation at prominent sites (BeO particles, impurities, etc.) and the ultrasonic bath cooled the melt rapidly to prevent grain growth. The cast Be_4B disk was dense with a fine random-oriented grain structure (see Fig. 26).

While promising specimens ($\sim 1/2$ in. diam) were prepared with this casting procedure, targets large enough to ballistically test (≥ 3 in. diam) were not possible because of the size limitations of the existing equipment. We believe that the ballistic performance of cast Be_4B targets would be comparable to that found for hot-pressed Be_4B targets, provided the microstructures were similar.

The Ballistic Performance of Metal-Graded or Reinforced Beryllium Boride Armor

Improvements in the ballistic performance of ceramic armor can be achieved by finding the proper balance between compressive strength and ductility in tension.²⁻⁵ Part of the high compressive strength of the ceramics can be traded for ductility to delay failure in tension. Since the impact surface of the armor needs a high compressive strength to defeat the point of the projectile, the ideal solution would be to grade the amount of ductility through the thickness of the armor with the face opposite the impact face having the highest ductility. In practice, this trade-off has been accomplished by introducing the ductile behavior of metals into ceramics through the formation of cermet.

An excellent example of a cermet with the right properties (excluding its high density of ≥ 4.9 g/cc) for armor is the $\text{TiC}-(\text{Ni}, \text{Mo})$ cermet. Even without optimum grading of the Ni-Mo metal phase, its ballistic performance was significantly (22%) higher than that of TiC (see Fig. 27).⁵ These properties are largely attributed to

the excellent ability of the metal phase to "wet" the TiC . This "wetting" behavior produces a continuous, uniformly dispersed network of metal between TiC grains with relatively low amounts (< 20 vol%) of metal. Similar interaction between low density (< 3 g/cc) ceramics and metals should be sought for light armor applications. Wetting studies can be used to screen metal candidates for cermets.^{11,12}

A few attempts to obtain cermets with the more promising ceramic armors (Be_4B , Be_2B , B_4C , BeO , and B_4C) were reported earlier.³⁻⁵ Good wetting behavior such as found in the $\text{TiC}-(\text{Ni}, \text{Mo})$ system was not obtained during these early attempts. The ballistic performance of most cermet systems was low primarily due to one of three interfacial conditions: (1) little or no chemical bond between metal and ceramic, (2) high residual stress at the interface from thermal expansion mismatch, or (3) the presence of a brittle interfacial layer (i.e. TiO_2 layer in $\text{Ti}-\text{BeO}$ system, FeB in $\text{Fe}-\text{B}_4\text{C}$ system, AlB_2 in $\text{Al}-\text{B}_4\text{C}$).^{3,4}

Fig. 27. Ballistic limit versus metal content for TiC cermet.

Be_4B -Be

Controlled solid state diffusion provided an alternative technique to TiC-(Ni, Mo) type wetting,⁴ producing a chemical bond with no brittle interface. The interfacial bond between the Be and Be_4B was as strong as the parent materials. Residual stresses at the interface were low since all expansion coefficients were close. No brittle interfacial layer was formed between Be and Be_4B since no other compounds exist between these compositions according to the phase diagram (see Fig. A-1). Two methods of preparing the Be_4B -Be graded armor were described earlier⁵ (cross sections shown in Fig. 28). These initial Be_4B -Be graded targets had significantly higher V_{BL} 's ($\geq 10\%$ on an areal density basis) than hot-pressed Be_4B targets.

The graded-metal portion of the target shown in Fig. 28a was prepared from Be and Be_4B powder blends while the metal-containing portion shown in Fig. 28b was obtained with Be honeycomb sheets and Be_4B powder. Four more series of ballistic targets were prepared by these two methods in order to evaluate higher metal loadings and different geometries.

Both methods yielded graded-metal targets with higher V_{BL} 's (4-8%) than hot-pressed Be_4B targets, but values lower than found for earlier Be_4B -Be graded targets. The powder blended series with the highest (58 vol% Be) metal loading (see Fig. 29a) had the same ballistic performance as hot-pressed Be_4B targets. By reducing this metal content (32 vol% Be) in the other powder blended series (see Fig. 29b), the ballistic performance was

Fig. 28. Schematic diagram of early⁵ Be_4B -Be graded targets.

Fig. 29. Schematic diagram of Be_4B -Be graded targets prepared from powder blends.

increased to 8% above hot-pressed Be_4B targets. The relatively large grain-size range in the Be rich layers of these targets undoubtedly had some detrimental effect on their ballistic performance (see Fig. 30).

Graded targets prepared from alternate layers of Be sheets (50 vol% Be) and Be_4B powder also were found to be equal in ballistic performance to hot-pressed Be_4B targets (see Fig. 31a). Their per-

formance was not higher than Be_4B even with complete bonding along the Be sheet interface and obvious diversion of the fracture by the Be sheets (see Fig. 32). Ballistic performance was improved to 4% above the level found for Be_4B targets by replacing the eight layers of Be sheet (10 mils) with one thin layer (~10 mils) of blended powders (32 vol% Be- Be_4B) and two Be sheets (5 mils each) (Fig. 31b). The excellent bond between these layers

Fig. 30. Microstructure of the interface between the two Be rich layers of the Be_4B -Be graded targets prepared from powder blends (see Fig. 29).

Fig. 31. Schematic diagram of Be_4B -Be graded targets containing Be sheets.

after hot-pressing is apparent from Fig. 33. This figure also shows that a crack initiated in the Be_4B during ballistic impact was stopped (crack blunting) in the first Be sheet.

We believe a systematic investigation into the effect of relative amounts and dispersions of metal in the graded armor would be valuable. The reasons for using

the Be_4B -Be graded system for this investigation are as follows:

- demonstrated improvement in ballistic performance with certain graded compositions and geometries,
- relatively low fabrication temperatures ($<1100^\circ\text{C}$),
- simplicity of fabricating various graded compositions and geometries,

Fig. 32. Microstructure of the alternate layers of Be sheets (10 mils) and Be_4B hot-pressed powder region of Be_4B -Be graded targets (see Fig. 31a).

- and superior ballistic performance to any known light weight armor.

Be_4B -Ni OR Ni BASED ALLOY

Preliminary investigation of Be_4B -Ni graded systems were made because of the good ductility of Ni and the possible chemical compatibility of Ni and Be_4B at the fabrication temperature ($<1100^\circ\text{C}$) of Be_4B . It was also hoped that the high ductility of Ni (greater than Be) would improve the crack blunting behavior. However, the relatively high density of Ni (8.9 g/cc) does not make it a very likely candidate for light armor applications. Early results also showed that Ni was not completely stable in the presence of Be_4B at the fabrication temperatures. Nevertheless, ballistic tests of Ni- Be_4B and nichrome wire- Be_4B targets (Fig. 34) were prepared since the microhardness of the interface

Fig. 33. Microstructure of the hot-press bonded layers of target shown in Fig. 31b. Note that the crack initiated in the Be_4B during ballistic impact was stopped in the first Be sheet.

layer formed between the metals and Be_4B was not much harder (20-30%) than the Be_4B . The lower ballistic performances of these two graded series (24 and 8%, respectively as compared to Be_4B on an areal density basis) was attributed to the brittle fracture along the interface layers between the metal and Be_4B (see Fig. 35).

In anticipation of experiments with the Ni system, preliminary studies were made into the possibility of pressure bonding Ni to aluminum backup plates. It was thought that a ductile bond at this interface would improve ballistic performance and multi-hit capability. Good metallurgical bonds were obtained at the Ni-Al interface

Fig. 34. Schematic diagram of Be_4B -Ni and nichrome graded targets.

Fig. 35. Brittle fracture along the interface layer of a ballistically impacted Be_4B target reinforced with nichrome wires.

with an applied pressure of 1000 psi at 450°C for 20 min or 500°C for 5 min. The microhardness of this interfacial layer (400 kg/mm) was higher than the Ni (200 kg/mm) or Al alloy (180 kg/mm). This bond was not ballistically tested since the studies on the Be_4B -Ni graded targets were discontinued after the brittle interfaces between Be_4B and Ni failed during ballistic tests. We believe that the pressure bonding technique should be applied to the more successful graded targets, especially Be_4B -Be. The Be surface of a Be_4B -Be graded armor plate could be bonded to a metal backup plates to improve ballistic performance and multi-hit capability.

Toxicity Studies

A proposal advocating the fabrication and use of beryllium containing compounds must include a toxicity study. The

toxicities of compounds that might be used in the fabrication of the beryllium borides (i.e. BeSO_4 , $\text{Be}(\text{OH})_2$, BeO , beryllium

powder) are known and these materials are presently handled on a production scale at many plants. The preparation of the beryllium boride powders or blends of Be and B powders for hot pressing or casting of Be_4B can be handled similarly.^{13,14} However, little information was available on the toxicity of the beryllium boride powders themselves. Such information could only simplify the procedures used in the handling of these powders.

Previous studies concerned with the use of beryllium in armor have concluded that, "Based on the information provided, the risk of increased morbidity due to the use of beryllium containing armor is considered negligible from the viewpoint of inhalation of respirable particles or contamination of soft tissue wounds."¹⁵ Although the preceding statement could include the beryllium borides, additional information was desired in two areas: (1) the effect of direct exposure to the blood through open wounds and to the lungs by inhalation of fine debris; and (2) the amount and size distribution of beryllium boride debris generated by a ballistic impact.

The toxicity of both the beryllium boride powders used in the fabrication of targets and the debris from targets is currently being investigated by the Department of Health, Education and Welfare (HEW) in Cincinnati, Ohio. The toxicity studies at HEW are being performed by intratracheal injection of beryllium boride particles ($\geq 5 \mu$ diam) in the lung tissues of rats. This technique was selected because it provides information relating to the effect that these particles might have upon lung inhalation and open wound

exposures. These studies are being done with Be_4B , Be_2B , and BeB_6 debris as well as commercially available Be_4B and Be_2B powders. Inconclusive results were obtained after the first 6 months period. Experiments over 6, 12, and 18-month periods are in progress. A separate report will be prepared when all of these results are available.

Should an unusually high toxicity potential for debris be established by the above toxicity studies, information about the amount and size of this debris would also be required to determine the potential hazards involved in specific armor applications. A method of obtaining this information was developed at LLL. This method was designed to collect the maximum amount of debris generated during ballistic impact. In most light armor systems significant spall suppression ($\leq 400\%$ suppression¹⁶) is obtained with spall shields. This factor was not taken into account in our work. The significance of this type of suppression can be estimated later for specific applications if the general efficiency of the specific spall shield is known. The toxicity of most inhaled powders depends on the following interrelated variable factors¹³:

1. the physical and chemical properties, of the powder,
2. the quantity of debris deposited in the airways and the lungs,
3. the relative solubility of the debris in the tissue fluids,
4. and retention and release of the powder.

Considering only the density ($\sim 2 \text{ g/cc}$) of the beryllium borides, particles of approximately $\geq 5 \mu$ diam would deposit in

Fig. 36. Typical size-distribution curves of all the debris collected from the impact side of ballistically fractured beryllium boride targets.

the airways, and particles of approximately $\leq 1 \mu$ diam would not be retained in the lungs.¹⁷ As indicated above, chemical factors also influence the particle size range that can be deposited in the lungs. For the present investigations it was assumed that particle retention in the lungs would be in the diameter range of 1 to 5μ . The particle size limit of major interest as far as contamination of wounds is concerned was considered to be $\leq 45 \mu$ diam. Larger particles have a lower chemical activity (less surface per wt unit) and are relatively easy to remove.

When the particle size limits of major interest, 1 to 5 and $\leq 45 \mu$ diam, had been defined, techniques were incorporated into the existing ballistic testing procedures to collect and characterize these particles. A description of the collection and characterization techniques used for the ballistically generated debris is given in Appendix D.

All the size distribution curves of the beryllium boride debris collected from

Fig. 37. Size-distribution curves of $<45 \mu$ diam debris collected from the impact side of ballistically fractured beryllium boride targets.

Fig. 38. Size-distribution curves of all the debris collected from the back side of ballistically penetrated beryllium boride targets.

Fig. 39. Size-distribution curves of $<45\mu$ diam debris collected from the back side of ballistically penetrated beryllium boride targets.

the impact side of the targets lay between the two curves shown in Fig. 38. Size distribution curves of the debris in the most interesting portion ($<45\mu$ diam) of these curves are shown in Fig. 37. Comparable boundary distribution curves for the debris collected from the back side of ballistically penetrated targets are shown in Figs. 38 and 39. The debris collected in front of targets was characterized only when the impact velocity was near ($\pm 5\%$) the V_{BL} of that target. The debris collected from the backside of penetrated targets was characterized only when the target was impacted slightly above (≤ 120 ft/sec) the V_{BL} . These impact velocity limitations reduced the influence of impact and exit velocity to the range of greatest interest; near the V_{BL} .

The most pertinent information obtained from these size-distribution curves was the correlation between debris size and V_{BL} . Finer particles were generated from targets with higher V_{BL} 's. This correlation was also proposed from the

fracture theory described in a prior section. The amount of fine debris should also increase with increasing V_{BL} . The amounts of the two most interesting size fractions (<5 and $<45 \mu$ diam) are plotted against V_{BL} in Figs. 40 and 41 for debris

Fig. 40. Quantity of beryllium boride debris collected from the impact side of targets versus ballistic limit.

Fig. 41. Quantity of beryllium boride debris collected from the back side of penetrated targets versus the exit velocity of the projectile.

collected in front and behind the targets, respectively. These results are also consistent with the fracture theory: the amount of debris increases with increasing V_{BL} (Fig. 40).

The number of $<5 \mu$ diam particles generated on the impact side of the target increases at a greater rate with increasing V_{BL} than does the number of $<45 \mu$ diam particles (see Fig. 40). Conversely the quantity of $<45 \mu$ diam particles generated on the back side of the target increases at a greater rate with increasing exit velocity than does the number of $<5 \mu$ particles (see Fig. 41).

A first approximation of the potential hazard from this debris for a specific armor application might be calculated from equations like the following:

$$(P.H.)_W \text{ or } I = \frac{D}{V} (1-SS)(TF)_W \text{ or } I$$

Symbol	Description
P.H. =	Potential hazard
W =	Wound exposure ($<45 \mu$ diam debris)
I =	Inhalation exposure ($<5 \mu$ diam debris)
D =	Amount of debris (μg)
V =	Volume into which debris is dissipated (m^3)
SS =	Spall shield efficiency (constant ≤ 1)
TF =	Toxicity factor established from toxicity studies (in progress at HEW).

Environmental Tests

The behavior of beryllium borides in likely fabrication and application environments was studied in order to better assess potential uses.

Fabrication (hot-pressing or casting) environments could give rise to the following problems: the adsorption and surface reaction of moisture with starting powders and finished products, and the oxidation and carbonization of the compounds at elevated temperatures. Exposure to moisture during handling and storage had little or no adverse effect on the Be_4B or Be_2B powders. Fine powders (~ 400 mesh) with large surface areas ($\sim 2 m^2/g$) from two different vendors were exposed to distilled (75 and 100% humidity) and salt water (95% humidity) atmospheres for 104 days. Weight gains of 0.02 to 1.3%

were reduced to -0.01 to 0.9% by vacuum drying the exposed powders. X-ray diffraction results showed no shift ($<1\%$) in the original compositions.

An indication of the maximum oxidation rate of Be_4B and Be_2B powders (~ 400 mesh) in air at elevated temperatures was obtained by thermogravimetric analyses (TGA). The Be_4B powder was observed not to gain weight until the temperature reached $410^\circ C$ (see Fig. 42). After a 30-hr exposure at this temperature, the rate of weight gain had decreased from $\sim 0.1\%/hr$ to $0.02\%/hr$. The latter rate was maintained even after the temperature was increased to $506^\circ C$. The tests were terminated when the weight gain exceeded 4% , since oxidation above this level was considered undesirable. According to

Fig. 42. Weight gain of Be_4B powder at elevated temperature in air.

x-ray diffraction results, this weight gain was due to the formation of BeO . Similar results were obtained (see Fig. 43) for Be_2B powder. However, significantly lower rates of weight gain (0.013 and 0.005%/hr) at the same temperatures (410 and 506°C, respectively) were observed.

The above results indicate the desirability of a protective atmosphere when these finely powdered compounds are consolidated at elevated temperatures (>400°C). Casting operations with Be_4B would also benefit from a vacuum or inert atmosphere. The self-generated reducing atmosphere of graphite dies and punches is sufficient protection for the consolidation of the Be-B blends or Be_4B

and Be_2B powders during hot-pressing. No significant increase in BeO content was detected by x-ray diffraction techniques when the Be_4B , Be_2B , or B-Be blended powders were hot pressed in graphite dies and cooled to <400°C before removal from the dies. A Be_4B disk (3 in. diam, 0.32 in. thick) showed a significant increase in BeO content (~6%), as compared with the starting powder (~3% BeO), when the disk was extracted from the die at ~800°C and air cooled. Extraction of the hot (>400°C) disks into a protective atmosphere (or carbon black) would be required to reduce this surface oxidation. Hot extraction of a disk this size (3 in. diam) did not reduce its ballistic performance which indicates good thermal shock

Fig. 43. Weight gain of Be_2B powder at elevated temperature in air.

resistance. The shock resistance would allow a faster hot-pressing cycling and more efficient use of the hot-pressing facilities.

Slight carbonization of Be_4B and Be_2B to form Be_2C has been observed under three conditions: (1) hot-pressing Be_4B and Be_2B powder in graphite dies, (2) reaction hot-pressing Be-B powder blends in graphite dies, and (3) chill-casting Be_4B in graphite molds. In the first two conditions partial surface carbonization (<2 mils) occurred after prolonged (>30 min) hot-pressing at 1075°C for Be_4B and 1100°C for Be_2B . Similar carbonization was obtained on Be_4B surfaces exposed to the graphite mold while chill-casting Be_4B plates (4 × 5 × 0.4 in.) from 1300°C. These thin contaminated surfaces have no apparent effect on the ballistic performance of these materials. Beryllium carbide (Be_2C) is easily hydrolyzed in moist air giving methane.¹⁴ This surface contamination was eliminated by employing one of the following procedures: lining the hot-press dies with a BN slurry coating; grinding the surface (~2 mils) of the component;

reacting the carbide surface with water and wasting away the products; or by lining the casting molds with BeO . Lining the graphite dies with a thin layer (~2 mils) of boron or Be_2B powder not only reduced the amount of Be_2C formed but also increased the hardness and corrosion resistance of the target surface.

Ceramic armors are exposed to numerous environmental conditions as a result of their various applications. To determine the effect of all these conditions on the beryllium borides is beyond the scope of this program. Some general observations and tests have been made to provide guidance in determining the viability of these borides in certain environments.

The excellent corrosion resistance of borides with boron contents above 66 at.% (BeB_2) is apparent from their insolubility in acids.^{15,18} This resistance is not found for Be_4B and Be_2B , which are the most attractive compounds for light armor applications. The chemical stability of these beryllium-rich compounds (≤33.3 at.% B) decreases with decreasing boron content.

Fig. 44. Profile views of surfaces of Be_2B eroded by a 20-mil-diam stream of salt water.

A severe test for water damage was made by directing a stream of distilled or salt water at the surface of Be_4B or Be_2B targets. A pressure of 30 psig was maintained on a 20-mils-diam nozzle to form a single stream. The nozzle was perpendicular to and 1/2 in. away from the boride surface. The recycling bath temperature was 105°F. No erosion or weight change was observed with distilled water impinging on Be_4B or Be_2B after 350 hrs.

Severe erosion and weight loss of the Be_4B and Be_2B surfaces were apparent with salt water after 32 hrs exposure (see Fig. 44). These surfaces can be protected from direct erosion by salt water by installing spall shields or by providing a thin surface layer of high boron content (BeB_2 or BeB_6). Such a surface layer can be obtained by the use of B or BeB_2 in slurries used to coat the pressing die and punches.

The excellent behavior of Be_4B and Be_2B under high-temperature ($\leq 800^\circ\text{C}$)

thermal-shock conditions has already been mentioned in regard to hot extraction of hot-pressed disks. This same behavior was observed in the temperature range of +150 to -320°F. No degradation of boride disks (3 in. diam, 0.32 in. thick) was detected after they were heated to 150°F and quenched in liquid nitrogen. Larger disks (6 in. diam) were also subjected to similar thermal shock tests and showed no degradation.

A simple test to qualitatively determine shock resistance and thermal conductivity of the beryllium boride targets was performed on Be_4B , Be_2B , BeB_2 , and BeB_6 disks. The centers of the boride disks (3 in. diam, 3 in. thick) were rapidly heated with an oxygen-acetylene torch to their melting points and air cooled. Be_4B , Be_2B , and BeB_2 showed no spalling or cracking. The relatively lower thermal conductivity of BeB_6 caused it to behave as do most ceramics (i.e. B_4C , Al_2O_3 ,

and AlB_{12}) under these conditions: it immediately spalled at the point of contact with the flame.

The oxide (B_2O_3 and BeO) films formed at the surface of the Be_4B , Be_2B , and BeB_2 displayed the anticipated resistance to further oxidation. Although many more

quantitative studies would be needed to establish the value of these materials in severe environments, they show promise as multiple purpose materials. Their physical and mechanical properties will hopefully be determined in future programs.

Summary

The potential of beryllium boride for use as light-weight armor is apparent from its ballistic performance. Its use however will probably rest on economic factors. Be_4B and Be_2B armor is very easy to fabricate. This is in contrast to other ceramic armor systems where economical approaches to fabrication are not available due to the refractory nature of most ceramics. The combination of superior ballistic performance and low fabrication temperature make the beryllium borides the most outstanding candidates for advanced light armor applications. Hot-pressing, reaction hot-pressing, and casting all appear to be practical processes for fabrication. Inexpensive techniques for increasing the hardness and corrosion resistance of hot-pressed surfaces were found.

The low temperature of fabrication allows the addition of metals to the ceramic to form graded armors. The performance of metal-graded armors was improved by varying the amount and location of the metal phase. Beryllium boride-nickel graded targets failed because of the detrimental effect of the brittle interface between the ceramic and the metal.

Our results have also brought performance parameters into sharper focus.

Microstructure has been shown to be a critical performance factor. A direct correlation between grain size and ballistic performance can be drawn and then related to the mechanism of fracture. Fracture can occur transgranularly, intergranularly, or by a transitional mechanism. The transitional mode is operative for a particular range of grain sizes. When transitional fracture occurs, it results in the ballistic limit being higher than the limits found with the other fracture modes. Grain size can be influenced by process variables such as temperature, pressure, and the composition of the starting materials.

The excellent thermal shock and spall resistance of Be_4B and Be_2B in combination with its likely oxidation resistance suggests multipurpose applications. On the negative side, erosion of these materials was observed when a jet of salt water was impinging on their surfaces for several hours. Under these conditions, a spall shield or higher boride surface layer would be required to prevent this erosion.

Toxicity studies are currently underway at HEW laboratories in Cincinnati, Ohio. We have developed a method for assessing the amount and size of debris generated by ballistic impact. There

exists a good relationship between the ballistic limit of a material and the character of its debris.

For the future, the most promising way of improving the ballistic performance of beryllium borides seems to lie in the use of the graded armor concept. The goals in this area should include: increased ductility of the ceramic, increased bonding between the ceramic

and the backup plate, and compressive-reinforced loading of the ceramic with surface coatings, metal fibers, wires or sheets.

Lastly, we believe that the initial cost of raw materials could be operationally offset by recycling the waste, broken and obsolete armor plates, and that the long term cost would be similar to other ceramic armors.

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Appendix A: Preparation of Materials and Analytical Evaluation

The Be-rich side of the working Be-B phase diagram was followed in the preparation of the beryllium boride compounds by

reaction hot-pressing (see Fig. A-1).

Fig. A-1. Rough estimate of the beryllium-boron phase diagram (prepared by Gordon Godfrey and Van Frechette at ORNL in 1968).

The two phases of primary interest, $\text{Be}_4\text{B}(\delta)$ and $\text{Be}_2\text{B}(\alpha)$, were prepared by reacting Be and B powder blends below their liquidus temperatures ($\sim 1110^\circ\text{C}$ and $\sim 1165^\circ\text{C}$, respectively). According to Fig. A-1, attempts to prepare these compounds from a melt would result in the formation of a two-phase material, since both Be_4B and Be_2B decompose below their melting points ($\sim 1165^\circ\text{C}$ and $\sim 1370^\circ\text{C}$, respectively). The low melting point of the Be_4B does suggest the possibility of preparing a two-phase (~ 30 vol% Be_2B - Be_4B) armor material by casting. Preliminary evaluation of casting was reported in Ref. 5 and was continued in a previous section of this report.

Several analytical techniques were used in the evaluation of these compounds. Total Be and B contents were analyzed by wet chemical methods,^{19,20} trace impurities by emission spectroscopy, and total oxygen content by vacuum fusion analysis.²¹ Phase identification and quantitative phase analyses of BeO were accomplished by x-ray diffraction. Quantitative analyses by x-ray diffraction of BeO in the as-received beryllium boride powders required standards of fine ($< 5 \mu$ diam), low-fired ($< 1200^\circ\text{C}$) BeO particles uniformly dispersed in high-purity beryllium boride powder (~ 400 mesh). Analyses of hot-pressed beryllium boride.

Table A-1. Typical analyses of Be_4B and Be_2B powders (~ 400 mesh) from two vendors.

Powder type	Vendor	Analysis performed by	Wet chemistry (wt%)					X-ray diffraction ^a					Vacuum fusion (wt%)		
			Be_4B	Be_2B	BeO	Be	B	Be_4B	Be_2B	BeO	Be	Others	O	N	H
Be_4B (No. 4)	A	Vendor LLL	97		1	2		S	T	T	T	T of WC			
Be_4B^b (Heat 6)	A	Vendor LLL	97		1	2	21	S		T	T		2.04	0.18	0.05
Be_4B^b (Lot 2131)	B	Vendor LLL				74.5	22.9	S	T	T			2.02	0.22	0.02
Be_2B (Heat 16)	A	Vendor LLL	10	85	2.5	2.5		M	S	T	T		3.18	0.18	0.01
Be_2B (Lot 1832)	B	Vendor LLL				58.7	34.9	T	S	T					
Be_2B^b (Lot 2135)	B	Vendor LLL				56.1	35.9	M	S	S	5.0 wt%		3.19	0.64	0.02

^aT—trace; S—strong; M—medium.

^bSee Table A-2.

Table A-2. Spectrochemical analysis of Be_4B and Be_2B from two vendors.

Powder type	Vendor	Spectrochemical analysis at LLL (ppm)														
		Fe	Mg	Al	Si	Cr	Ni	Mn	Zn	Ca	Cu	Ti	Co	Sn	Ag	Sr
Be_4B (Heat 6)	A	5,000-10,000	1000	500	500	600	500	400	≤ 300	300	300	20	40	20	≤ 5	< 6
Be_4B (Lot 2131)	B	1,500	2000	1500	1000	80	100	250	≤ 300	150	150	150	≤ 6	< 6	< 5	< 6
Be_2B (Heat 16)	A	2,000	150	2000	1000	200	200	400	< 200	500	80	40	< 6	< 6	< 2	< 6
Be_2B (Lot 2135)	B	1,500	400	2000	1000	≤ 75	75	300	< 200	600	100	200	< 3	< 6	60	10

parts required that the standards had a similar hot-pressing history.

The Be_4B and Be_2B powders (-400 mesh) were supplied by two vendors for evaluation. The impurities varied slightly with each batch at the beginning of these programs, since these compounds were not routinely produced by any vendor. Typical analyses of these powders from suppliers are listed in Tables A-1 and A-2. The wet chemical results from one vendor were reported as compounds (Be_4B , Be_2B , and BeO), while the LLL results were reported according to the element (Be or B)

analyzed in Table A-1. The weight percent BeO was reported in LLL's x-ray diffraction results.

The only limitation on the impurities listed in Table A-2 to be met by the vendors was that no trace of these impurities show up in the x-ray diffraction analyses. The suppliers are capable of providing lower impurity levels in the future if desired.

The properties of the beryllium-boron compounds that were reported in Ref. 5 are also listed in Tables A-3 and A-4 along with more recent data.

Table A-3. Properties of beryllium boride compounds (Ref. 6).

Compound	Theoretical density $\rho^0(\text{g/cm}^3)$	Crystal structure	Melting point (°C)	Hardness (HK ₁₀₀)
Be_4B	1.94	Tetragonal	~1160	1370
Be_2B	1.89	Cubic	~1500	~1300
BeB_2	2.42	Hexagonal		3180
BeB_6	2.35	Tetragonal	2020-2120	~3500
BeB_{12}	2.42	Hexagonal	—	—

Table A-4. Measured elastic properties of beryllium compounds (Ref. 6).

Compound	Density, $\rho^0(\text{g/cm}^3)$	Longitudinal sound speed, $C_l(\text{cm}/\mu\text{sec})$	Shear wave velocity, $C_s(\text{cm}/\mu\text{sec})$	Elastic impedance $\rho^0 C_l$	Bulk modulus, K (Mbar)	Shear modulus, μ (Mbar)	Yield strength σ^0 (Mbar)
BeO^a	2.84	1.15	0.703	3.27	1.85	1.43	0.064
TiBe_{12}	2.28	1.14	0.750	2.60	1.23	1.28	0.045
Be_4B	1.94 ^b	1.275	0.838	2.45	1.32	1.35	0.058
Be_2B	2.03 ^b	1.27	0.800	2.58	1.52	1.30	0.057
BeB_2	2.25 ^c	1.28	0.828	2.88	1.63	1.54	—
BeB_6	2.31						0.135

^aBrush-thermalox grade BeO.

^bThe fabricated density includes contributions from BeO and BeB_2 impurities and from some porosity.

^cDensity is lower than the theoretical density ($\rho^0 = 2.42$) because of a small amount of Be_2B .

Appendix B: Average Grain-Size Determination

The average grain size was determined by the Heyn's intercept method.⁷ This method was selected because the grains were not equiaxed (width/length ratio = 0.8).

The average grain size was determined by counting line intercepts in two directions; parallel and perpendicular to the hot-pressing axis. The intercepts on two lines in each of these directions were counted on four typical microstructural views. The microstructure was magnified on a metallograph until approximately 20 intercepts/70.7 mm were obtained. The average number of grains/mm in both directions was multiplied together to get the number of grains/mm² or converted to grains/ μ^2 .

These grain-size counts are too high by a factor which reflects the probability of intercepting a grain across its largest chord in the direction of measurement. No exact correction factor is known for irregular grains. Since this error equally affects all sizes, the method is still use-

ful in evaluating the effect of grain size on ballistic performance of a material.⁸

A less accommodating error is introduced in this method of determining average grain size when the range of grain size is large (greater than a factor of ~3). Since the mode of fracture is affected by grain size and grain boundaries, the ballistic performance of two ceramics with the same composition and average grain size can still be different if the grain size ranges are not similar. Several available methods of calculating the average grain size might adjust this average to more closely represent the behavior of the fracture. Due to the complex nature of fracture in a polycrystalline material with a large range in grain size, we would not expect to develop a simple relationship between fracture and grain diameter. At present, our best means of studying this relationship is achieved by keeping the grain size range as narrow as possible.

Appendix C:

Evaluation of Fractured Surfaces with Electron Microscopic Techniques

The features revealed by examining ballistically fractured surfaces with the electron microscope are useful in determining modes of fracture. The two major features of interest in this investigation were 1) the amount and orientation of hackle marks (river line patterns),^{9,10} and 2) the general roughness of the surface in relation to the grain size. Hackle marks in fractured surfaces provide information about 1) the amount of transgranular fracture, 2) the direction of fracture, and 3) the relative amount of energy required to propagate the fracture. Hackle marks only appear across transgranularly fractured grains. The fracture velocity is decreased as a result of the increased surface energy generated during the formation of hackle.^{9,10} Hackle marks indicate the direction of fracture, since they are parallel to the direction of fracture.

The roughness of the fractured surface is also related to energy required to propagate the fracture. Smooth fractured surfaces across large grains (transgranular fracture) with little or no hackle indicate relatively low resistance to the initiation and propagation of the fracture. The fine or shallow roughness of intergranular

fracture between fine grains also indicates low resistance to the propagation of fracture. Slight adjustments in the fracture front must occur to maintain intergranular fracture. If a grain in the path of the fracture exceeds a certain critical size, the portion of the fracture front that encounters this grain may be converted to an alternative mode of fracture (transgranular, crack branching, etc.) to sustain the fracture front. This conversion or initiation of new fracture consumes energy.

The ballistically fractured surfaces of the targets were evaluated with the aid of the electron microscope techniques. Ballistically fractured surfaces near the point of impact were recovered for these evaluations. Misleading conclusions could be drawn from comparing fractures formed by different impact velocities. To avoid this problem, the fractured surfaces of each material were examined over a range of ballistically impacted velocities. The fractured surfaces were examined directly on the scanning electron microscope of magnifications of $\leq 10,000\times$. Replicas of the fractured surfaces were examined with other electron microscopes to magnifications of $\leq 100,000\times$.

Appendix D:

The Collection and Characterization of Powders Generated by Ballistic Impact

The methods used to collect and evaluate the debris from ballistically impacted targets of Be_4B and Be_2B bonded to 6061-T6 aluminum backup plates are described below. The reasons for developing these methods are discussed in the section on beryllium boride toxicity.

Two collection systems were incorporated into our existing ballistic test facilities to collect ballistically generated

target debris. Wax-coated aluminum plates were positioned to face the ceramic plates for collection of the debris in front of the targets, and wax-coated cardboard plates were positioned in back of the aluminum backup plates to collect the debris from the targets that were penetrated (see Fig. D-1). Particles greater than $\sim 5000\ \mu$ in diameter are not considered as debris for these studies.

Fig. D-1. Schematic diagram of the two collection systems used to collect the ballistically generated debris in front and in back of composite armor targets.

When the projectile penetrated the target the debris that was carried through the hole in the backup plate was collected in the wax-coated cardboard plate. Thin cardboard plates were used in this position since the thin cardboard did not significantly reduce the velocity of the projectile, and the velocity of the debris was generally low enough so that the cardboard was not penetrated by the debris. Since the velocity of the projectile was not significantly reduced by the cardboard, the existing methods of estimating the velocity of the projectiles that penetrate the target were not altered.¹ The small amount of debris carried along with the projectile was lost. The debris imbedded in the wax was removed for particle size determinations.

The debris was removed from the wax by 1) dissolving the wax in water, 2) con-

centrating the debris in the bottom of a test tube with a centrifuge, 3) decanting the solution, and 4) repeating (~6 times) the above steps until the wax was removed. An intermediate step to dissolve projectile debris was included in this operation by using dilute acid solution instead of water during the third rinse. After the final decanting the debris was vacuum dried and weighed. The debris was screened through sieves to determine the upper portion ($>45 \mu$ diam) of the size distribution curve. The finer debris ($<45 \mu$ diam) was weighed before determining its size distribution curve by a centrifugal sedimentation technique (MSA particle-size analyzer from the Mine Safety Appliances Company). Examples of these results are plotted in Figs. 38-41.

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