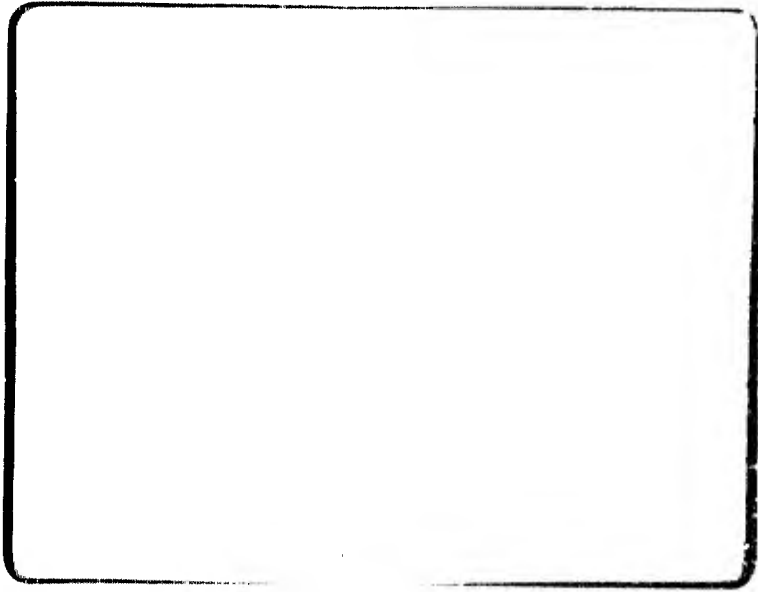


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ARMY MATERIALS AND MECHANICS RESEARCH CENTER

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**A SURVEY OF POTENTIAL CERAMIC ARMOR
MATERIALS**

Monograph Series by

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March 1968

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER

A SURVEY OF POTENTIAL CERAMIC ARMOR MATERIALS

ABSTRACT

A list of materials having potential armor application is presented along with values of density, Young's modulus, and hardness for each material if such data is available. Some ideas for future research and development work in this field are presented to illustrate the directions in which the writer believes future improvements lie in the field of ceramic armor.

INTRODUCTION

The present report is the result of a broad, comprehensive review of the field of ceramic and metal/ceramic materials. The materials tabulated and the topics discussed in Remarks and Recommendations comprise the writer's choices and suggestions for fruitful ceramic armor research.

The table contains those materials having at least one property (hardness, density, or Young's modulus, Y.M.) satisfying the following criteria while the other two properties are "reasonably" close. The criteria are: hardness > 2000 Knoop; Y.M. > 40×10^6 psi; density < 3.00 g/cc. The table is subdivided into two classes of materials: individual materials (i.e., borides, carbides, etc.) and potentially interesting combinations of materials such as composites, cermets, and alloys. The present capability for commercial production of the materials listed is included with the properties summary of each (i.e., its availability in commercial quantities, pilot-plant runs, or laboratory quantities only). Density is measured in grams per cubic centimeter; Y.M., is in terms of 10^6 psi and should be assumed measured by a "static" test except where indicated; hardness is according to the Knoop method and should be assumed measured with a 100-gm load except where indicated.

Sources consulted in compiling the table of materials are as follows:

Engineering Properties of Selected Ceramic Materials, American Ceramic Society, Columbus, Ohio, 1966.

Thermophysical Properties of Materials, Vol. III & Vol. IV, Armour Research Foundation, WADC Tech. Rept. 58-476.

Helpful comments and suggestions were obtained from Capt. M. Robinson, Ceramics Research Laboratory, and Mr. F. Hannon, Engineering Materials Branch, both of AMMRC, and from Capt. D. Martin, Clothing and Organic Materials Laboratory, ANLAB.

MATERIALS AND PROPERTIES

Material	Density	Young's Modulus	Knock Hardness	Availability
Individual Materials				
Borides				
SiB ₆	2.43	60	2000 to 2400	Laboratory
Various hexaborides (CaB ₆ , SrB ₆ , BaB ₆)	2.46 to 4.32	Unknown	2700 to 3000	Laboratory
BeB ₂	2.33	Unknown	Unknown	Laboratory
TiB ₂	4.52	55 (90% dense) to 65 (95% dense)	3000 (90% dense) to 3500 (95% dense)	Laboratory
Various borides of Sc and Y (YB ₂ , SeB ₂ , YB ₃ , YB ₄ , YB ₆)	2.91 to 4.36	Unknown	2630 (ScB ₂) 3260 (YB ₆)	Laboratory
Various borides of Al (AlB ₁₀) (α-AlB ₁₂ , β-AlB ₁₂ , γ-AlB ₁₂)	2.56 to 3.16	Unknown	1000 to 2700	Laboratory
Carbides				
Be ₂ C ^(a)	2.44	46	2700	Laboratory
Al ₄ C ₃ ^(h)	2.99	Unknown	Unknown	Laboratory
B ₄ C	2.52	65	3000 to 4200 ^(c)	Commercial
SiC ^(d)	3.2	50 to 80 (single crystal) 30 to 55 (polycrystal)	2200 to 3000 (single and polycrystal)	Commercial, small quantities
ScC	3.06	Unknown	2700	Laboratory
TiC	4.0 to 4.8	40 to 65	3200	Commercial, small quantities
Nitrides				
Be ₃ N ₂	2.71	Unknown	Unknown	Laboratory
Mg ₃ N ₂	2.06	Unknown	Unknown	Laboratory
α-Ca ₃ N ₂	2.06	Unknown	Unknown	Laboratory
Sr ₃ N ₂	Unknown	Unknown	Unknown	Laboratory
BN (hexagonal) ^(e)	2.27	Unknown	300	Commercial
AlN	3.26	50	1300	Commercial
Si ₃ N ₄ ^(f)	3.2	31 (100% dense)	1800 to 2300	Commercial, in whisker form
Single Oxides				
Al ₂ O ₃	3.6 to 4.0	45 (90% dense) 60 (100% dense)	3000	Commercial ^(g)
BeO	2.7 to 3.0	40 (90% dense) 60 (100% dense)	1800 to 2200	Commercial, small quantities
MgO	~3.6	40 (90% dense) 55 (100% dense)	800	Commercial
B ₂ O ₃	2.58 (theo- retical = 2.62)	Unknown	Unknown	Laboratory
CaO	3.2	16.5 (98% dense)	600	Commercial

MATERIALS AND PROPERTIES (continued)

Material	Density	Young's Modulus	Knoop Hardness	Availability
Individual Materials (continued)				
Mixed Oxides				
Mullite (a complex silicate) (h)	2.5 to 3.0	20	600 to 1200	Commercial
Silicides				
Mg ₂ Si	2.00	Unknown	Unknown	Laboratory
Ca ₂ Si	Unknown	Unknown	Unknown	Laboratory
CaSi	3.21	Unknown	Unknown	Laboratory
CaSi ₂	2.41	Unknown	Unknown	Laboratory
SrSi	3.47	Unknown	Unknown	Laboratory
BaSi ₂	3.98	Unknown	Unknown	Laboratory
B ₄ Si	2.46	Unknown	2400	Laboratory
B ₃ Si	2.64	Unknown	5350 (30-g load)	Laboratory
Metalloid Elements				
B	2.3 to 2.5 (various allotropes)	33	3300	Commercial (also fibers and whiskers)
Si	2.3 to 2.55	15 to 16	700	Commercial
Ge	5.3 to 5.8	23 (single crystal <111> direction)	700	Commercial
Metalloid Compounds (i)				
Be ₃ P ₂	2.06	Unknown	Unknown	Laboratory
Mg ₃ P ₂	2.02	Unknown	Unknown	Laboratory
Ba ₃ P ₂	3.18	Unknown	Unknown	Laboratory
BP	2.97	Unknown	3200	Laboratory
AlP	Unknown	Unknown	Unknown	Laboratory
ScP	3.28	Unknown	Unknown	Laboratory
Intermetallic Compounds				
TiBe ₂	3.23	Unknown	Unknown	Laboratory
TiBe ₁₂	2.3	Unknown	960 (j)	Laboratory
Zr ₂ Be ₁₇	3.05	45	1130 (j)	Laboratory
ZrBe ₁₃	2.72	47	1000 (j)	Laboratory
VBe ₁₂	2.35	Unknown	Unknown	Laboratory
Nb ₂ Be ₁₇	3.28	43 (dynamic) 48 (static)	1000 (j)	Laboratory
Nb ₂ Be ₁₉	3.15	Unknown	Unknown	Laboratory
NbBe ₁₂	2.91	47	500 (j)	Laboratory
Ta ₂ Be ₁₇	Unknown	28 (dynamic) 54 (static)	Unknown	Laboratory
MoBe ₁₂	3.03	Unknown	950 (j)	Laboratory
WBe ₂₂	3.23	Unknown	Unknown	Laboratory

MATERIALS AND PROPERTIES (continued)

Material	Density	Young's Modulus	Knoop Hardness	Availability
Cermets, Composites, Alloys				
Cermets (dispersed metallic phase with or without compound formation)				
SiC + 35% Yttrium by volume ^(k)	3.13 (13.6% porosity)	Unknown	Unknown	Laboratory
70 Al ₂ O ₃ /30 Cr (wt %)	4.6 to 4.65	52	~1500	Laboratory
B ₄ C-Fe bonded (36.4% Fe)	3.24	52	~1500	Laboratory
BeO-Be bonded (8% Be)	2.86	52	~1500	Laboratory
SiO ₂ -Al bonded	Unknown	52	~1500	Laboratory
TiC cermets (0 to 50 wt % Co or Ni)	5.5 to 6.8	45 to 55	85 to 90 Rockwell A	Laboratory
Composites				
TiC with additions of ZrB ₂ or TiB ₂ or Mo ₂ C have been investigated and found to have fairly high melting points (>2970 K), but no other property data seems to be available.				
SiC-silicon nitride bonded	2.5 to 2.8 (13 to 15% porosity)	17	Unknown	Commercial
SiC-silicon oxynitride bonded	~2.7 (~18% porosity)	17	Unknown	Commercial
SiC + graphite	2.3 to 2.8 (8 to 26% porosity)	35	Unknown	Commercial
Alclad B ₄ C	2.5	Unknown	Unknown	Laboratory
Cr-reinforced Al ₂ O ₃ (30 wt % Cr)	4.6 to 4.65	52.3	1100 to 1200	Laboratory
Alloys				
Al ₂ O ₃ ·P ₂ O ₅ (melting point 2900 F)	2.6	Unknown	Unknown	Laboratory
Al ₂ O ₃ ·MgO	3.6	35	1200 to 1400	Laboratory

- (a) Be₂C is possibly sensitive to moist air at room temperature.
 (b) Al₄C₃ is unstable in moist air.
 (c) Various investigators.
 (d) See also various SiC composites in "Cermets, Composites, Alloys". Also, doping of SiC with B has raised the Y.M. to 95.
 (e) Cubic BN has been made from hexagonal BN by methods used for synthetic diamond and has a hardness in the same range as diamond and a density of 3.48 g/cc.
 (f) Properties of Si₃N₄ are heavily dependent on percent density (porosity).
 (g) Now available in continuous single crystal (both sapphire and ruby) filaments which can take various cross-sectional shapes (i.e., L, I, tubing, ribbon, etc.)
 (h) Many silicates have densities <3.0 but no other properties are listed for these.
 (i) Other possibilities in this subsection are the antimonides and bismuthides, which all have melting points above 2800 C and might be expected to have hardnesses in the desirable range. However, no densities or mechanical properties for these materials could be found.
 (j) 2500-gram load.
 (k) 62% Co + 30% Cr + 5.5% Mo + 2.5% Ni + 2% Fe.

REMARKS AND RECOMMENDATIONS

The viewpoint taken here is that of the materials scientist only. No attempt will be made to reconcile or discuss the points made below with the "cold, hard facts" of the "real" engineering and/or economic world.

By this is meant that many potentially promising areas of research in armor materials/processes are mentioned. The questions: "Can the materials be made or the processes engineered?" and "Can the previous aims be accomplished economically with regard to both time and money?" will remain to be answered. The following list of ideas is certainly not exhaustive; they serve merely to introduce the topic.

A résumé of materials is perhaps in order at this point. Retaining the subsection headings from the tables of properties, the following materials seem to have the most promise and to merit consideration as individual armor materials.

Borides

SiB_6 Low density, acceptable Y.M. and hardness

CaB_6 Low density, high hardness

SrB_6 Low density, high hardness

BaB_6 Low density, high hardness

Other hexaborides Low density, high hardness

BeB_2 Lowest density boride, no other properties known

TiB_2 Poor density, good Y.M. and hardness with possibility of large improvement in Y.M. and hardness with reduction in porosity.

Carbides

Be_2C Good density and hardness

B_4C Presently in use material

TiC High hardness

Nitrides

Cubic BN Good hardness, should have very good modulus

Single Oxides

B_6O Good density, should have good modulus and hardness

Mixed Oxides

None

Silicides

B_4Si ,
 B_3Si Good densities, acceptable hardness values

Metalloid Elements

B Very good density and strength for use as fiber reinforcer

Metalloid Compounds

BP Very good hardness

Be_3P_2 ,
 Mg_3P_2 Very good densities, no other properties available

Intermetallic Compounds

Zr_2Be_{17} Good hardness

$ZrBe_{13}$ Good densities and hardnesses, acceptable moduli

VBe_{12} Good densities and hardnesses, acceptable moduli

Cermets

None

Composites

Alclad B_4C Good density, other properties not available

This résumé should *not* be taken to mean that none of the other materials listed have potentially useful properties. One of the main contentions of this survey is that instead of looking for individual (single) materials to substitute for existing materials in ceramic armor, an effort should be spent in designing a combination armor which will use the favorable properties of two or more materials while minimizing the effects of their unfavorable properties. The term combination should be substituted for composite in armor usage because composite has a specific meaning in materials science terminology, which is discussed later.

First, with regard to "pure" materials, such as those in the foregoing tables, some generally known features should be emphasized. Materials available at present, even in commercial quantities, are not well characterized with respect to impurity content, porosity content, and porosity size and distribution. All of these factors directly influence mechanical properties

such as hardness and Young's modulus. For instance, it has been shown that reduction of porosity content by as little as 1 percent (for example, a density increase from 98 percent theoretical density to 99 percent) increases the Y.M. by as much as a factor of 1.3. Impurities may affect mechanical properties by creating complex second phases in otherwise pure and homogeneous materials. These second phases may have deleterious properties with respect to the matrix (such as being more brittle than the matrix, thus serving as crack initiators).

It should be emphasized in regard to the materials discussed that in most cases, techniques such as hot pressing, which have been found to reduce porosity and refine grain size, have *not* been tried. The property data available are for the most part from as-cast or pressed and sintered material. Most of this data is from fairly porous samples (containing as much as 10 to 15 percent porosity in extreme cases); this is especially true of the borides, carbides, and nitrides. Efforts to reduce porosity and increase purity of individual pure materials must be expected to yield significant increases in mechanical properties.

An interesting effect found in the beryllides is related to the generalizations on purity and homogeneity made above. It has been shown that for a given metal atom, Me, a mixture of different beryllides of the same metal (say $MeB_2 + Meb_6$, for example) may yield higher strengths than are obtained from either of the individual beryllides.

Still another property related to purity and homogeneity and having an important effect on mechanical properties is the degree of off-stoichiometry which may be present in certain ceramic materials. Examples are the transition metal oxides of the iron series and the carbides of Ti, Zr, and V. If a material such as TiC_x exists over a range of values of x (in this case $1.00 \geq x \geq 0.5$), its mechanical and physical properties are expected to vary significantly over this range.

One technique which has great promise for armor application and which has not received its due share of attention is the application of composite materials. The term composite here refers to materials having a matrix in which fibers of another material are embedded. It is expected that the composite will possess the desirable properties of both matrix and filler material. Much application of such materials has been made in the aerospace and high temperature materials fields. There has been, to the writer's knowledge, no attempt to "build" or "design" a composite material specifically for an armor application.

Extensive research is currently underway both in government laboratories and in private industry toward investigating the basic (or theoretical) questions of fiber and whisker composite behavior and toward developing and improving currently successful composites. Restricting consideration for the present to ceramic fibers in metal matrices (neglecting, for instance, ceramic fibers in polymers and graphite fibers in metals and in polymers), the following are examples of composites having potential in the armor field.

Fibers and whiskers of boron, silicon, and germanium have been successfully embedded in metal matrices, and more or less thorough investigations have been conducted to determine their properties. The distinction between fibers and whiskers implies that whiskers are usually very thin single crystals (~ 0.001 inch or less in thickness), whereas fibers are usually polycrystalline and of slightly larger diameter (> 0.001 inch in thickness). Generally whiskers are placed in metal matrices while fibers are placed in polymers or epoxies. Their purpose in both cases is to add strength to the composite while preserving as much ductility and energy-absorbing capacity as possible.

A commercial development of potentially great application to armor (especially personnel armor) is the idea of placing boron fibers (~ 0.002 - to 0.005 -inch diameter) in an epoxy sheet. Very thin sheets may be made and then built up as an armor backing (or possibly as a facing material in an epoxy-ceramic-epoxy sandwich), thus allowing very fine gradations in thickness. This in turn will enable designers to more carefully control the weight factor to get precisely the ballistic protection needed with minimum weight.

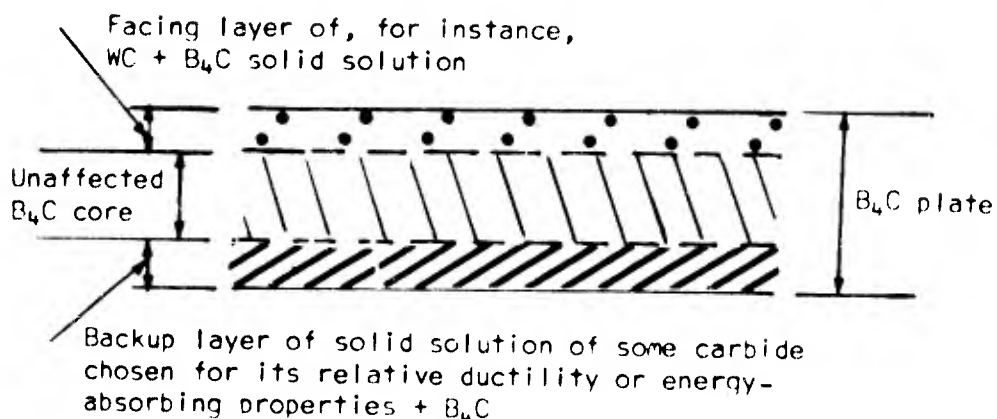
Cermets, that is metals or ceramics containing fine (\sim a few microns in size), dispersed particles of a second phase, have been available commercially for 10 to 12 years. Certain properties of cermets which have a finely dispersed ceramic phase in a metal matrix may be desirable for armor applications. For instance, their high tensile strength combined with a capacity to absorb energy would make them candidates for armor which could perform a load-bearing or structural function. The usually appreciable density coupled with fairly low hardness of the metal matrices of cermets may preclude their use in bulk in personnel armor, but a thin sheet or plate of a cermet material used in combination (i.e., as a backup plate) with a hard, brittle facing plate may yield improved performance in lightweight armor.

It has been found that optimum properties in a given cermet usually result from the finest possible matrix grain size and/or complete dispersion (no coagulation) of the hard phase. The shape of the second phase is also important, spheroids being most desirable. These desirable features have proved attainable in cermet materials currently of interest.

Still another interesting area which might yield immediate improvements in present materials is the development of a dual-hardness ceramic armor. An example using B_4C as the basis material is shown in the following sketch. (This proposal is currently being investigated by the author.)

Success with this principle should result in a thickness reduction on the B_4C plates presently used and possibly a weight reduction also. It must be realized that any weight saving resulting from reducing the overall thickness of the ceramic may be offset by a weight gain due to a higher density in the surface layers.

The last idea to be discussed here concerns the surface characteristics of armor plates. One wonders whether there is a reason for having ceramic

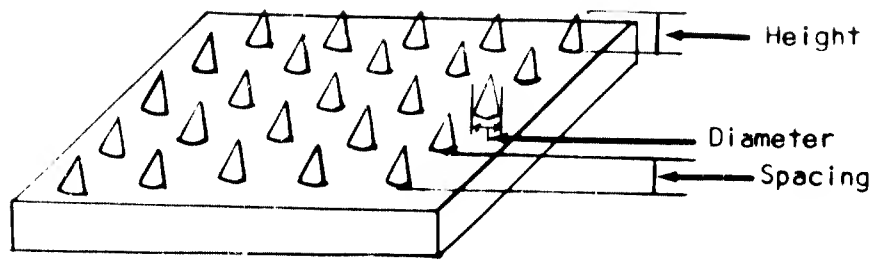


- NOTE:
1. Facing and backup layer thicknesses and starting plate thickness to be determined by experimentation.
 2. Facing and backup layers to be formed by (possibly simultaneous) diffusion of the two metals.
 3. It is recognized that simultaneous or post-diffusion high pressure (~10 kbar) treatment at temperature may be necessary to cause compound formation in the diffusion layers.

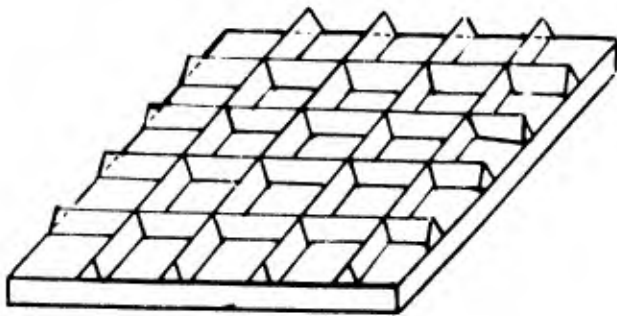
armor plates smooth-surfaced. Even though research* has shown that the bullet is fragmented on impact, the fragments stay together and the bullet continues as if it were integral, having a certain velocity and momentum, for some finite time after it actually has fragmented. Might not one expect the ballistic limit of a given piece of armor to improve if some way were found to separate these fragments earlier after impact? A possible way to accomplish this is the following.

The impact surface of the ceramic plate might be designed to possess protrusions or ridges of some (to be determined) optimum dimensions as in the accompanying sketches. These features, which may be imparted during final forming processes such as hot pressing, have the additional desirable property of deflecting the incoming projectile so as to reduce the possibility of impact at 0 degrees obliquity. Ideas similar to this have been tried before, but in all cases were attempted more than five years ago. However, the increasing interest in and development of ceramic processing technology since those attempts would seem to warrant another look at these possibilities.

*FLORENCE, A., and AIHRENS, T. *Interaction of Projectiles and Composite Armor*. Stanford Research Institute, Menlo Park, California, 31 January 1967.



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