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Westinghouse Astronuclear Laboratory

DEVELOPMENT OF A CbC-ZrC MATERIAL FOR
USE AS A HOT HARDNESS INT^PENTER
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J. L. Godshall and J. Alfred Berger*

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*Mr. Godshall is engineer with the Westinghouse Astronuclear Laboratory. Dr. Berger is Professor and Chairman of the Department of Metallurgical Engineering at the University of Pittsburgh. This paper is based in part upon a thesis submitted by Mr. Godshall to the University of Pittsburgh in partial fulfillment of the requirements for the degree of Master of Science.

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Development of CbC-ZrC Material for Use as a Hot Hardness Indenter

Major Advisor: Dr. J. Alfred Berger*

A pseudo-binary columbium** carbide - zirconium carbide (CbC-ZrC) of 96 per cent theoretical density was prepared by hot pressing of powdered carbides for use as a hot hardness indenter to measure the hardness of refractory alloys at elevated temperatures. Attempts to further densify the carbide by high energy rate (Dynapak) extrusion, arc-melting, high temperature sintering in graphite, and liquid phase sintering in vacuum were generally unsuccessful. The carbide, prepared without any contaminating binder, showed excellent hardness values at 1315°C (2400°F), good compatibility with columbium and tantalum base alloys, and was capable of being ground to a fine point Vickers configuration. However, when the CbC-ZrC carbide was used as the indenter at 1315°C (2400°F) the fine point flattened during the indentation.

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**Alternately referred to as niobium

FOREWORD

The Author wishes to express his appreciation to the Astronuclear Laboratory of the Westinghouse Electric Corporation for the generous use of their facilities. In addition, appreciation to the following Westinghouse personnel: Mr. W. Marcom, Bloomfield Division, for his suggestions on hot pressing, Mr. C. Schenone for his efforts in obtaining the x-ray films, Mr. R. T. Begley for his discussions throughout the investigation and to Mr. D. C. Goldberg for his support of the experimental work. Finally, my appreciation to Prof. J. Alfred Berger of the University of Pittsburgh for his guidance in the selection and completion of this research topic.

TABLE OF CONTENTS

	Page
FOREWORD	
I. INTRODUCTION	1
A. Carbide Technology	5
B. Selection of the Pseudo-Binary CbC-ZrC	8
II. METHODS OF CARBIDE PREPARATION	17
A. Powder Metallurgical Approach	17
1. Preparation of Alloyed Powders	18
2. Consolidation of Powders	18
3. Arc-Casting Metallurgical Approach	19
4. Other Processing Techniques	19
III. EXPERIMENTAL APPROACH	21
A. Pressing and Sintering	24
B. Hot Pressing	27
C. Arc Melting	32
D. High Temperature Sintering in Carbon	35
E. High Temperature Extrusion	40
F. Vacuum Annealing and Liquid Phase Sintering	49
G. Hot Hardness Measurements	53
IV. DISCUSSION	59
V. CONCLUSIONS	68
VI. BIBLIOGRAPHY	70

LIST OF TABLES

	Page
1. Chemical Analysis of CbC Powder Supplied by Kennametal Lot No. BL-1 -325 mesh	22
2. Chemical Analysis of ZrC Powder Supplied by Atlantic Equipment 1-5 μ size	23
3. Hardness and Density of Pressed and Sintered CbC-ZrC Compacts	25
4. Hot Hardness of TaC as a Function of Temperature	55

LIST OF FIGURES

	Page
1. Correlation of Hot Hardness with Tensile Strength for Columbium Alloys	3
2. Columbium-Columbium Carbide Phase Diagram	9
3. Zirconium Carbon Phase Diagram	10
4. Lattice Parameter Composition Curves for the Carbide Pairs ZrC-TaC, CbC-ZrC, CbC-TaC and TiC-ZrC	12
5. Lattice Parameter vs Carbon Composition Comparison of Lattice Parameters Results for Zr-C System	13
6. Lattice Constant and Theoretical Density vs C/Cb Molar Ratio for CbC	14
7. Pressed and Sintered Compacts of CbC, 60CbC-40ZrC, and 80CbC-20ZrC	26
8. Variation of Relative Density of 4 TaC-1 HfC with Hot Pressing Parameters	28
9. Variation of Relative Density of 4 TaC-1ZrC with Hot Pressing Parameters	29
10. Hot Pressed 50CbC-50ZrC	31
11. Hot Pressed ZrC	33
12. Hot Pressed CbC	33
13. Hot Pressed 50CbC-50ZrC	33
14. Arc-Melted 50CbC-50ZrC Hot Pressed Compact	34
15. Arc-Melted 20CbC-80ZrC Hot Pressed Compact	36
16. Schematic of High Temperature Sintering Furnace	37

LIST OF FIGURES

	Page
17. Hot Pressed 40CbC-60ZrC after Sintering in Carbon	39
18. Model 1220C Dynapak	41
19. Canning Configuration of ZrC and CbC Carbides in Tungsten Prior to Extrusion	42
20. Pressed and Sintered ZrC Canned in Tungsten and Extruded	44
21. Pressed and Sintered CbC Canned in Tungsten and Dynapak Extruded	44
22. Pressed and Sintered CbC Canned in Tungsten and Dynapak Extruded	45
23. Canning Configuration for Pressed and Sintered Carbide in Molybdenum Prior to Extrusion	47
24. Pressed and Sintered 60CbC-40ZrC Canned in Molybdenum and Heated to 1980°C (3600°F)	48
25. Canning Configuration of Hot Pressed Carbide in Molybdenum Prior to Extrusion	50
26. X-ray of Hot Pressed 50CbC-50ZrC Canned in Molybdenum and Extruded	51
27. Hot Pressed 50CbC-50ZrC Canned in Molybdenum and Extruded	52
28. Hot Hardness Tester	54
29. Vickers Impression of B ₄ C Indenter after 1st Indentation in Complex Ta Base Alloy	56
30. Vickers Impression of B ₄ C Indenter after 9th Indentation in Complex Ta Base Alloy	56

LIST OF FIGURES

	Page
31. Vickers Impression of B_4C Indenter after 15th Indentation in Complex Ta Base Alloy	56
32. TaC Specimen	57
33. TaC Hot Hardness Sample Mounted in Molybdenum	57
34. 50CbC-50ZrC Hot Pressed Compact Ground to a Vickers Configuration	62
35. 50CbC-50ZrC Indenter Mounted on a Molybdenum Shaft	62
36. Hardness Indentation Taken at $1315^{\circ}C$ ($2400^{\circ}F$) on a Cb-26W-4Re-2Hf-0.067C Alloy Using the 50CbC-50ZrC Indenter	64

I. INTRODUCTION

As the ever increasing needs of space age technology push the operating temperatures higher, the need for higher strength materials at elevated temperatures has become acute. In the development of materials for service above 1000°C (1800°F), the metals in groups IV, V, and VI of the periodic table have received considerable emphasis. The more promising of these alloy systems encompass one or more of the following elements used for various strengthening purposes: tungsten, molybdenum, tantalum, columbium, * hafnium and zirconium. The high cost of the basic materials and the extreme difficulty of obtaining reliable and reproducible test data to temperatures in excess of 1650°F (3000°F) has led to the development of several screening techniques, one of which is the hot hardness tester.

To extend the upper temperature limitation of hot hardness testing beyond the present limit of 1205°C (2200°F) for refractory alloys, an indenter material of high strength at high temperature, with densities in excess of 96 per cent of theoretical, compatible with the refractory alloys, relatively insensitive to thermal shock and capable of being ground to a fine void free point will have to be developed.

The use of room temperature measurements to determine the ultimate and yield strengths, the elastic limit, and various fracture mechanisms has been well established.^{(1-3)**} The utilization of hardness measurements up to 800°C (1470°F)

*Alternately referred to as niobium.

**Parenthetical references placed superior to the line of text refer to the bibliography.

has also been well established to determine the above properties as well as aging reactions and kinetics. (4-9) However, virtually no reliable data have been obtained on the higher strength materials at temperatures in excess of 1200°C (2200°F).

The principal advantages of the hot hardness procedure are the simple shape of the specimen required and the large number of specimens that can be measured at the same time. Additionally the trend of hardness with increasing temperature can generally be made on the same sample eliminating other processing variables between similar samples. The correlation of hot hardness data with those of other conventional high-temperature tests has been adequately demonstrated as shown in Figure 1. However, there is as yet no standard for inter-calibration between the various investigators and most of the data accumulated must be analyzed within this limitation. While there are numerous advantages associated with the hot hardness tests in conjunction with the specimen design and inherent brittleness of the harder materials, the use of the hot hardness technique is beset with several problems of its own. In general these problems become more prominent with higher temperatures, lower loads, and the harder, more brittle materials.

Extensive development of operating and design features have eliminated many of the difficulties in the static type tests. Controlled programming of the indenter speeds, dwell times, heating and cooling cycles, etc., have allowed the engineer to circumvent the more obvious difficulties until the limiting feature has become a suitable material for the indenter and its mounting.

The choice of the indenter geometry is particularly important. There are three forms that have found considerable use in micro-hardness testing; the square based

FIGURE 1 - Correlation of Hot Hardness with Tensile Strength for Columbium Alloys (After Begley, Buckman, Godshall, and Stickler Ref. 7).

pyramid, the cone, and the rhombohedral-based pyramid or Knoop shape. The ball is not favored because of the change in geometry with increasing depth. The pyramid design allows a constant kg/mm^2 ratio to be applied regardless of the depth of the penetration. The pyramid, as compared to the cone, produces undesirable stress concentrations at the corners of the impression limiting its use for the extreme brittle ceramic materials. As each face of the pyramidal indenter must be cut and polished separately it is extremely difficult to cut the pyramidal indenter to a truly sharp point. The sharpest point commercially available to date is approximately 0.5 micron.

There are several factors which must be included in the selection of the indenter material. Chemical inertness with the material to be tested, stability, and commercial availability are among the more critical aspects. At the present time, the data on the high temperature properties of the available materials are severely limited, and therefore the selection must usually be based on room temperature properties and available thermal-chemical data.

Diamond, one of the hardest materials available, has the unfortunate property of reverting to its more stable form of graphite at elevated temperatures under high vacuum conditions.⁽¹⁰⁾ In addition diamond reacts chemically with many of the alloying additions such as titanium.⁽¹¹⁾

The second choice of an indenter material, sapphire, possesses good stability, can be ground to the desired configuration, and has good low temperature hardness. However, sapphire has an upper temperature limitation due to its decrease in hardness. It is generally recognized that the hardness of the indenter should be at least two and one-half times that of the material being tested. The hardness of sapphire falls off

linearly with an increase in temperature over the temperature range of 20 to 800°C (68 to 1470°F) limiting its use for the very hard high temperature materials. ⁽¹²⁾

Various cemented carbides have been utilized. All of these suffer from the softening point of the binder (usually less than 800°C). In addition, any binder or material used as a sintering activating complex could react with the alloys causing degradation of the indenter or erroneous hardness measurements. A substantial amount of work has been described in various Russian and German publications. However, only a small portion of this literature has been translated.

The use of arc-cast W_2C has been established at Battelle ⁽¹³⁾. However, the hardness generally is low ranging below 200 VHN at 1200°C (2200°F).

Recent work at NASA ⁽¹⁴⁾ has indicated that B_4C produced by the Norton Company under the trade name "Norbide" possesses adequate strength at 1205 to 1315°C (2200 to 2400°F). As discussed later, boron reacts chemically with some of the refractory materials.

The conclusion therefore results that with respect to either material or geometry there is no material known or developed which at present can be utilized for refractory metals in the temperature range of 1200 to 1650°C (2200 to 3000°F).

A. Carbide Technology

Recognizing that virtually all of the refractory alloys being developed today utilize zirconium or hafnium to form stable carbides, nitrides, or carbo-nitrides as a strengthening mechanism by precipitation hardening; it seemed feasible to investigate a pseudo-binary alloy carbide system relying on solid solution strengthening for a high

temperature, high hardness, chemically inert with respect to refractory metals indenter material.

A recent publication⁽¹⁵⁾ contained the following statement:

"The carbides of the transition metals of the IVth, Vth and VIth group of the periodic table have found many useful applications when formed into structural parts by combining the powder with an auxiliary metal such as cobalt or nickel as a binder. The full potential of these refractory substances, however, cannot be realized until they can be fabricated into dense bodies of the desired shape without the use of the auxiliary binder. In spite of a great deal of effort, this has not yet been done successfully."

Norton and Lewis⁽¹⁵⁾ have investigated the TiC system and from their results have drawn many conclusions on the properties of the ZrC system which they state to be entirely analogous to the TiC system. Their review will be utilized to present a detailed theoretical model of the defect structure found to exist in the refractory metal carbide systems. In particular they give a rational explanation for the observed fact that the refractory metal carbides are never found in stoichiometric compositions but always contain a slight excess of the metal phase. The electrons responsible for the bonding energy occupy a band of states derived from the outer s and d states of the metal atoms and the 2s and 2p states of the carbon atom. One would then predict that this band of states has a capacity of 80 electrons per unit cell (cubic cell containing 4 metal atoms), where the complete 2s and 2p shells could contain 2 and 6 electrons respectively in the carbon atom while the 3d and 4s shells of titanium could contain 10 and 2 electrons respectively. For a unit fcc cell structure containing 4 atoms per cell, there is a potential for 80 electrons if all the s and d shells were completely filled.

However, somewhat less than half of the states are occupied by electrons since at the stoichiometric composition only about 32 electrons per unit cell are available. As the carbon content of the substance increases from $MC_{0.75}$ to $MC_{1.00}$, the electron concentration increases from 28 to 32 electrons per unit cell, and one would expect the Fermi energy to increase. It has been postulated that less than one per cent of the electrons near the Fermi level contribute to the electric conductivity. The remaining electrons essentially of p and d character contribute to the bonding in a manner similar to the covalent bonds. From this it is expected that the bond strength would increase as the carbon concentration increases.

This model predicts that there are two competing forces at work as the carbon concentration is increased. First, if the metal atoms are close packed, the octahedral hole is smaller than the carbon atom which is to occupy it and the lattice constant should increase progressively as the carbon content is increased. The increase in lattice parameter may not be linear, but it should not present any maximum with a subsequent reduction. Alternately, the electron concentration increases with the carbon content and this results in an increase in bond strength which would operate in a direction to decrease the lattice parameter. This combination results in values of the parameters less than predicted on the hard sphere model and the curve might well show a broad maximum. This has been observed in the ZrC system and is expected to a lesser degree in the CbC system at values very close to $CbC_{0.98}$.

The refractory metal carbides all show some defect structure in that a stoichiometric composition is never attained although it is sometimes closely approached. One explanation for this is that the carbon atoms prefer to combine as graphite rather

than to fill the last remaining few sites in the carbon lattice.⁽¹⁵⁾ The shape of the Fermi surface and its possible approach to a zone boundary at the critical electron concentration has been suggested as an explanation for the stoichiometric composition being less stable than the graphite phase with which it is competing as the composition approaches a 1:1 atom ratio.

Many investigators (Santoro⁽¹⁶⁾ for example) have shown the correlation of the carbon/metal ratio on the hardness and approach to theoretical density. Unfortunately all of these systems have been limited to the pure binary systems at low temperatures and there are no data available for pseudo-binaries such as are examined in this investigation.

B. Selection of the Pseudo-Binary CbC-ZrC

The choice of the columbium carbide-zirconium carbide (CbC-ZrC) system was dictated on the basis of certain theoretical and experimental data. It should be realized that there are many other systems that could have been investigated. However, the high temperature data for any carbide system are sparse, and any selected system would require a similar investigation.

CbC and ZrC are both fcc of the sodium chloride structure. The metal atoms are essentially close packed in a fcc arrangement with the carbon atoms placed in the interstices. Both carbides are isomorphous, have a wide variation of non-stoichiometric stability, have similar melting points, and have atomic diameters of less than 7.5 per cent variation. Phase diagrams are shown in Figures 2 and 3 for the CbC and ZrC

FIGURE 2 - Columbium-Columbium Carbide Phase Diagram (After Storms and Krikorian Ref. 22).

FIGURE 3 - Zirconium Carbon Phase Diagram
(After Sara Ref. 17).

systems respectively. These carbides should follow Vegard's law and possess mutual solid solubility over the entire composition range. Norton and Mowry⁽¹⁸⁾ have presented some data reproduced in Figure 4 where they have examined a number of refractory metal carbides and show complete mutual solid solubility for the CbC-ZrC system. The increase in lattice parameter with increasing concentration of ZrC follows a nearly straight line relationship and therefore is in agreement with Vegard's law. The authors do not present any density determinations but from their processing techniques it can be assumed that a value below 95 per cent was achieved.

The ZrC system shows a definite maximum in the lattice parameter as the carbon/metal ratio is increased to 0.85 as shown in Figure 5 reproduced from the work of Dolloff as reported by Norton and Lewis⁽¹⁵⁾ for samples which are probably close to the true oxygen free value. At carbon concentrations greater than this limiting value, the lattice parameter decreases. The CbC system reproduced from the work of Kempter, Storms, and Fries⁽¹⁹⁾ shown in Figure 6, shows a general increase in the lattice parameter with increasing amounts of carbon until a concentration of about 0.98 has been attained. (The curve is extrapolated to stoichiometric composition in the figure). The theoretical density shows a minimum at a carbon/metal ratio of about 0.78 rising to a maximum as the carbide approaches the stoichiometric composition. It appears from this that a system composed of these two carbides with competing lattice parameter variation as stoichiometry is approached could be produced in which the density would be greater than either of the two component carbides.

There is considerable disagreement in the literature on the mode of vaporization of these carbides. This mode of vaporization would be important in high

FIGURE 4 - Lattice Parameter Composition Curves for the Carbide Pairs ZrC-TaC, NbC-ZrC, NbC-TaC, and TiC-ZrC (After Norton and Mowry Ref. 18).

FIGURE 5 - Lattice Parameter vs Carbon Composition Comparison of Lattice Parameter Results for Zr-C System (After Norton and Lewis Ref. 15).

FIGURE 6 - Lattice Constant and Theoretical Density vs C/Cb Molar Ratio for CbC (After Kempter, Storms and Fries Ref. 19).

temperature sintering where the composition of the carbides could be altered if the vaporization were markedly different from congruent resulting in a non-stoichiometric carbide. Pollock⁽²⁰⁾ stated that zirconium carbide vaporizes with an excess of metal in the vapor leading to an enriched carbon content in the substance. This was disputed by Coffman, Kibler, Lyon and Acchione⁽²¹⁾ who reported that ZrC vaporizes congruently at temperatures in excess of 2000°C (3600°F). However, the authors state that the results are similar after about one per cent of the carbide has vaporized leading to the conclusion that the initial vaporization could be impurity volatile elements in the compacts.

Storms and Krikorian⁽²²⁾ have stated that CbC vaporizes with a resultant loss of metal in the specimen at temperatures in excess of 2300°C (4200°F).

Nelson, Berger, and Foster⁽²³⁾ using a modified Langmuir technique have concluded that CbC vaporizes with two atoms of carbon per columbium atom in the vapor. The starting material consisted of CbC and Cb₂C precipitated on certain planes. These authors also state that ZrC vaporizes with an excess of carbon in the vapor. However, their starting material had a significant excess of carbon beyond the stoichiometry that would have been desired.

The foregoing data clearly indicate the variation in the literature between different authors. It is generally recognized that a large portion of the differing data is caused by the difference in the purity of the starting materials and the method of preparation. In most references cited, the detailed chemistry and processing data are omitted despite the significant variation in the final compacts which could result.

The data cited above indicated that a pseudo-binary CbC-ZrC carbide could be prepared by powder metallurgy which would have properties substantially better than either of the pure carbides; that is, very high density, moderate size, chemical stability with the refractory alloys and the capability of being ground to a Vickers configuration.

II. METHODS OF CARBIDE PREPARATION

While there are a number of methods of producing high purity dense carbides of controlled composition, all suffer from some basic limitation. To date most of the research effort has been directed at either arc melting in vacuum or pressing and sintering. Many novel techniques have been developed to overcome some of the limitations, but to date none of the methods is capable of generating a large size highly dense material.

A. Powder Metallurgical Approach

At the outset, it is imperative to mention that production of alloys by mixing the component metal and carbon powders and sintering them is almost impossible because of the vast differences in diffusion rates of the various components. This nonuniformity in diffusion rates leaves behind porosity due to volume changes and also results in a very inhomogeneous material. To circumvent this difficulty it is generally desirable to start with prealloyed powders and then to densify them. For the more simple systems where the atom sizes are somewhat similar, a homogeneous compact could theoretically be produced if the time-temperature-pressure relationships could be controlled. Many other factors such as eutectics, melting points, vaporization rates, etc., would all have to be favorable.

The powder metallurgy of any alloy could be subdivided into two distinct parts:

- (1) Preparation of high-purity prealloyed powders, and;
- (2) Consolidation of these prealloyed powders in a dense, homogeneous material.

1. Preparation of Prealloyed Powders

The most widely used technique for production of prealloyed powders involves a process of mechanical comminution of an arc-cast ingot of the alloy. This process inherently contains a large impurity content which increases as the powder size is reduced.

Hydriding an arc-cast alloy ingot has been used with limited success. However, this technique is limited to those metal systems whose hydrides decompose rather readily at low temperatures and which do not have an excessive affinity for oxygen. Obviously these limitations rule out the refractory metal carbides.

2. Consolidation of Powders

The primary mechanism of densification of powdered metals is volume diffusion. When particles employed in sintering are very fine (one micron or less), the surface diffusion contributes appreciably towards densification. As mentioned previously the decrease in size also increases the contamination of the particles. During sintering an activating energy sufficient to cause densification must be supplied to the compact.

The technique of hot pressing takes advantage of the increased plasticity of the refractory metals at high temperatures. The application of this process requires that a graphite die be used to contain the powders and has the inherent limitation of changing the carbide stoichiometry.

3. Arc Casting Metallurgical Approach

As an alternative to the powder metallurgical approach the use of consumable arc melting has been increasingly utilized to make large ingots of widely varying composition. In this process the carbide itself would have to be the electrode creating very difficult problems in the electrode fabrication. Non-consumable arc-melting has been utilized to make smaller size ingots, where a tungsten electrode is utilized to maintain an arc with the powders. This technique suffers from the loss of certain constituents as the metal is liquified or vaporized at the point of contact. Utilization of a partial pressure of inert gas reduces this tendency. Further the compacts are generally melted in a water-cooled copper mold which causes severe thermal shock to the cast structure.

4. Other Processing Techniques

A number of alternate methods for producing carbides are now in the developmental stage. Since none of these are well enough advanced for utilization in this investigation, only a few will be briefly discussed.

One technique, vapor deposition, occurs when a layer of carefully controlled chemical composition is built up on a very fine wire. Processing control for complex compositions is extremely difficult.

Another method, adding a thermite mixture to the alloy powders, triggers and supplies the high temperatures required for densification without the need to heat the graphite die. This circumvents the limitation placed on the pressing force by the relatively weak graphite dies.

A third process, liquid phase sintering, mixes a small volume of a lower melting metal with a refractory metal. Densification is accomplished by sintering above the melting point of the lower melting addition. This method has had very little success in refractory metal carbides.

III. EXPERIMENTAL APPROACH

Any investigation into the high temperature refractory carbides requires the utilization of very complex, expensive, and sometimes hazardous equipment. The approach taken in this investigation was formulated to utilize the existing equipment located at the Astronuclear Laboratory of the Westinghouse Electric Corporation.

The carbide powders were purchased from commercial vendors to maintain a uniformity of composition throughout the program. The starting chemistry is listed in Tables 1 and 2 for the CbC and ZrC respectively. It is evident that while this material is supposed to be of the highest purity commercially available, the analysis indicates a substantial degree of contamination. It was felt that purification of the starting material was beyond the scope of this investigation and consequently the carbide powders were used in basically the as-received condition.

A number of approaches were taken to produce a compact of better than 95 theoretical density, using various ratios of CbC/ZrC. The size limitation was determined by the hot hardness tester discussed in a later section. Initially, both cold pressed and sintered, and hot pressed compacts were made. These were then extruded through a Dynapak Extrusion press to attempt further densification. Alternately arc melting in both argon on a water-cooled copper mold, and in an electron beam welder were attempted. High vacuum annealing of the compacts, sintering at very high temperatures in graphite, and the use of a liquid phase to

Table 1

Chemical Analysis of CbC Powder Supplied
by Kennemetal Lot No. BL-1 -325 Mesh

<u>Element</u>	<u>Analysis (ppm)</u>
Ag	5.4
Al	<1.3
B	1.3
Ba	<2
Be	<0.2
Bi	<6
Ca	18
Cd	<600
Co	<20
Cr	56
Cu	220
Fe	350
In	<200
Mg	<0.2
Mn	5.3
Mo	<20
Ni	120
P	<200
Pb	<20
Sb	<20
Si	28
Sn	19
Sr	<6
Th	<60
Ti	<6
Ta	<600
V	<6
W	<200
Zn	<200
Zr	<6
% Nb 88.66 ^A 88.65 ^B Avg.	= 88.66
% C 11.28 ^A 11.29 ^B Avg.	= 11.29

Table 2
Chemical Analysis of ZrC Powder Supplied
by Atlantic Equipment 1-5 μ Size

<u>Element</u>	<u>Analysis (ppm)</u>
Ag	<4
Al	<4
B	720
Ba	<40
Be	<0.4
Bi	<40
Ca	12
Cd	<400
Co	<40
Cr	190
Cu	<4
Fe	320
In	<150
Mg	0.6
Mn	<1
Mo	1020
Nb	460
Ni	38
P	<400
Pb	<150
Sb	<40
Si	3.6
Sn	<40
Sr	<4
Th	<400
Ti	2000
Ta	<400
V	240
W	1000
Zn	<150

% Hf	1.51
% Zr	87.69
Σ Metals	1.73
% C by Δ	10.58

serve as an activating complex were all investigated. It should be stated that since each of these techniques represented a substantial endeavor, a limited number of samples were prepared in any one process. These approaches are discussed in detail in the following sections.

A. Pressing and Sintering

In view of the uncertainties and conflicting data in the literature, it appeared that the use of powder metallurgy processing would be the most promising approach in attaining the desired properties. One of the main limitations imposed on this study was the requirement that the samples which were to be tested in the hot hardness tester be either one-half inch in diameter by one-half inch long or that they be capable of being mounted in a molybdenum holder to achieve the required size.

Both cold pressing and sintering, and hot pressing were utilized in this investigation. The procedure followed in the cold pressing operation consisted of the following sequence:

- (1) Weigh the powders to the nearest 0.01 gram;
- (2) Dry blend the mixture for one hour by tumbling the powder in a rotating jar taped to the inside of a can;
- (3) Add 2 w/o Carbowax from a 50/50 water solution;
- (4) Add sufficient water to thoroughly wet the mixture;
- (5) Dry in a circulating air oven at 60°C (140°F);
- (6) Sieve through a -16 mesh;

- (7) Press in a one-inch diameter die at 20,000 pounds load;
- (8) Pre-bake in argon to 600°C (1110°F) using a controlled temperature rise of 100°C per hour;
- (9) Sinter in 2/3 argon atmosphere to 2300°C (4170°F). Soak for one-half hour using a graphite crucible.

This procedure provided compacts of CbC/ZrC in the following ratios:

CbC, 50CbC-50ZrC, 60CbC-40ZrC, 80CbC-20ZrC, ZrC

Photomicrographs of the pressed and sintered compacts are shown in Figure 7.

The relative densities of these compacts varied from 57 to 62 per cent of the theoretical density, apparently independent of the composition. Vickers hardness impressions were taken on the samples using a 10 Kg load at room temperature. The hardness values are listed in Table 3. From the analysis of the data it appeared obvious that the limitations of this process precluded its application to obtain the desired properties needed for a hardness indenter. Many of the compacts were retained for later experiments to attempt further densification.

Table 3

Hardness and Density of Pressed and Sintered CbC-ZrC Compacts

<u>Composition</u>	<u>Hardness VHN (10 Kg Load)</u>	<u>Density g/cm^3</u>
CbC	716	4.67
50CbC-50ZrC	483	4.52
60CbC-40ZrC	410	4.42
80CbC-20ZrC	468	4.33

500X

7-a

500X

7-b

500X

7-c

FIGURE 7 - Pressed and Sintered Compacts of CbC; 60CbC-40ZrC; and 80CbC-20ZrC.

B: Hot Pressing

As discussed in the previous sections, the use of hot pressing supplied a significant amount of energy to aid in densification as well as to increase the plasticity of the powders under a compressive load. However, under high temperature applications the load is severely limited by the strength of the graphite dies and is generally held to below 6500 psi.

Two different approaches were utilized in this investigation. A recent publication by Fischer⁽²⁴⁾ on the TaC-HfC and TaC-ZrC systems presents some data on the effect of varying the 3 parameters -- time, temperature, and pressure. These data are reproduced in Figures 8 and 9. Considering the results on a homologous temperature basis it appeared that comparable densities could be achieved on the CbC-ZrC system.

Initially a hot pressing sequence was utilized as outlined below. In this process the powders were generally used in the as-received condition.

- (1) Outgas the system to approximately 15 microns;
- (2) Apply pressure to 1000 psi;
- (3) Heat to 1500°C (2730°F);
- (4) Backfill to 10 inches Hg negative pressure of argon;
- (5) Increase pressure to 2000 psi;
- (6) Heat to 2300°C (4170°F) and soak for 10 minutes;
- (7) Shut off power;
- (8) Allow approximately 50 pounds of pressure to aid in cooling for 15 minutes.

FIGURE 8 - Variation of Relative Density of 4TaC-1HfC with Hot Pressing Parameters (After Fischer Ref. 24).

FIGURE 9 - Variation of Relative Density of 4TaC-1ZrC with Hot Pressing Parameters (After Fischer Ref. 24).

A heating rate from room temperature to 2000°C in 2 minutes was utilized. Cooling from 2000°C to 600°C occurred in approximately one and one-half minutes.

A number of samples were hot pressed to one-half inch diameter by one-half inch lengths for immediate analysis and for further densification treatments. The results of this treatment produced material of densities ranging from 76 to 83 per cent of theoretical density with Knoop hardness values reaching a maximum of 1200.

A photomicrograph of the 50CbC-50ZrC as hot pressed compact is shown in Figure 10.

Recognizing that the above processing could not yield material in excess of 90 per cent of the theoretical density desired, an alternate pressing schedule was adopted. It was believed that the low densities obtained were a result of either the low pressing pressure, the relatively large size of the powder, or the pressing temperature. To alleviate this difficulty, the powders were ball milled and processed as follows:

- (1) Load 40 grams of powder in a tungsten carbide ball mill 1-1/2 inches in diameter by 1-1/2 inches long;
- (2) Add 10-12 ml of water with Photoflow wetting agent in solution of 200:1;
- (3) Ball mill for 48 hours;
- (4) Wash twice in distilled water. Decant excess water and dry at 80°C (176°F);
- (5) Crush the dried powder;
- (6) Load into an ATJ graphite mold;
- (7) Press at 6500 psi and 2000°C (3630°F);
- (8) Hold temperature and pressure until plunger advance decreases to less than 0.0005 inch per minute;

400X

FIGURE 10 - Hot Pressed 50CbC-50ZrC

(9) Cool overnight and remove from the mold.

Three compacts were pressed in this manner, CbC, 50CbC-50ZrC, and ZrC. The CbC compact was calculated to have a density of 91 per cent of theoretical, the ZrC compact 87 per cent of theoretical and the pseudo binary had a density approaching 96 per cent of the theoretical. Photomicrographs of each of these compacts are shown in Figures 11-13.

C. Arc Melting

To overcome the apparent density limitations in the powder metallurgy processing, two arc melting techniques were investigated.

In the first run, low density hot pressed samples of 20CbC-80ZrC and 50CbC-50ZrC were arc melted using a non-consumable tungsten electrode. The compacts were melted under 10 inches of helium partial pressure. In the first melt, a current of 200-450 amps at 30 volts was utilized for 30 seconds. The buttons were then turned over and the other side melted using a current of 450-550 amps at 30 volts for 20 seconds. A weight loss of approximately 7 per cent occurred during melting. Two melts were required to completely melt the button as the first melt was prevented from achieving full penetration so the copper molds would not be destroyed.

After melting, the buttons contained a number of cracks apparently resulting from thermal shock due to the water cooled copper hearth on which the buttons were melted.

One section of the 50CbC-50ZrC arc melted button was examined metallographically as shown in Figure 14. A substantial loss of carbon occurred on the

500X

FIGURE 11 - Hot Pressed ZrC

500X

FIGURE 12 - Hot Pressed CbC

500X

FIGURE 13 - Hot Pressed 50CbC-
50ZrC

100X

14a. Edge

100X

14b. Center

FIGURE 14 - Arc-Melted 50CbC-50ZrC Hot Pressed Compact

surface, resulting in the appearance of a M_2C structure. The center appeared to be stoichiometric but porous and cracked. A photo-macrograph of a 20CbC-80ZrC sample after melting is shown in Figure 15. Severe cracking is evident throughout the entire structure.

Attempts to arc melt a hot pressed compact of the 50CbC-50ZrC composition in the electron beam welder resulted in failure. As soon as the arc hit the compact there was a violent splatter and the carbide was ejected from the mold.

D. High Temperature Sintering in Carbon

Both of the techniques discussed above lead to a change in the chemistry of the samples. Attempts were made to provide high temperature sintering in graphite to retain the stoichiometric composition.

The apparatus used in this study is discussed in a paper by Zometsky, Cadoff, Adelsberg, and Tobin.⁽²⁵⁾ A schematic of the chamber is shown in Figure 16.

This system is simple in design, construction, and requires relatively little power. A Westinghouse Electric Corporation 450 kc - 5 kw generator was used as the power source. A temperature of $3640 \pm 100^\circ\text{C}$ ($6550 \pm 212^\circ\text{F}$) was obtained with the 5 kw generator.

The crucible and stem were designed to approximate a black body at the temperature of operation. The equipment was constructed to eliminate optical losses due to light transmission through air-glass interfaces. The pyrometer was sighted on a surface reflecting mirror, and the light was transmitted through gas only.

10X

FIGURE 15 - Arc-Melted 20CbC-80ZrC Hot Pressed Compact

603403-6B

FIGURE 16 - Schematic of High Temperature Sintering Furnace

Temperature measurements were made with a Leeds and Northrup optical and Milletron two color pyrometers, all of which were calibrated against a standard tungsten bulb which in turn was calibrated by the National Bureau of Standards. Temperature was controlled by manual adjustment of the plate current of the generator. Once thermal equilibrium had been obtained, the system could be held for hours at temperature. Fluctuations of only $\pm 20^{\circ}\text{C}$ ($\pm 60^{\circ}\text{F}$) were observed with the two color pyrometer once thermal equilibrium was achieved.

At operating temperatures greater than 3000°C (5430°F), the lampblack insulation tends to sinter and hence become a conductor, thus drawing more power into the system, causing a temperature rise and eventual devitrification of the vycor container.

The lampblack provides the required insulation and thermal inertia necessary for efficient utilization of the available power and for good thermal stability. Vaporization of graphite at temperatures above 2600°C (4710°F) is also inhibited by the lampblack. The lampblack must be baked for at least one hour in vacuum at 1900°C (3450°F) and then kept in a desiccator to prevent pickup of volatiles.

Compacts, which had been hot pressed as described previously, were sintered for periods up to 8 hours at temperatures between 2600 and 2800°C (4700 and 5070°F). A typical photomicrograph of a $40\text{CbC}-60\text{ZrC}$ compact after sintering is shown in Figure 17. In all of the samples there is a homogeneous dense structure approaching the stoichiometric composition on the outside. However, in all of the samples, regardless of the time-temperature profile, the surface became cracked and the central portion of the compact appeared to contain a large number of voids.

5X

FIGURE 17 - Hot Pressed 40CbC-60ZrC After Sintering in Carbon

E. High Temperature Extrusion

One of the limiting factors of powder metallurgy is the very high activation energy needed to attain diffusion controlled densification. An approach was made to provide a large energy input in a very short time to a powdered compact by means of very high energy impact extrusion. The extreme heat and compressive forces generated during the extrusion were believed capable of significant improvements in the densification without changing the chemistry of the compacts.

The Dynapak Model 1220 C, shown in Figure 18, produced by the General Dynamics Corporation was used as the extrusion press. The machine can produce energies up to 275,000 ft-lbs. in a period of a few milliseconds. Power to drive the Dynapak is derived from the adiabatic expansion of gas at high pressure.

The compacts were canned as described below and extruded at a 6:1 reduction ratio. The dies for all the billets were conical having a 90 degree entry angle and a 7 degree relief and were plasma sprayed with zirconia.

Initially two pressed and sintered compacts (CbC and ZrC) were prepared as discussed above utilizing a sintering period of two hours at 2500°C (4530°F). These compacts were canned in molybdenum or tungsten as shown in Figure 19. The billets were press sealed to ensure a tight fit, heated inductively in an argon atmosphere to 1540°C (2800°F), soaked for 30 minutes at temperature, rapidly transferred to the extrusion press (5 seconds or less) and extruded. The resultant extrusion was sectioned and found to contain a powdery substance.

FIGURE 18 - Model 1220C Dynapak

FIGURE 19 - Canning Configuration of ZrC and NbC Carbides in Tungsten Prior to Extrusion

A second extrusion was prepared similar to the first, except that tungsten was used for the canning material instead of molybdenum. The billet was heated to 1950°C (3540°F) in 30 minutes, soaked at temperature for an additional 30 minutes and extruded. The extrusion was sectioned to remove the carbides. As before, a powdery substance was found near the tail of the extruded bar as shown in Figure 20. However, the nose portion of the extrusion contained what appeared to be a dense compact.

The canning was ground off to remove the specimen shown in Figure 21. It appears that when the billet was hit by the ram, the compact side forged into the tungsten wall. As the extrusion was forced through the die, the rapid deceleration caused the compact to fragment.

A section of the fragmented compact was removed and examined microscopically. The photomicrograph shown in Figure 22 is of a very dense small grained structure. Room temperature Knoop hardness measurements were taken and found to be between 1700 and 1800 across the entire cross-section using a 300 gram load.

As the nose of the billet contained the dense CbC compact and the ZrC initially in the tail was powdery, there was some confusion as to the cause of the different results. It was concluded that possibly the ZrC compact had become contaminated with oxygen during the transfer of the billet or immediately after the extrusion was made since the extrusion contained a rather large pipe. At this stage it was also realized that the flow characteristics of the tungsten canning and the carbides would inhibit the production of a fully dense large sized carbide.

4X

FIGURE 20 - Pressed and Sintered ZrC Canned in Tungsten
and Dynapak Extruded

2X

FIGURE 21 - Pressed and Sintered CbC Canned in Tungsten
and Dynapak Extruded

3X

22a. As-Extruded

500X

22b. As-Polished and Etched

FIGURE 22 - Pressed and Sintered CbC Canned in
Tungsten and Dynapak Extruded

Two additional pressed and sintered compacts were obtained. The first containing 60CbC-40ZrC was canned in molybdenum as shown in Figure 23. The use of both pressed and sintered, as well as arc cast molybdenum was dictated by the knowledge that pressed and sintered molybdenum could not be electron beam welded but was about half as expensive as the arc melted material.

The compact canned in molybdenum was heated in argon as before to 1980°C (3600°F). Difficulty was encountered in holding the temperature stable as the inductive coupling tended to fluctuate. At 100 per cent of the rated current input, (1980°C) the billet catastrophically melted as shown in Figure 24. The starting billet is also shown. A recent publication by Wallace, Gutierrez, and Stone⁽²⁶⁾ on the Mo-Zr-C system indicated that there should be no melting below 2440°C (4425°F). It seems difficult to believe that any additions of columbium would lower the eutectics to less than 2000°C (3630°F).

The power source utilized in the induction heater was of 3,000 cps producing a skin effect depth in the molybdenum of 0.3 inch at 2000°C . The conclusion was that the skin depth had been locally deeper than expected or more probable that the relatively high resistance of the pressed and sintered compact led to localized hot spots and subsequent failure.

An additional specimen of 80CbC-20ZrC pressed and sintered was similarly prepared and canned in molybdenum. This billet was extruded at 1500°C (2730°F). Again this extrusion resulted in a powdery type compact.

There were now two conclusions that could be drawn.

FIGURE 23 - Canning Configuration for Pressed and Sintered Carbide in Molybdenum Prior to Extrusion

FIGURE 24 - Pressed and Sintered 60CbC-40ZrC Canned in Molybdenum and Heated to 1980°C (3600°F)

- (1) That the pressed and sintered compacts could not be given the required activation energy under stress to cause densification.
- (2) That some contamination still existed during the extrusion from the tail containing the large pipe.

To clarify the problem, a 50CbC-50ZrC compact hot pressed as before was canned in molybdenum as shown in Figure 25. The billet was heated to 1500°C (2730°F) and extruded as before except that a disc of molybdenum was placed on the bottom of the extrusion ram. After extruding, the composite was examined and found to be completely intact over the entire surface. The carbide shown in Figure 26 was located by x-rays taken of the extrusion. When the compact was removed by cutting the molybdenum canning, a powdery substance was obtained as shown in Figure 27.

F. Vacuum Annealing and Liquid Phase Sintering

Throughout this investigation, the effect of the impurities on the results had been subjected to some doubt. To resolve the confusion, a hot pressed compact of 50CbC-40ZrC-10Zr was vacuum annealed in a Model 1064 Brew furnace. The sample was carefully wrapped in tantalum foil to insure that the furnace components would not be damaged. The temperature was gradually increased maintaining the vacuum below 2×10^{-5} Torr until the sample was at 2800°C (5070°F). At this temperature, the zirconium should be liquid and aid in any densification. A soak of 4 hours at temperature was utilized followed by controlled cooling to 800°C (1470°F) in one hour. The power was cut at this time and the sample furnace cooled to room temperature.

FIGURE 25 - Canning Configuration of Hot Pressed Carbide in Molybdenum Prior to Extrusion

FIGURE 26 - X-ray of Hot Pressed 50CbC-50ZrC Canned in Molybdenum
and Extruded

10X

FIGURE 27 - Hot Pressed 50CbC-50ZrC Canned in Molybdenum
and Extruded

The sample was removed from the furnace and the Knoop hardness test using a 100 gram load was attempted. However, the structure had a large percentage of void area and accurate measurements were not obtainable.

G. Hot Hardness Measurements

Hot hardness measurements were made on a Westinghouse designed and built testing apparatus (shown in Figure 28). This tester is capable of operating at temperatures in excess of 1315°C (2400°F) under a vacuum better than 5×10^{-5} Torr.

The furnace is tungsten wound, on a tantalum frame, capable of a maximum temperature of 1600°C (2912°F). The heating element is surrounded by a shield pack of four 10 mil thick molybdenum radiation shields and a 1/4 inch thick copper water cooled cold wall.

The pumping system incorporates an NRC Purifying Oil Diffusion Pump backed by a Welch No. 1397 Mechanical Pump. Vacuum at temperature ranges from 3×10^{-5} to 1×10^{-5} Torr. Volume of the system is 29.79 liters, with a leak rate of 5 micron per hour (5.46cc atmos./sec.).

The impressions are made using a standard Vickers 136 degree pyramid indenter fused into a molybdenum rod under a static load of 2.5 kilograms. The specimen is placed on an anvil and driven up into the indenter lifting the 2.5 kg weight off its support. The normal dwell time of indentation is 9 seconds and over-all time is 15 seconds. The tester can be loaded with 1 to 12 individual samples. Each sample is held 10 minutes at temperature before testing to allow equilibrium conditions to exist.

FIGURE 28 - Hot Hardness Tester

To determine the feasibility of conducting tests at 1315°C (2400°F) a B_4C Norbide cylinder was obtained from the Norton Company. The cylinder was ground and polished by the F. F. Gilmore Company to the standard Vickers configuration and utilized to take a series of indentations. Photomicrographs of the 1st, 9th, and 15th impressions are shown in Figures 29-31 respectively. The photographs clearly show the rapid contamination encountered with this indenter material.

During the course of this investigation, a sample of TaC was received from a research laboratory.⁽²⁷⁾ The as-received material is shown in Figure 32 and the cut, polished and mounted sample is shown in Figure 33. The hardness as a function of temperature was determined using a sapphire indenter. The results are shown in Table 4.

Table 4

Hot Hardness of TaC as a Function of Temperature

<u>Temperature C/F</u>	<u>Hardness VHN (2.5kg Load)</u>
RT/RT	1040
980/1800	306
1095/2000	212
1205/2200	198
1315/2400	168

While the limit of 168 VHN was far too low for utilization of any indenter material, it is interesting to note the effect of density and stoichiometry on the hardness values. The room temperature density calculated by x-ray determinations was 14.514 g/cc . The a_0 value was 4.4540 and the C/Ta ratio was 0.92. The

FIGURE 29 - Vickers Impression of B₄C Indenter After
1st Indentation in Complex Tantalum Base Alloy

FIGURE 30 - Vickers Impression of B₄C Indenter After
9th Indentation in Complex Tantalum Base Alloy

FIGURE 31 - Vickers Impression of B₄C Indenter After
15th Indentation in Complex Tantalum Base Alloy

1X

FIGURE 32 - TaC Specimen

4X

FIGURE 33 - TaC Hot Hardness Sample Mounted on Molybdenum

density as determined by water displacement was 88 per cent compared to 99.1 per cent determined by the lattice parameters. It is obvious that any entrapped voids in the sample will not be reflected in the x-ray measurements although they are very effective in lowering the hardness values.

IV. DISCUSSION

This investigation resulted in a CbC-ZrC compact of 96 per cent of theoretical density. Hot pressing of a comminuted powder prepared without any detrimental contaminating binder being added represents a significant step in the development of materials suitable for a high temperature high vacuum indenter material. Attempts to further densify the compact were universally unsuccessful.

A photomicrograph of the 50CbC-50ZrC sample shown previously in Figure 13 reveals two definite areas. In the clear areas, room temperature Tukon hardness measurements using a 200 g load showed hardness values between 1800 and 2400. In the darker areas outlined by grain boundaries values of 1400 to 1800 were obtained. While the spread appears to be large, the variation of hardness value per change in the length could result in substantial error. The major portion of the surface gave Knoop readings of 2000.

An x-ray powder pattern taken on the samples was analyzed and generally broad lines were observed indicating a non-equilibrium structure in the compact. The a_0 value of 4.576 as measured falls between that of ZrC and CbC being very close to the mid-portion of these parameters. This agrees with the curve presented by Norton and Mowry⁽¹⁸⁾ for a composition of equal parts CbC and ZrC. Our determination showed a composition of 48 ± 5 per cent ZrC and 52 ± 5 per cent CbC.

Initial attempts to measure the elevated temperature hardness were unsuccessful. A sapphire indenter used at 815°C (1500°F) flattened under a 2.5 kg load. No indication could be found of the hardness impression on the carbide.

A B_4C Norbide indenter was substituted for the sapphire and another test taken at $1315^{\circ}C$ ($2400^{\circ}F$). To insure that the hardness tester was operating correctly, two complex tantalum base alloys were measured immediately before and after the carbide. The first alloy had a VHN of 150 which compared favorably with its prior determination of 148. The second tantalum base alloy following the carbide had a VHN of 252 compared with its previous determination of 251. Readings on the carbide were not obtainable as there was no apparent impression. Examination of the indenter point after the test revealed that the point had become blunted. However, the indentation produced sharp diagonal lines which could be read even though the center of the impression was somewhat erratic.

Since these readings had been obtained on a specimen polished on 4-0 polishing papers, it was felt that there could have been an impression too small to be found at 400X magnification. The sample was again repolished and etched to produce the finish shown in Figure 13. When the sample was being removed from the Hysol mount, it fractured in half.

Both of these pieces were sent to the F. F. Gilmore Corporation to determine if they could be ground into the Vickers configuration.

An additional sample was prepared in an identical manner and analyzed for room temperature hardness, x-ray parameters, and elevated temperature hardness. To correlate the physical constants of the pseudo binary with the experimental data, two hot pressed binary compacts of ZrC and CbC were also analyzed.

Lattice parameters were attempted through back reflection x-ray techniques on the CbC, ZrC and the alternate CbC-ZrC compacts. The CbC produced the

sharpest lines and was accurately measured at the high angle lines showing a_0 to be between 4.4672 and 4.4674 Å indicative of a C/Cb ratio of 0.94. The ZrC pattern was not as sharp as the CbC and produced an a_0 between 4.6920 and 4.6924 Å indicative of a C/Zr ratio of about 0.85. Unfortunately the CbC-ZrC compact produced very broad lines and no accurate measurement of the parameter could be made. Evidently the CbC-ZrC compact possesses substantial solid solution variation. It was estimated that the limit of solid solution ranged between 30 and 70 per cent CbC in ZrC. Additionally the x-ray pattern indicated that throughout the sample there was a significant variation in the carbon content as the lines tended to overlap between the relatively sharp reflections.

Room temperature hardness measurements were made on the Tukon scale using a load of 200 grams. The ZrC and CbC compacts were not dense enough to obtain accurate readings. The pseudo-binary CbC-ZrC showed a Tukon hardness range of 1750 to 2100.

Hot hardness measurements of the polished pseudo-binary were obtained using a B_4C indenter at 1315°C (2400°F) producing an average value of 633. As there are no data in the literature with which to make a comparison, the only result which can be stated is that the carbides are substantially stronger than any other suitable indenter material available today.

The 50 CbC-50 ZrC compact was successfully ground to a Vickers configuration by the F. F. Gilmore Corporation. The ground carbide is shown in Figure 34 and the mounted indenter is shown in Figure 35. Initial evaluation revealed the carbide to have a sharp point and clean diagonal edges. There was some indication of voids on the ground surface away from the point.

10X

FIGURE 34 - 50CbC-50ZrC Hot Pressed Compact
Ground to a Vickers Configuration

1/2X

FIGURE 35 - 50CbC-50ZrC Indenter Mounted
on a Molybdenum Shaft

In order to determine the hardness and chemical stability of the carbide, a series of nine complex columbium and tantalum base alloy compositions was prepared for hardness measurements at 1315°C (2400°F). The first impression taken on a Cb-26W-4Re-2Hf-0.067C alloy flattened the tip of the carbide indenter. The indentation shown in Figure 36 reveals the lack of clear diagonals normally present in a good Vickers impression. However, the shape of the impression is clean along the edges indicating that there was little or no chemical reaction between the carbide and the alloy. The remaining alloys were tested during the same run utilizing a total of thirty impressions. The indentation configuration remained the same for all indentations throughout the series confirming the good chemical stability of the indenter and the base alloys.

The lack of the clean diagonals across the indentation showed that the tip of the indenter had become blunted. This was subsequently confirmed when the indenter was removed from the hardness tester and examined under the microscope. The hardness value of 149 taken on the complex columbium base alloy was higher than would have been expected at 1315°C (2400°F) based on the tensile and hardness-temperature data.

While it is impossible to accurately state the cause of the failure of the indenter, there are two general postulates which can be made. The first is that while the point could be ground to the Vickers configuration without any voids in the point area, it can be assumed that there were some small voids in the carbide interior immediately adjacent to the point. These voids allowed the point to collapse when the load was applied during the indentation process. The high hardness

250X

FIGURE 36 - Hardness Indentation Taken at 1315°C (2400°F) on a Cb-26W-4Re-2Hf-0.067C Alloy Using the 50CbC-50ZrC Indenter

of the carbide determined earlier using the B_4C indenter indicates that the separation of the void and the point must have been very small.

A second postulate is that the carbides have an inherent low compressive strength at these high temperatures. The low strength would limit the load carrying ability of the sharp point and edges under the compressive load. As there are no data available on the compressive strength of these mixed carbides at elevated temperatures, there is no way in which these postulates can be confirmed or rejected.

Attempts to increase the density of the pressed and sintered as well as the hot pressed carbides were not successful. Arc-melting, Dynapak extrusion, high temperature sintering in a carbon atmosphere, and vacuum annealing with liquid phase sintering were all investigated.

The arc melting technique produced very small pieces of dense uniform stoichiometric composition. Unfortunately, none of these pieces were of sufficient size to obtain any high temperature hardness data. The complex problem of maintaining an arc requires the utilization of a partial pressure of an inert gas atmosphere. It is also quite probable that during melting a significant change in surface composition has occurred. However, the limiting factor in arc melting appears to be the inherent susceptibility to thermal cracking of the carbides in contact with the water-cooled copper hearth.

Extruding by means of the Dynapak high velocity extrusion press produced some promising results. It appears that a closer control of temperature, where the interior temperature is measured instead of the exterior casing, would produce a

plastic structure. If the canning material could be better matched in terms of the flow stresses; or if an interfacial metal layer could be utilized so that the carbides could flow during the extrusion compaction, a larger compact would result. However, there are no data available for the flow stresses of carbides at high temperatures.

The results obtained on the CbC compact approached the theoretical density. Hardness measurements at room temperature indicated that little if any compositional changes had occurred during heating and extrusion.

Electron beam welding of the sealed can to reduce any oxygen contamination, combined with very pure starting materials should result in a fully densified homogeneous structure.

As tungsten or molybdenum appear to be the only suitable canning materials for use at these high temperatures, further refinements in the deceleration of the extruded bar through variation of the Dynapak parameters should be determined. The utilization of a molybdenum disc on the bottom of the extrusion ram resulted in a sound extrusion completely free of any pipe defects in the canning material. In addition the plug extending beyond the top of the canning should initially depress into the compact at the instant of contact providing some compaction before the canning starts to flow through the die.

High temperature sintering in a carbon atmosphere to obtain a fully dense structure of stoichiometric composition appears to be a potentially useful process. The hot pressed carburized compacts all had a very dense hard outer layer extending about 1/8 inch radially inward. While for the purposes of this investigation a completely homogeneous cross-section would be needed, there is a possibility that

altering the specimen configuration or using a larger specimen and utilizing only a small portion of the final compact should be investigated. Generally the inherent thermal shock coupled with the very slow diffusion rates limit the present application to relatively small sample sizes.

Annealing in a high vacuum, high temperature furnace to take advantage of the purification and liquid phase sintering would not be applicable. While the literature indicated a loss in carbon during vaporization at very high temperatures for the carbides, it is probable that the metallic phase would be preferentially vaporized. A large precise experimental program would be needed to determine the relative constituent losses encountered and the extent to which these losses could be compensated for by altering the starting chemistry. Finally, the cost of replacing the furnace components after they become contaminated would be prohibitive.

V. CONCLUSIONS AND RECOMMENDATIONS

(1) A pseudo binary 50CbC-50ZrC hot pressed compact having a density greater than 96 per cent of theoretical can be made without the use of any binder.

(2) By utilizing a pseudo binary, densities can be attained which are significantly greater than those of the pure binary constituents.

(3) The hot pressed carbide could be ground to a Vickers configuration free of cracks or voids in the tip area.

(4) The CbC-ZrC indenter possessed adequate chemical stability to be utilized in the high temperature hardness measurements of complex columbium and tantalum base alloys.

(5) The resultant carbide indenter could not withstand the compressive stresses imposed during the 1315°C (2400°F) indentation process even though the compact had a Vickers hardness of 633 at this temperature when measured with a B₄C indenter.

(6) The cause of failure during the indentation cannot be stated at the present time with the limited data available on the high temperature properties of carbides.

(7) It does not appear feasible to produce stoichiometric carbides approaching the theoretical density which is required without the expenditure of a vast amount of time and effort. Single crystals, if they can be produced, should supply many of the missing data and lead to a better understanding of the carbide properties.

(8) It is recommended that future effort be directed to determining the compressive strength data of carbides at high temperatures.

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