

PROCESSING AND PROPERTIES OF TiZrC AND TiZrB₂ SOLID SOLUTION MATERIALS

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TiZrC and TiZrB₂ solid solution materials were synthesized by conventional powder production methods. These materials exhibited non-linear, and generally superior, mechanical properties when compared to the end member constituents.

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INTRODUCTION

Non-oxide ceramics, such as borides and carbides, exhibit excellent mechanical and chemical properties which make them suitable for a wide variety of applications.^{1,2,3} These materials generally possess a high melting point, high strength, chemical inertness, high wear resistance, and high hardness which make them useful for such applications as armor, wear guides, high temperature supports, cutting tools, etc. The average flexural strengths of titanium carbide (TiC) and titanium diboride (TiB₂) have been measured to be greater than 400 MPa, with fracture toughnesses (K_{Ic}) in the range of 3 - 5 MPa·m^{1/2}. The mechanical properties of these sintered materials are dependent upon the purity and processing of the starting powder as well as the densification technique and residual porosity.

To further increase their thermal, mechanical, and electrical properties, these carbide and boride materials can also be combined, with other oxide and non-oxide materials such as alumina (Al₂O₃), silicon carbide (SiC), or tungsten carbide (WC) to form such composites as SiC-TiB₂, Al₂O₃-TiB₂, and TiC-WC. These materials exhibit improved mechanical properties due to particulate toughening mechanisms. Al₂O₃-TiB₂ composites containing 20 volume % TiB₂ obtained flexural strengths of 700 MPa, whereas Al₂O₃-TiC composites obtained a flexural strength of 550 MPa at the same loading of TiC.^{4,5} The addition of titanium diboride to a silicon carbide matrix improved the average strength of the composite by 28% and the fracture toughness by 45%.⁶ A fracture toughness of up to 8.9 MPa·m^{1/2} has been reported for a 16 volume % TiB₂ - SiC composite.⁷

Solid solutions of refractory metal boride and carbides have been produced by a number of synthesis techniques including direct synthesis of the solid solutions from the elements and mixing of the metal borides and carbides. These mixtures are heated to temperatures near or beyond the melting point of the boride and carbide end members to form the solid solution.^{8,9} Complete solid solution formation, however, does not always occur due to the differences in atomic radii between the metal atoms.¹⁰ The physical, chemical, and electrical properties of these solid solutions have previously been measured which illustrate a non-linear or parabolic relationship between the end member compositions and the solid solutions. An example of this is the TaC-HfC solid solution with a melting point of ~ 4000°C, which is substantially higher than

the single components (TaC, HfC) exhibit.¹¹ The mechanical properties of these solid solutions, however, have not been extensively reported.

In this study, solid solutions of titanium and zirconium borides and carbides were synthesized by borothermal and carbothermal reduction.¹² Five compositions per system were evaluated, as are shown in Table I. Physical and chemical analyses, as well as X-ray diffraction analysis, were used to confirm the formation of the solid solutions. The synthesized powders were consolidated by hot pressing and pressureless sintering. The mechanical properties of these solid solutions, including flexural strength, fracture toughness, and indentation hardness, were determined.

POWDER SYNTHESIS AND CHARACTERIZATION

The solid solution and end member compositions were synthesized from oxide raw materials by carbothermal and borothermal reduction in a continuous graphite furnace at temperatures between 1975°C and 2025°C. A non-aqueous slurry of the raw materials was prepared in the correct stoichiometric proportions, mixed, and dried. The mixed powder was screened to provide a uniform feed powder for the furnace. The raw material mixes were then loaded into graphite tubes and synthesized at 2025°C for the carbide compositions, and 1975°C for the boride compositions. The yield after furnacing was approximately 50% for each of the powders compared to the raw material input due to the loss of gaseous by-products of the oxide raw materials which occurs during the carbothermal and borothermal reduction process. For each composition, the synthesis times were adjusted to synthesize a single phase solid solution as confirmed by x-ray diffraction. After synthesis, the fired powders were milled to reduce the sintered agglomerates to single particles. A sample of each powder was then analyzed for a number of physical and chemical characteristics which are summarized in Table II.

The density of each of the synthesized powders was determined by helium pycnometry. The pycnometer density for all of the compositions evaluated were within 3% of the calculated theoretical densities. X-ray diffraction analysis was used to verify the formation of the solid solution compositions in the carbide and boride systems. For the carbide system, full formation of the $Ti_{0.7}Zr_{0.3}C$ solid solution did not occur despite numerous synthesis attempts in which the synthesis temperature and time at temperature were varied. This material was not composed of the end members or the single phase solid solution but rather it appeared to have formed two solid solution phases, one rich in titanium and one rich in zirconium. The boride solid solutions was generally easier to synthesize than the carbide solid solutions. The $Ti_{0.7}Zr_{0.3}B_2$ powder, however, did not fully form the solid solution. X-ray diffraction analysis showed that there was a small amount of a second solid solution phase present after synthesis.

PRESSURELESS SINTERING AND HOT PRESSING

Densification of these compositions was conducted by two methods: pressureless sintering and hot pressing. A number of sintering aids as well as consolidation parameters (time, temperature, pressure) were examined to determine the optimum amount and type necessary in order to assure a fully dense part.

Pressureless sintered parts were produced by wet mixing the synthesized powder with 2 wt. % organic binder and 2 wt. % nickel powder as the sintering aid for the carbides or 2 wt. % iron powder as the sintering aid for the borides. The mixtures were then dried and screened to -60 mesh and dry pressed into 2.54 cm discs at 75 MPa. A variety of sintering times and temperatures were examined with the highest densities achieved by sintering at 2100°C for 2 hours. Sintered densities for the solid solutions compositions were generally greater than 98% of theoretical density.

Hot pressed plates of each of the compositions were also produced for use in mechanical properties testing. These 10.0 cm x 10.0 cm x 1.0 cm plates were hot pressed at 1900°C and 21 MPa in argon for 1 hour. These conditions were found to yield the maximum fired density in all of the compositions. A sample of each of the hot pressed plates was crushed and characterized by gas pycnometry and x-ray diffraction analysis. The density of each of the plates was determined by the Archimedes method and compared to the gas pycnometer density of the crushed powder. The solid solution compositions typically exhibited a higher percentage of theoretical density after hot pressing than the end member compositions. Densities of the solid solution materials typically exceeded 99% of the theoretical density for the materials. Examples of hot pressed, pressureless sintered, and machined solid solution parts are shown in Figure 1.

X-ray diffraction analysis of each of the hot pressed compositions was obtained. In all cases, the phase composition of the hot pressed part varied from that of the powder. The single phase solid solution powders appear to have separated into two solid solution phases during hot pressing. These new patterns suggest segregation of each composition into a two phase solid solution composite. It was determined that the presence of the single or two phase solid solution in the hot pressed samples was dependant on the cooling rate after hot pressing. A fast cooling rate, resulted in the two phase solid solution, whereas a slow or "furnace cool" cooling rate, which was approximately four times slower, resulted in the presence of the single phase solid solution for the boride solid solutions. The carbide materials formed two phase solid solutions independent of hot pressing conditions. Although mechanical property measurements were obtained for both the single and two phase solid solutions, only the two phase results will be discussed.

MECHANICAL PROPERTIES TESTING

Alumina plates^α (99.9% Al₂O₃) were used for baseline mechanical properties measurements. All test samples were obtained from hot pressed plates, as described above. Test bars for flexural strength testing of all the compositions were machined to 5.0 cm x 0.4 cm x 0.3 mm with a surface finish of less than 20 microinches rms. At least 20 bars from each composition were measured in order to calculate the Weibull modulus for each composition, except for the two phase Ti_{0.5}Zr_{0.5}B₂ composition. Extreme difficulty in cutting this material by conventional methods limited the number of specimens to only ten (10) test bars. Approximately 5 times the amount of time was needed to cut the boride solid solution compositions as compared to the other solid solution compositions. Because of the difficulties encountered with cutting these samples,

^α Obtained from Naval Surface Warfare Center, Dahlgren, VA

flaws may have been introduced during the machining process.

The results from this mechanical property testing were varied. Flexural strength testing of the carbide compositions revealed a parabolic strength relationship, with the $Ti_{0.5}Zr_{0.5}C$ solid solution obtaining a strength of 706 MPa. The boride system exhibited a nearly linear relationship in strength, with the strength decreasing as the amount of Zr increased (Figure 2). The sample bars from flexural strength testing were then polished to a surface finish of less than 1 microinch rms and used for microhardness and fracture toughness testing. The Weibull modulus for each of the materials was also determined. In general, the carbides compositions achieved higher Weibull moduli than the boride compositions as is shown in Table III. Hardness was determined by Vickers indentation with a 500 gram load. Five to 10 tests per composition were conducted. The carbide and boride materials exhibited a parabolic relationship with respect to hardness as is shown in Figures 3, with the solid solution materials exhibiting an increased hardness with respect to the end member compositions. A maximum hardness of 2500 kg/mm² was obtained for the $Ti_{0.5}Zr_{0.5}C$ composition.

Fracture toughness testing was conducted on the ten test compositions using the Vickers indentation method with a 2.0 kilogram load to promote cracking in the samples. Five samples per composition were measured and the following formula was used to determine the fracture toughness:⁴

$$K_{Ic} = 0.016 \cdot [E/H]^{1/2} \cdot [P/c^{3/2}]$$

where E = elastic modulus (GPa), H = hardness (kg/mm²), P = load (kg), and c = average crack length (mm). Analysis of the carbide compositions shows a nearly linear relationship between the fracture toughness and Zr content, with the fracture toughness increasing as the amount of ZrC increases. The boride compositions also exhibit a linear relationship, but the fracture toughness decreased with increasing Zr content. This information is shown in Figure 4.

The elastic and shear moduli for each of the synthesized compositions were determined by transient vibration analysis using samples machined from hot pressed plates. From these values, the Poissons ratio for each of the compositions was calculated and is shown in Table IV. The elastic modulus for each of the compositions was then used in the calculation of K_{Ic} , as is shown above.

SUMMARY AND CONCLUSIONS

TiZrC and TiZrB₂ solid solutions were formed and consolidated to produce parts which exhibited increased mechanical properties when compared to those exhibited by the end member compositions. These materials can be used to produce higher strength products without the additional costs and processing concerns associated with reinforced materials. Potential uses for these materials include armor, wear applications such as cutting tools, wear guides, or sandblast nozzles, or applications where increased strength at high temperature is required. The production of these materials as either single or two phase solid solutions may lead to the ability to tailor the microstructure of these materials to increase mechanical properties to an even greater extent.

This increase may hold true for other solid solution materials and may offer an alternative way to increase the end use strength and/or toughness of these materials without the addition of particulate, whisker, or fiber reinforcements.

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Table I: Solid Solution and End Member Compositions Evaluated

Carbide Compositions (mole fraction)	Boride Compositions (mole fraction)
TiC	TiB ₂
Ti _{0.7} Zr _{0.3} C	Ti _{0.7} Zr _{0.3} B ₂
Ti _{0.5} Zr _{0.5} C	Ti _{0.5} Zr _{0.5} B ₂
Ti _{0.3} Zr _{0.7} C	Ti _{0.3} Zr _{0.7} B ₂
ZrC	ZrB ₂

Table II: Physical and Chemical Property Data

Composition	Surface Area ^α (m ² /g)	Average Particle Size ^β (μm)	Powder Density ^δ (g/cm ³)	Total Oxygen ^λ (wt. %)
TiC	3.3	2.3	4.9	0.5
0.7 TiC / 0.3 ZrC	0.9	5.1	5.4	0.3
0.5 TiC / 0.5 ZrC	0.9	6.4	5.8	0.5
0.3 TiC / 0.7 ZrC	0.5	7.6	6.1	0.2
ZrC	0.6	7.5	6.5	0.1
TiB ₂	0.7	5.3	4.5	0.6
0.7 TiB ₂ / 0.3 ZrB ₂	0.5	6.8	5.0	0.4
0.5 TiB ₂ / 0.5 ZrB ₂	0.6	7.0	5.3	0.8
0.3 TiB ₂ / 0.7 ZrB ₂	0.3	10.3	5.6	0.3
ZrB ₂	0.3	12.7	6.0	0.4

^α Micromeritics Flowsorb II Surface Area Analyzer

^β Coulter Counter Model TA-II Particle Size Analyzer

^δ Quantachrome Gas Micropycnometer (Model MPY-2)

^λ Leco TC-436 Oxygen/Nitrogen Determinator

Table III: Average Flexural Strength, Standard Deviation and Weibull Modulus for Compositions Evaluated

Composition	Flexural Strength (MPa)	Standard Deviation (MPa)	Weibull Modulus
TiC	412	27.1	16.0
0.7 TiC / 0.3 ZrC	623	54.0	12.0
0.5 TiC / 0.5 ZrC	706	50.9	14.2
0.3 TiC / 0.7 ZrC	643	55.5	11.5
ZrC	566	26.1	22.6
TiB ₂	579	42.6	14.2
0.7 TiB ₂ / 0.3 ZrB ₂	478	47.9	12.9
0.5 TiB ₂ / 0.5 ZrB ₂	420	50.8	9.6
0.3 TiB ₂ / 0.7 ZrB ₂	374	38.4	16.9
ZrB ₂	377	75.3	4.8

Table IV: Elastic Modulus, Shear Modulus, and Poissons Ratio for Compositions Evaluated

Composition	Elastic Modulus (GPa)	Shear Modulus (GPa)	Poissons Ratio
TiC	345	140	0.23
0.7 TiC / 0.3 ZrC	415	169	0.23
0.5 TiC / 0.5 ZrC	403	166	0.21
0.3 TiC / 0.7 ZrC	412	169	0.22
ZrC	399	164	0.22
TiB ₂	512	216	0.19
0.7 TiB ₂ / 0.3 ZrB ₂	549	245	0.12
0.5 TiB ₂ / 0.5 ZrB ₂	523	232	0.13
0.3 TiB ₂ / 0.7 ZrB ₂	539	240	0.13
ZrB ₂	463	206	0.13

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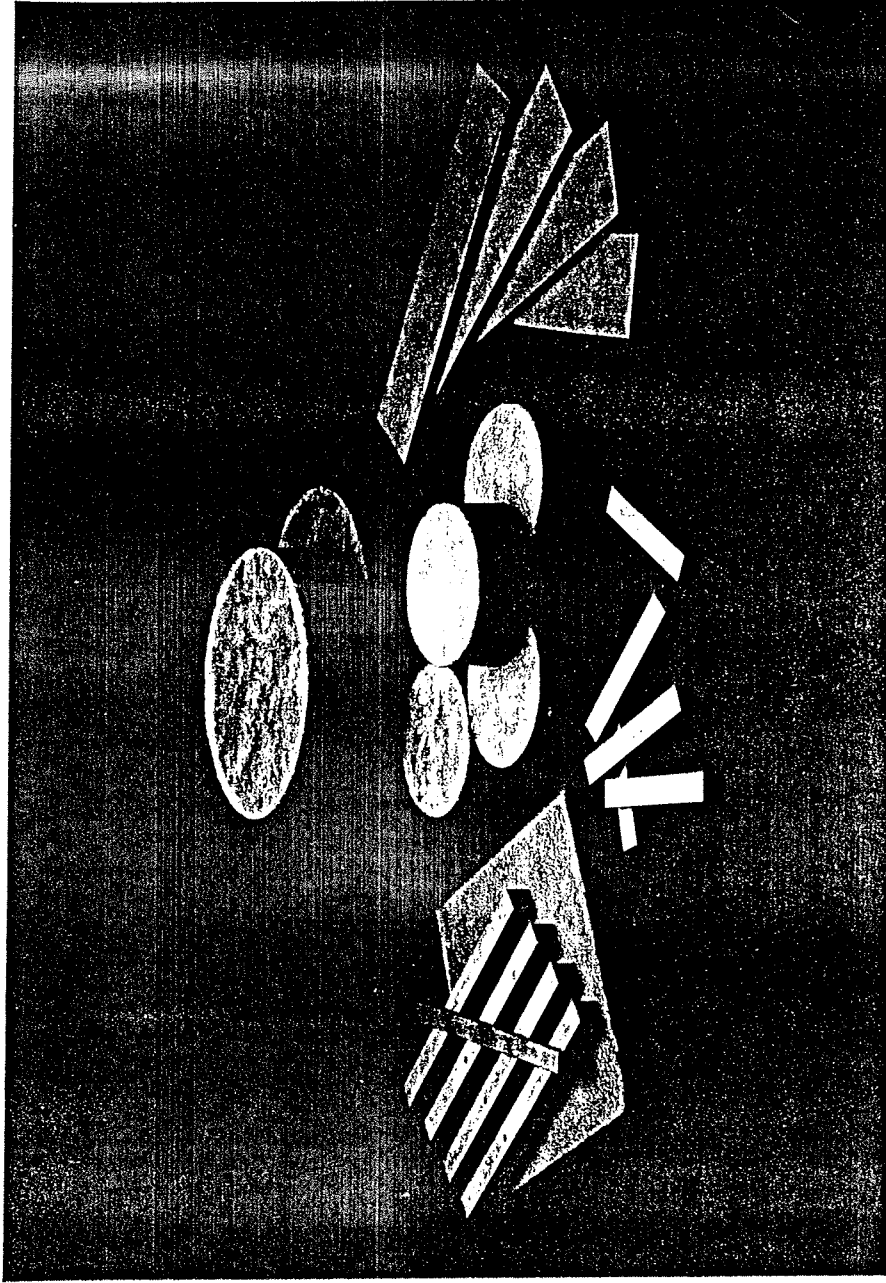
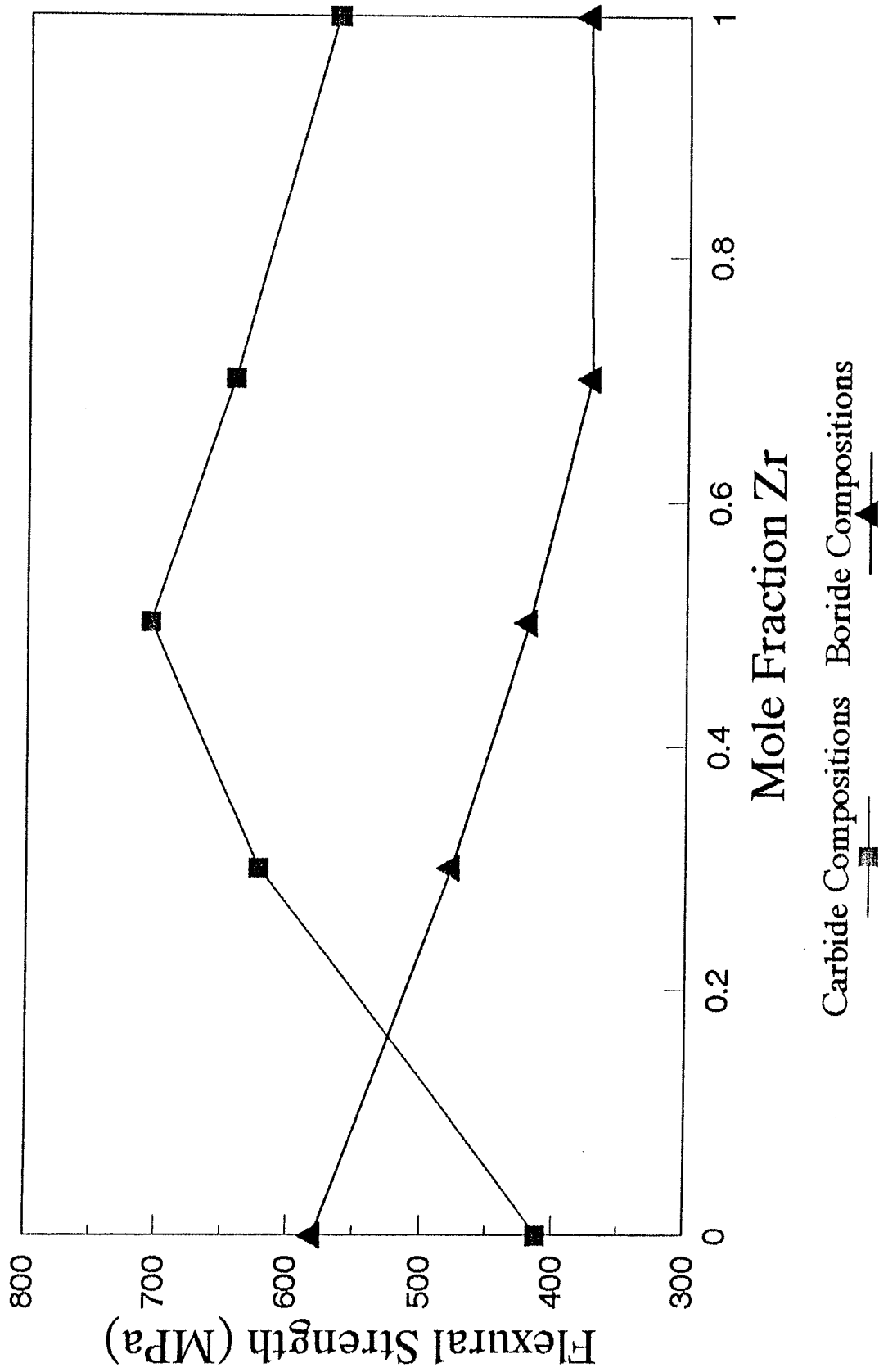
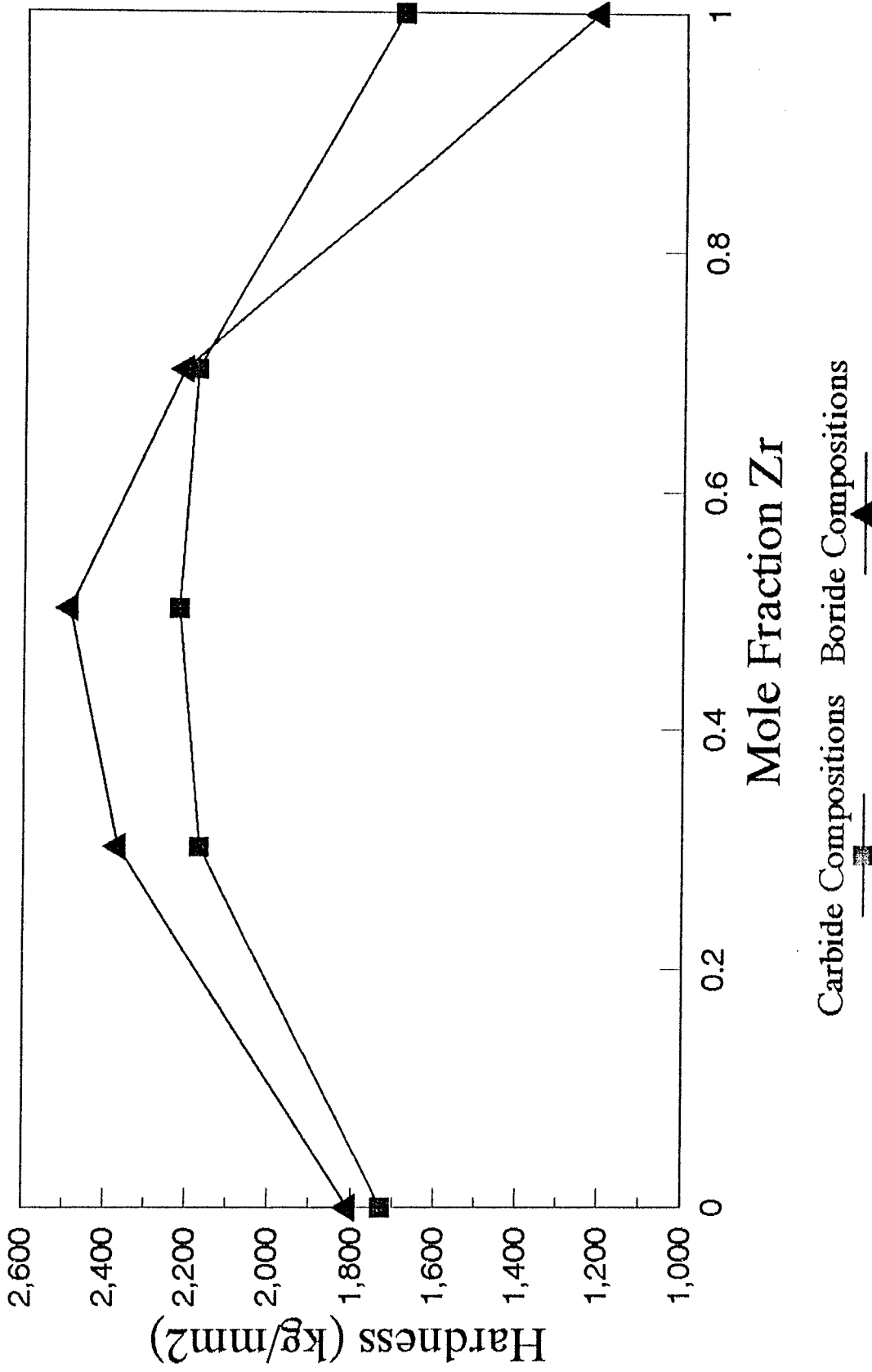


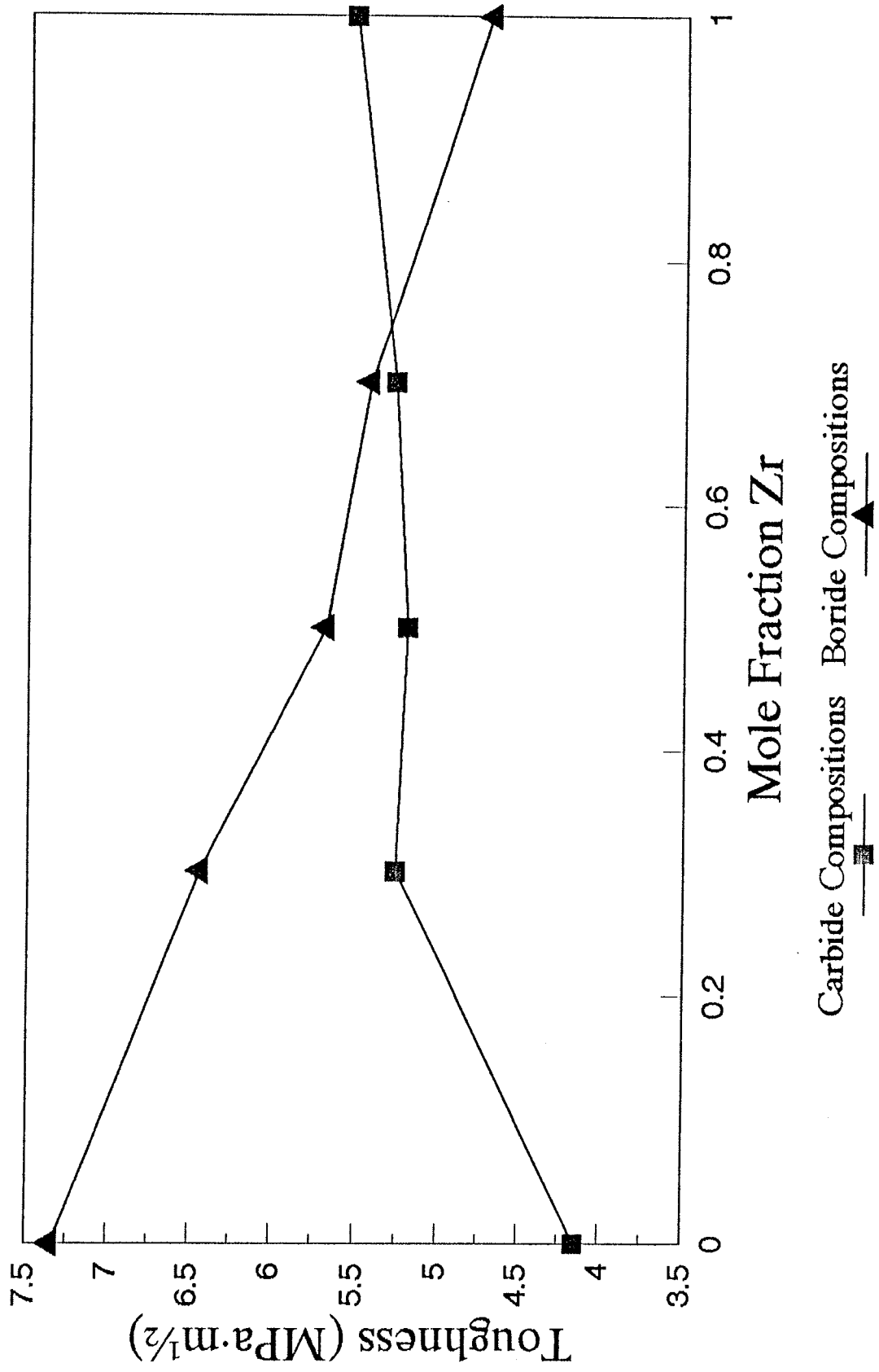
Figure 1: Hot Pressed, Pressureless Sintered,
and Machined TiZrC and TiZrB2 Parts



**Figure 2: Flexural Strength Results
Carbide and Boride Compositions**



**Figure 3: Hardness Results
Carbide and Boride Compositions**



**Figure 4: Fracture Toughness Results
Carbide and Boride Compositions**