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Mechanical and Physical Properties of Particulate Composites in the System Titanium Nitride-Alumina-Aluminum Nitride

By K. J. Liles

BUREAU OF MINES

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	angstrom	μm	micrometer
°C	degree Celsius	mol pct	mole percent
cm	centimeter	MPa	megapascal
DPH	diamond pyramid hardness	$\mathrm{MPa \cdot m^{1/2}}$	megapascal times square root meter
$\mathrm{g/cm^3}$	gram per cubic centimeter	m/s	meter per second
h	hour	N	Newton
kPa	kilopascal	pct	percent
L	liter	rpm	revolution per minute
min	minute	wt pct	weight percent
mm	millimeter		

MECHANICAL AND PHYSICAL PROPERTIES OF PARTICULATE COMPOSITES IN THE SYSTEM TITANIUM NITRIDE-ALUMINA-ALUMINUM NITRIDE

By K. J. Liles[1]

ABSTRACT

The U.S. Bureau of Mines evaluated the physical properties of ceramic particulate composites made from titanium nitride (TiN), alumina (Al_2O_3), and aluminum nitride (AlN) as part of a program to meet the high-performance demands on structural materials for new and emerging technologies. Samples containing from 20 to 80 wt pct TiN were pressed and fired, and their composition, Vickers hardness, modulus of rupture (MOR), and fracture toughness were determined. X-ray diffraction and scanning electron microscope (SEM) analyses showed that, depending on the amount of TiN added, the microstructure of the samples consisted of either a titanium-aluminum-oxynitride (TiAlON) particulate in a spinel matrix or a spinel particulate in a TiAlON matrix. The best results of the physical tests were achieved on a mixture of 40 wt pct TiN, 30 wt pct Al_2O_3, and 30 wt pct AlN. Sintering aids were added in 1- and 3-mol-pct increments to the 40-30-30 mixture to determine their effect on microstructure and physical properties. Results of an analysis of variance on a 4 by 4 factorial analysis showed significant effects on density, MOR, and Vickers hardness.

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[1] Research chemist, Tuscaloosa Research Center, U.S. Bureau of Mines, Tuscaloosa, AL.

INTRODUCTION

The continued growth of the U.S. economy and assurance of national security is based on a broad range of high-performance engineering materials. In support of this growth and security, technological innovation is required throughout the entire material cycle, from mining to consumer product to disposal and recycling. Some of the materials used today have been developed only recently from new technologies. At the forefront of these materials are the advanced ceramics, e.g., sialons, stabilized zirconia, silicon carbide whisker-reinforced alumina, and hot-isostatically-pressed silicon nitride.

There has been an increasing interest in structural materials that can withstand severe conditions of temperature, pressure, and environment and can substitute for high-temperature alloys that require imported critical materials such as chromium and cobalt and, to a lesser extent, nickel. The nonoxide ceramics (nitrides, carbides, borides, etc.) have shown promise as high-temperature structural materials for a variety of high-technology applications covering energy, metallurgical, and electronic areas because of their superior thermomechanical properties and hardness.

Although monolithic materials, such as silicon nitride and silicon carbide, have high-temperature strength and are resistant to wear and corrosion, they are very brittle and have low resistance to fracture.

Exploratory research by the U.S Bureau of Mines showed that a hard, dense composite material could be made from metallic nitrides such as titanium or zirconium when combined with Al_2O_3 and AlN. Of these nitrides, TiN showed the best results and was chosen for further investigation. This report describes the research on combinations of these materials and the results of physical and mechanical testing on the samples that were produced.

This work is part of the Bureau's program to stimulate development of domestic substitutes for materials that require significant quantities of imported strategic and critical minerals.

SAMPLE DESCRIPTION

The properties and elemental percentages of the starting materials used in this work are listed in table 1.

Table 1.-Elemental percentages and properties of starting materials used in composites

Compound	Constituent, pct Ti	N	C	O	Al	Fe	Metal impurities	Grain size, µm	Bulk density, g/cm^3
[1]TiN	77.3	20.5	0.1	2.0	NA	NA	0.10	1.8-2.0	0.79
[2]Al_2O_3	NA	NA	NA	40.1	52.9	NA	NA	.25	.56
[1]AlN	NA	31	.1	2	65.0	0.15	NA	1.3-2	.36

NA Not analyzed.
[1]Supplier: Hermann C. Starck, Inc., New York, NY.
[2]Supplier: Baikowski International Corp., Charlotte, NC.

SAMPLE PREPARATION

One of the more important requirements for obtaining a dense, strong material is to ensure a thorough mixing of the starting materials. By utilizing the Bureau's 6-L turbomill,[2] an intimate mix of the starting materials was obtained. A cutaway sketch of the turbomill is shown in figure 1.

Because of the reaction between AlN and water ($2AlN + 3H_2O \rightarrow Al_2O_3 + 2NH_3$), kerosene was used as the mixing medium. The specific gravity of the kerosene was 0.81 g/cm^3. Half the liquid was added to the mill, the solids were then added while the mill was rotating at reduced speed, and then the remaining liquid was added. Al_2O_3 balls, approximately 2 mm in diam, were added to the total mixture to prevent agglomeration of the solids. After the mill was fully charged, the speed was increased to 1,500 rpm, resulting in a peripheral rotor speed of 6.8 m/s. Mixing was allowed to continue for 30 min, after which the material was screened to remove the Al_2O_3 balls. Solids were allowed to settle, the excess kerosene was siphoned off, and the slurry was filtered and washed with acetone to remove the remaining kerosene. The filter cake was dried at 70° C and the dried powder screened through 200 mesh. Exploratory research indicated that the percentage of TiN to be used lay in the range of 30 to 60 wt pct. Compositions with 20 and 80 wt pct TiN were also used to give an indication of "end member" effect. The compositions are shown in table 2.

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[2] Wittmer, D. E. Use of Bureau of Mines Turbomill to Produce High-Purity Ultrafine Nonoxide Ceramic Powders. BuMines RI 8854, 1984, 12 pp.

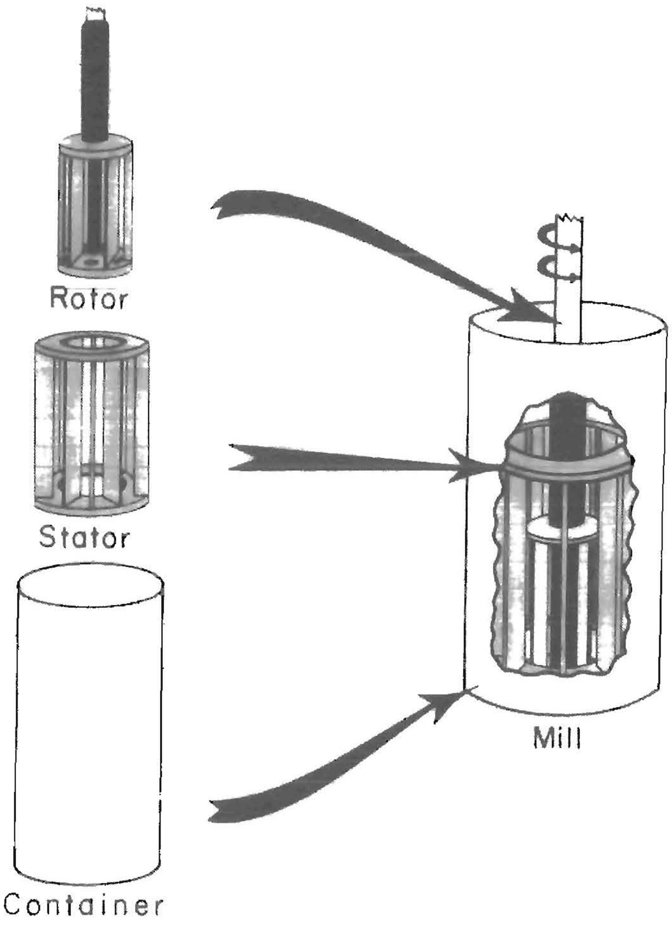

Figure 1.–Cutaway view of U.S. Bureau of Mines turbomill.

Table 2.–Composition and X-ray diffraction analysis of fired products

(1,850° C, 2-h hold, 34.5 kPa N_2)

Composition	Composition, wt pct			X-ray diffraction analysis		
	TiN	Al_2O_3	AlN	TiN	Spinel	Unidentified
1	20	40	40	M	M	m
2	30	50	20	M	M	ND
3	40	30	30	M	M	m
4	60	30	10	M	M	ND
5	80	10	10	M	m	ND

M Major constituent.
m Minor constituent.
ND Not detected.

The minus 200-mesh material was compressed into 2.54- by 5.08- by 0.953-cm billets using a hardened steel die. Pressed samples were then encapsulated in a latex sheath, evacuated, and pressed isostatically to 276 MPa. The pieces were fired in a graphite element furnace at 1,850° C with a 2-h hold. The furnace was under a positive pressure of 34.5 kPa N_2.

The pieces were then ground to shape using 80-, 200-, and 325-grit diamond wheels. Shapes for test procedures were sliced with a diamond impregnated blade.

The 40-wt-pct-TiN mixture was used to determine the effects of yttria (Y_2O_3) and mischmetal[3] additions as sintering aids when fired at 1,850° C for 2 h in 34.5 kPa N_2.

Samples of the 40-30-30 mixture were produced for a factorial analysis study. The factors included were sintering aid (Y_2O_3) addition, time at temperature, firing temperature, and internal furnace pressure. These factors, along with their respective levels, constituted a suite of 16 tests. The layout of the factorial analysis is shown in figure 2. All of the samples in the factorial study were prepared in the same manner as those for the previous tests.

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[3] A waste product of rare-earth production (major constituents are cesium and lanthanum).

		A+		A−	
		B+	B−	B+	B−
C−	D−	7	9	4	2
	D+	15	1	12	6
C+	D−	13	16	3	8
	D+	5	10	11	14

KEY

A+	1 pct Y_2O_3
A−	No Y_2O_3
B+	2 h
B−	No hold
C+	1,850 °C
C−	1,950 °C
D+	34.5 kPa N_2
D−	103 kPa N_2

A	Additive
B	Hold time
C	Temperature
D	Pressure

Figure 2.–Layout for factorial analysis.

TEST RESULTS

X-RAY AND SEM

X-ray diffraction patterns were made on all five of the compositions of samples that were used for MOR testing. Results indicated that TiN was a major constituent in all five compositions while an Al_2O_3-AlN spinel with a cell constant of 7.95 Å was major in compositions 1 through 4 and minor in 5. In compositions 1 and 3 there was a minor unidentified phase at 34° 2Θ. Results of X-ray analyses are shown in table 2.

The difference in microstructure of the compositions was shown dramatically in SEM photographs. Figure 3A, composition 1, shows a titanium-aluminum-oxynitride (TiAlON) particulate interspersed in a spinel matrix. Figure 3C, composition 5, shows a spinel particulate in a TiAlON-rich matrix. Figure 3B, composition 3, shows the two phases to be nearly equal. Grain sizes of the particulates ranged from 2 to 5 µm. Porosities of each of the compositions were made by area fraction calculations from the video image. Values for compositions 1 through 5 were 18.9, 6.2, 9.2, 3.1, and 14.0 pct, respectively.

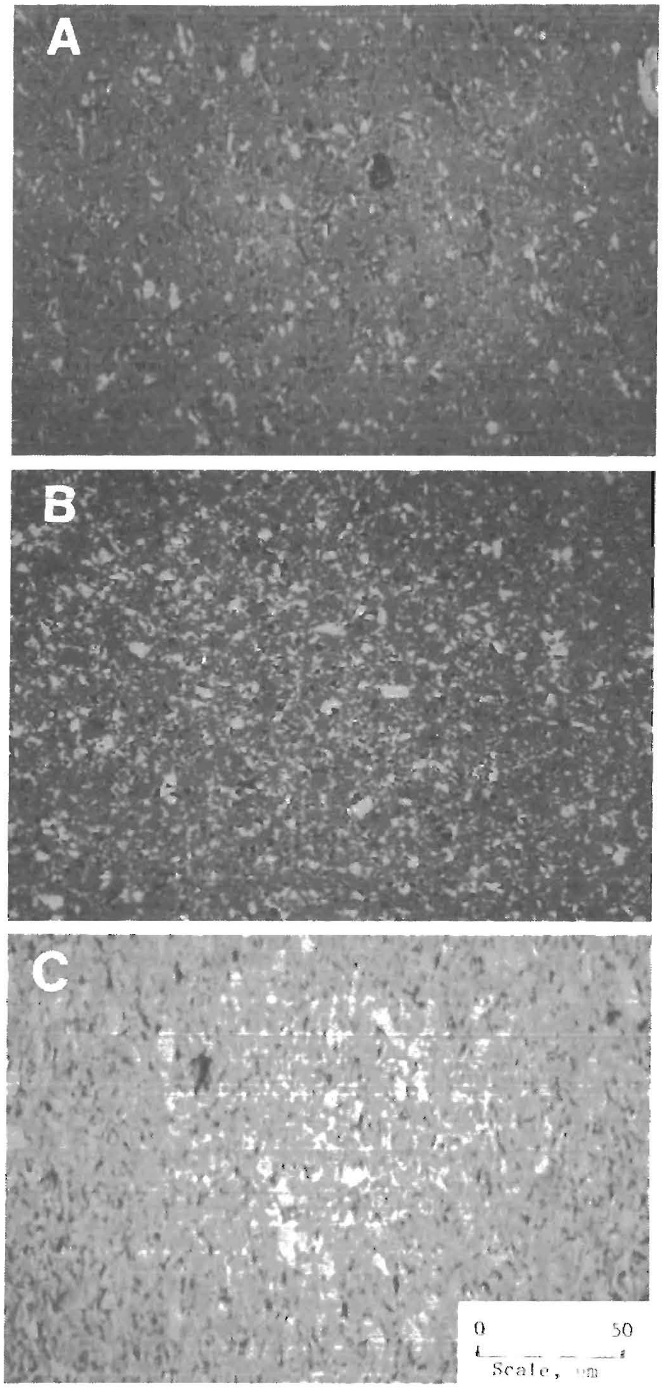

Figure 3.-TiAlON particulate in spinel matrix. A, Composition 1; B, composition 3; C, composition 5.

HARDNESS

Samples of each composition were mounted in transparent plastic and diamond polished for hardness testing. Indentations were made using a diamond point indentor with the angle between opposite faces at 136°, which results in a Vickers hardness. Five separate indentations were made on each piece and the results averaged. Values ranged from 469 DPH on composition 5 (80 wt pct TiN) to 1,564 DPH on composition 1 (20 wt pct TiN). A commercial reaction-sintered silicon nitride (Si_3N_4) was tested by the same method and found to have a value of 741 DPH. Results of the tests, along with error bars, are shown in figure 4.

MOR

MOR tests were made on ground and polished pieces approximately 0.635 by 0.635 by 5.08 cm, using a four-point bending device on a universal testing machine. A minimum of six pieces of each composition were broken, and the MOR was calculated using the formula[4]

$$MOR = \frac{3Pa}{bd^2},$$

where P = applied load, N,

a = moment arm, mm,

b = breadth, mm,

and d = depth, mm.

Test results ranged from 92 MPa for composition 5 (80 wt pct TiN) to 229 MPa for composition 3 (40 wt pct TiN), compared with 130 MPa for the commercial reaction-sintered Si_3N_4. Results for all compositions, along with error bars, are shown in figure 5.

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[4] Richerson, D. W. Modern Ceramic Engineering. Dekker, 1982, 399 pp.

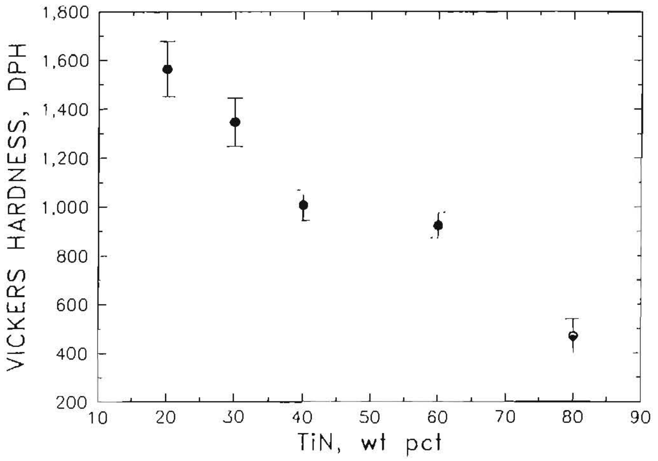

Figure 4.–Results of Vickers hardness tests in respect to weight-percent TiN.

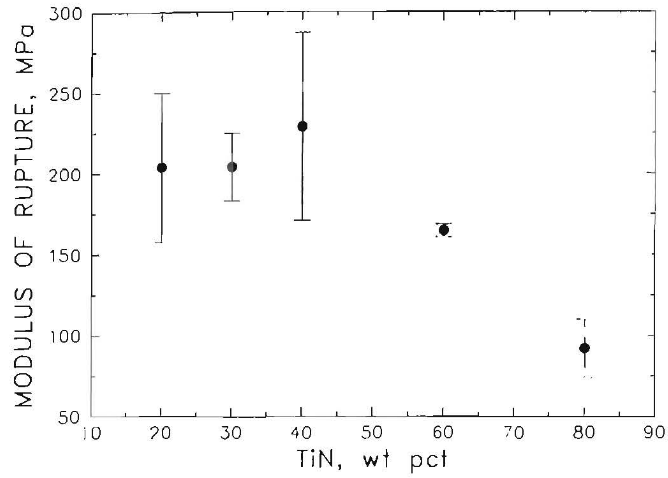

Figure 5.–Results of MOR tests in respect to weight-percent TiN.

FRACTURE TOUGHNESS

Fracture toughness is defined as the critical stress intensity factor at which a crack will propagate and lead to fracture. Consequently, the higher the fracture toughness, the more difficult it is to initiate and propagate a crack. Tests were conducted on ground and polished pieces using the single-edge notched-beam method and a four-point bending device. Samples were approximately 0.318 by 0.635 by 5.08 cm with a notch depth of 0.198 cm. A minimum of five samples were tested for each composition. Fracture toughness (K_{Ic}) was calculated using the formula[5]

$$K_{Ic} = \frac{3Pa}{bw^2} d^{1/2} \cdot y^{1/2},$$

where P = applied load at fracture, N,

a = moment arm, mm,

b = specimen width, mm,

w = specimen thickness, mm,

d = notch depth, mm,

and y = geometric configuration factor calculated by

$$y = 7.68 \left(\frac{d}{w}\right)^2 - 2.30 \left(\frac{d}{w}\right) + 1.98$$ for four-point bend.[6]

Results ranged from 0.99 MPa•m$^{1/2}$ (80 wt pct TiN) to 1.63 MPa•m$^{1/2}$ (40 wt pct TiN). The reaction-sintered Si_3N_4 tested at 0.61 MPa•m$^{1/2}$. Test results on all compositions, along with error bars, are shown in figure 6. A summary of all the test results on all samples is given in table 3.

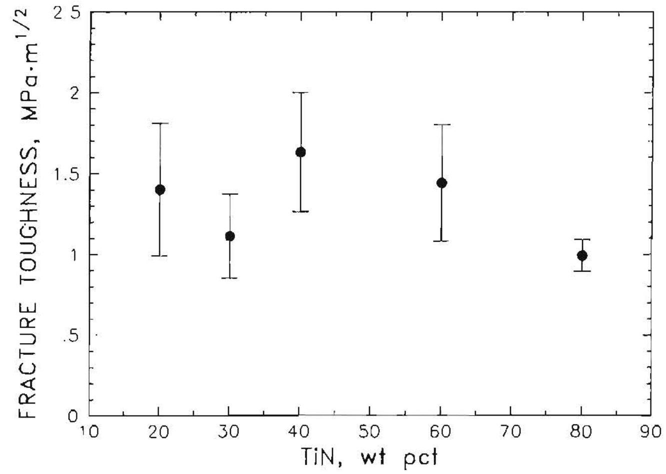

Figure 6.–Results of fracture toughness tests in respect to weight-percent TiN.

Table 3.–Summary of test results

(1,850° C, 2-h hold, 34.5 kPa N_2)

Sample	Vickers hardness, DPH	MOR, MPa	Fracture toughness, MPa•m$^{1/2}$	Density, g/cm^3
TiN, wt pct:				
20	1,564	205	1.40	3.55
30	1,346	203	1.11	3.86
40	1,005	229	1.63	3.72
60	922	165	1.44	3.77
80	469	92	.99	3.59
Si_3N_4	741	130	.61	NA

MOR Modulus of rupture.
NA Not analyzed.

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[5] Danforth, S. C., and M. H. Richman. Strength and Fracture Toughness of Reaction-Bonded Si_3N_4. Am. Ceram. Soc. Bull., v. 62, 1983, pp. 501-504.

[6] Hertzberg, R. W. Deformation and Fracture Mechanics of Engineering Materials. Wiley, 2d ed., 1983, 697 pp.

SINTERING AIDS

When 1 mol pct Y_2O_3 was added to the 40-30-30 mixture, strength results were considerably higher. Conversely, when 3 mol pct was added, results were lower. When 1 mol pct mischmetal was added, an increase in Vickers hardness and MOR was noted. A comparison of test results is shown in table 4.

Table 4-Results of tests using additives as a sintering aid

(1,850° C, 2-h hold, 34.5 kPa N_2)

Additive	Vickers hardness, DPH	MOR, MPa	Fracture toughness, $MPa \cdot m^{1/2}$
None	1,005	229	1.63
1 mol pct Y_2O_3	1,275	292	1.79
3 mol pct Y_2O_3	1,103	229	1.01
1 mol pct mischmetal ...	1,167	250	1.43

MOR Modulus of rupture.

FACTORIAL ANALYSIS

Test results of the factorial analysis are shown in table 5. Best results were achieved on a sample with no Y_2O_3 addition, a 2-h hold at 1,950° C, and 103 kPa N_2 pressure (sample 4). An analysis of variance (ANOVA) was calculated on the results in table 5 to determine the effects of the factors or interactions of factors on individual properties. The results of the ANOVA are shown in table 6. As seen in the table, the interaction between the presence or absence of Y_2O_3 and the firing temperature had the only statistically significant effect on both density and MOR. The interactions of Y_2O_3 and time at temperature, along with Y_2O_3 and firing temperature, both had an effect on Vickers hardness. None of the factors or interactions had a statistically significant effect on fracture toughness. The critical ratios are compared to f-values at the 95-pct (two-sided) confidence level.

Table 5.-Test results of factorial analysis

(Using 40 TiN, 30 Al_2O_3, 30 AlN)

Sample	Vickers hardness, DPH	MOR, MPa	Fracture toughness, $MPa \cdot m^{1/2}$	Density, g/cm^3
1	819	143.6	0.98	3.66
2	397	132.3	1.11	3.33
3	769	128.4	1.19	3.38
4	1,618	190.3	1.49	3.83
5	931	189.2	1.27	3.78
6	924	144.9	1.03	3.52
7	240	74.0	.95	2.90
8	243	74.6	1.00	2.91
9	641	107.2	.96	3.55
10	1,244	132.5	1.20	3.76
11	784	137.9	1.20	3.44
12	1,482	182.7	1.29	3.91
13	1,225	132.9	1.32	3.76
14	320	114.1	1.03	3.11
15	416	109.8	1.25	3.58
16	743	131.0	1.26	3.61

MOR Modulus of rupture.

Table 6.-Critical ratios of factors resulting from an ANOVA

Factor	Vickers hardness, DPH	MOR, MPa	Fracture toughness, $MPa \cdot m^{1/2}$	Density, g/cm^3
A (additive)	0.076	0.874	0.120	2.436
B (hold time) ...	4.453	3.295	10.324	2.272
C (temperature) .	.076	.236	.898	.500
D (pressure)	1.066	4.097	.005	3.950
Interactions:				
A vs B	[1]11.331	4.000	1.988	9.008
A vs C	[1]18.351	[1]14.504	10.624	[1]15.695
A vs D	.006	.699	1.082	.329
B vs C	.033	1.396	.898	1.167
B vs D	2.265	.002	.120	.064
C vs D	.195	.106	.065	.706

MOR Modulus of rupture.

[1] Exceed statistical significance value at 95-pct confidence level.

CONCLUSIONS

Based on the study of a range of TiN-Al_2O_3-AlN compositions that were turbomilled, compressed, and sintered, the following conclusions can be made:

1. A series of particulate composites was developed that produced a TiAlON particulate interspersed in a spinel matrix or a spinel particulate in a TiAlON matrix, depending on the quantity of TiN added.
2. MOR and Vickers hardness values for all but composition 5 (80 pct TiN) were higher than that for a commercial reaction-sintered Si_3N_4.
3. Fracture toughness values for all compositions were higher than that for a commercial reaction-sintered Si_3N_4 when tested by the single-edge notched-beam method.
4. When 1 mol pct Y_2O_3 was added to the mixture of 40 wt pct TiN, 30 wt pct Al_2O_3, and 30 wt pct AlN as a sintering aid, the strength values were considerably higher. Conversely, when 3 mol pct was added, the values were lower. When 1 mol pct mischmetal was added, an increase in Vickers hardness and MOR was noted.
5. According to an ANOVA, the only factors statistically significant in a factorial analysis were the interactions of the presence or absence of Y_2O_3 with firing temperature on density and MOR values and the presence or absence of Y_2O_3 with time at temperature and firing temperature on Vickers hardness.
6. The best results in the factorial analysis were achieved with no Y_2O_3 addition, a 2-h hold at 1,950° C, and 103 kPa furnace pressure (MOR = 190.3 MPa, fracture toughness = 1.49 $MPa \cdot m^{1/2}$, and Vickers hardness = 1,618 DPH).

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