

Novel Composites in the Aluminum Nitride–Zirconia and –Hafnia Systems

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Abstract

Solid-state displacement reactions in AlN–ZrO₂ and AlN–HfO₂ systems were investigated. The solid-state displacement reactions in the AlN–ZrO₂ system yield a ZrAlON phase after hot pressing in nitrogen and vacuum environments. The amount of ZrAlON formation increased with increasing AlN/ZrO₂ molar ratio and with increasing reaction temperature. AlN additions were found to stabilize the (cubic+tetragonal) ZrO₂ structure in composites. The relative amount of tetragonal phase was less than 30% volume; Y₂O₃ addition increased the amount of tetragonal phase to more than 70% volume. The amount of ZrO₂ was determined to decrease with increasing sintering temperature and increasing AlN/ZrO₂ molar ratio. No reaction occurred in the AlN–HfO₂ system, contrary to what is reported in the literature. The mechanical properties of the ZrAlON–Al₂O₃ composites were evaluated. The flexural strength of composites ranged from 300 to 490 MPa depending on the composition. The indentation fracture toughness of the composites ranged from 3 to 5 MPa√m but increased to 7 MPa√m with 2.5% mole Y₂O₃ additions because of the increasing tetragonal zirconia content. Hardness values of the composites were measured between 7 and 13 GPa. The composites initially showed a friction coefficient of 0.6, which increased with time to 0.85 against steel. © 1997 Elsevier Science Limited.

1 Introduction

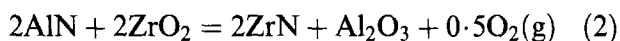
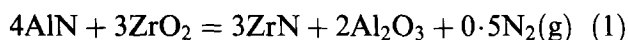
Interest has recently developed in the *in-situ* processing of ceramic matrix composites by solid-state displacement reactions, which incorporate a reactive, diffusional phase transformation to yield thermodynamically stable products in desired

microstructural arrangements.¹ Microstructures containing a specific proportion of grains with a distinctive morphological anisotropy can be formed in certain materials during sintering via solid-state displacement reactions without the use of initial crystals with anisotropic forms, i.e. whiskers.² A process of this kind has several advantages. The reinforcing phases are produced *in situ*, which is a low-cost processing route. The desired microstructures, such as interpenetrating phases and aligned reinforcements, can be produced. The mechanical properties obtained can be superior to those of similar composites processed by other routes because of the finely divided microstructures that naturally occur during reactions.

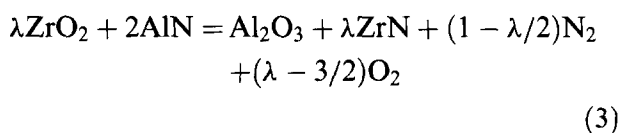
Displacement reactions in the AlN–ZrO₂ system^{3,4} and AlN–TiO₂ system^{5–7} were studied earlier. The TiO₂+AlN reaction goes to completion to produce TiN+Al₂O₃ composites,^{5–7} while the AlN+ZrO₂ reaction results in a combination of Al₂O₃, ZrN, ZrO₂, and AlN,^{3,4} depending on the heat treatment conditions. Savrun and Guinchi⁸ have studied the displacement reaction in the AlN–ZrO₂ system between 1600°C and 1900°C. The findings of Savrun and Guinchi are in agreement with those of Bayer and Mocellin³ and Mukerji,⁴ with the only exception being that a new ZrAlON phase formation was also determined. A quaternary Zr–Al–O–N phase has also been identified in the AlN–ZrO₂ system by others.⁹ The Fd3m space group was assigned to the ZrAlON phase, and several reaction paths were proposed for its formation.⁹ A similar lattice structure (fcc) with the same cell dimension was also identified in the ZrO₂–AlN system as ZrN(O) compound.¹⁰ However, the presence of Al₂O₃ in the reaction product was reported in the same study, which made that result questionable.⁹

Reactions (1) and (2) were proposed to occur between AlN and ZrO₂ in solid state, according to the X-ray results in studies by Bayer and Mocellin³ and Mukerji,⁴ respectively.

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Reactions (1) and (2) are special cases of reaction (3) [$\lambda = 1.5$ for the reaction (1) and $\lambda = 2.0$ for the reaction (2)] which was originally proposed by Mocellin and Bayer.^{3,5}



However, the recent studies^{8,9} suggest the presence of ZrAlON phase after displacement reactions in AlN–ZrO₂ system. ZrAlON phase formation was observed, not only when ZrN and Al₂O₃ powder mixture was vacuum hot pressed at 1800°C, but also when AlN and ZrO₂ powders were hot pressed at 1400°C.⁹ Similarly, pressureless sintering of AlN–ZrO₂ powder mixture in 4:3 ratio up to 1900°C showed the ZrAlON phase formation.⁸ Therefore, the ZrAlON phase does not appear to be an intermediate phase formation and the reaction (3) is questionable for AlN–ZrO₂ system. This study suggests a different reaction route to accommodate ZrAlON formation.

Reactions in the AlN–ZrO₂ system can be controlled to have residual AlN and ZrO₂ in the final product.^{3,4,8} Such composites of AlN–ZrN–Al₂O₃–ZrO₂ and/or AlN–ZrAlON–ZrO₂ could have promising properties for structural applications. The properties of ZrN–Al₂O₃ composites formed by solid-state displacement reactions have not been investigated to the best of our knowledge. If a new material will be considered for any application, its physical and mechanical properties must be determined to assess application limitations and permit tailoring of the physical and mechanical properties, including strength, fracture toughness, and coefficient of friction, all of which are discussed in this paper.

2 Experimental Approach

Commercially available powders of high-purity aluminum nitride (Tokuyama Soda, grade G), zirconia (Z-Tech, grade SF-Ultra 0.7), and hafnium oxide (CERAC Inc.) were used to fabricate composite samples. High-purity (99.99%) yttrium oxide powder (Rhone-Poulenc) was also used to increase the amount of tetragonal zirconia phase stabilized in the composites. Aluminum nitride and zirconia powders were mixed in different

ratios and reaction hot pressed. The composition 4AlN:3ZrO₂ (57% mole AlN) was selected as the baseline. Other compositions between 20% and 64% mole AlN were also prepared by changing the relative amounts of AlN and ZrO₂ to achieve ZrO₂, AlN, and ZrAlON phases or a combination thereof, in addition to Al₂O₃ and ZrN. Furthermore, one batch was prepared in the AlN–HfO₂ system equivalent to composition 2AlN:3HfO₂ to assess the feasibility of solid-state reaction. The effects of 2.5% mole Y₂O₃ additions were investigated for compositions 2AlN:3ZrO₂ and AlN:ZrO₂.

Powder mixtures were prepared by wet ball milling followed by spray drying to obtain homogeneous mixtures. A mixture of acetone and isopropyl alcohol was chosen as the solvent, while an amine-ester copolymer was used as the dispersant. The organics were removed from the mixture by heating in air. Total weight loss was measured after organics removal and found to be equal to the original amount used during the ball milling step.

The granulated powder mixtures were consolidated by hot pressing in a graphite die. The samples were hot pressed under 45-MPa pressure at 1500°C and 1600°C for 1 h under flowing nitrogen gas and vacuum conditions. The pressed blocks were ground, and densities were measured by a liquid displacement method. The samples were sectioned and polished for microstructural examination by light microscopy. X-ray diffraction was used for phase analysis; the relative volume fractions of the reaction products in the composites were calculated from X-ray diffraction data. The areas under the strongest peaks were compared for the following phases: monoclinic-ZrO₂ ($\bar{1}11$); cubic + tetragonal-ZrO₂ (111); Al₂O₃ (113); ZrAlON (444) and ZrN (111). ZrAlON ($a_0 = 1.834$ nm) is a superlattice of the ZrN ($a_0 = 0.458$ nm) structure.⁹ Thus, it is not easy to distinguish two phases from each other by X-ray diffraction. Therefore, the presence of both phases is reported in ZrAlON(ZrN) notation in this study. Relative proportions of cubic and tetragonal ZrO₂ were determined by considering the areas under (400) diffraction peaks of both phases.

Flexural strength test specimens 3.0 × 4.0 × 50.0 mm in size were prepared by diamond machining. The edges were chamfered to 45°, and the surfaces were polished through a 6- μ m diamond paste to eliminate machining flaws. Flexural strengths were determined in four-point bending with 1/4-point loading having an outer span of 40 mm. A cross-head speed of 0.05 mm min⁻¹ was used. At least five samples were tested for each composition, and the average failure stress was reported with a standard deviation.

All the microhardness measurements were conducted under a 4.9-N load for 30 s holding time. A large Vickers diamond indenter was also used to introduce indentation cracking patterns on polished specimen surfaces to determine fracture toughness values. A 98-N load was applied on an Instron universal testing machine. From the post-indentation analysis, the fracture toughness, K_{IC} , was calculated according to Anstis *et al.*¹¹ Elastic moduli of the composite materials were measured independently by using a resonant frequency technique, rather than relying on flexural stress-strain data. Standard ball-wear tests were conducted on specimens 20 × 20 × 4 mm in size. Specimen surfaces were polished with a series of diamond pastes down to 0.5 μm prior to testing. Wear tests were performed by using a ball velocity and wear track diameter during testing of 0.1 ms⁻¹ and 12 mm, respectively. Wear tests were carried out under a 5-N load at room temperature in air. In all of the wear tests, 4.76-mm-radius 440 carbon steel balls were used. Wear loss was determined from the scar dimensions left on the ball surface.

3 Results and Discussion

3.1 Densification and analysis of reaction

During hot pressing, densification of the powder mixtures started at about 1175°C under a pressure of 45 MPa, as evidenced by the rapid displacement of the hot-press ram. More than 90% of the densification process occurred during the heat-up cycle. Once the reaction temperature was reached, the densification process stopped after 30 min of holding at the reaction temperature. It may be possible that a reaction takes place between the AlN and ZrO₂ phases without the effect of a nitrogen environment in the furnace, because the early densification process may make it difficult for nitrogen gas to access the compact interior.

Figure 1 shows the X-ray diffraction data obtained from 40% mole AlN-containing AlN-ZrO₂ mixtures after hot pressing at 1500°C for 1 h under a nitrogen environment. The (cubic + tetragonal) form of the zirconia is the major phase, followed by the ZrAlON(ZrN) phase and the monoclinic form of the zirconia. Minor alumina peaks were also identified in the X-ray diffraction spectra. Because no AlN phase was detected for all the compositions studied, the AlN in the starting mixture must have completely reacted with the zirconia powder. Relative amounts of phases were calculated from the X-ray diffraction intensity data. The results are shown in Fig. 2. As seen from Fig. 2(a) and (b), the amount of ZrAlON(ZrN) phase increases with increasing AlN content.

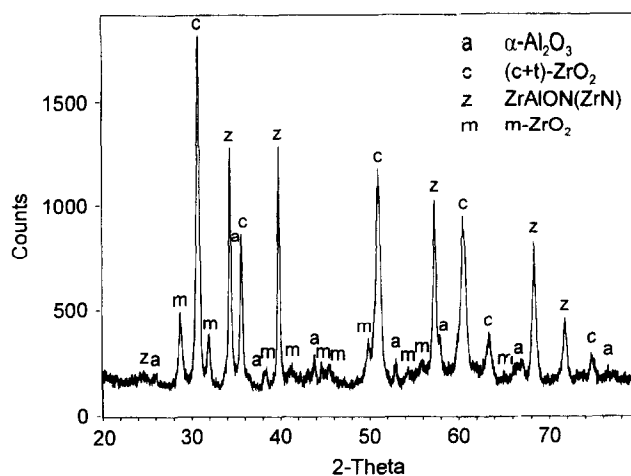
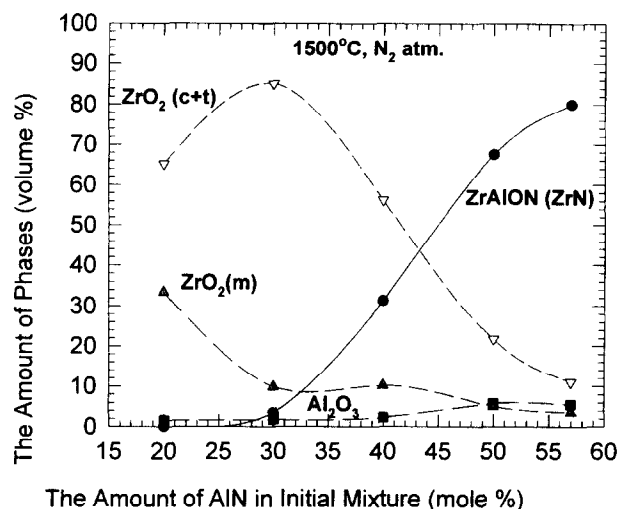
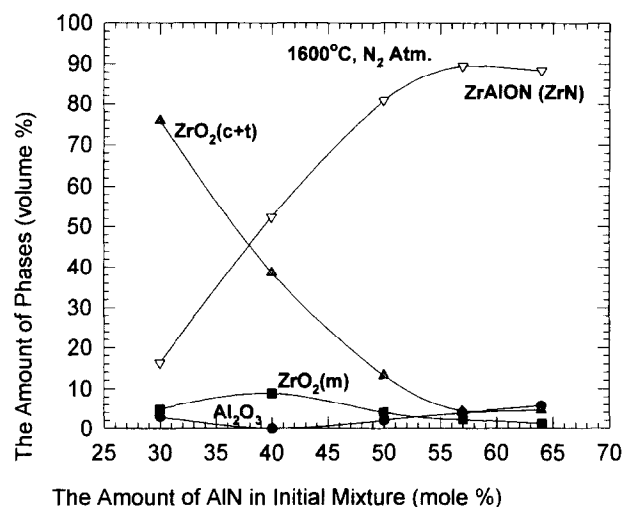


Fig. 1. X-ray diffraction spectra of 40% mole mixture after hot pressing at 1500°C in nitrogen.



(a)



(b)

Fig. 2. Relative volume percent of reaction products as a function of AlN content of starting mixtures (a) at 1500°C and (b) at 1600°C.

The alumina amount increases slightly with increasing AlN content. Increasing the ZrN content with an increasing AlN amount in the reaction mixture was reported by Mukerji.⁴ However, Mukerji's work also identified that the amount of cubic zirconia increased with an increasing AlN content in the reaction mixture. Our results show that the amount of (cubic+tetragonal) zirconia initially may increase with up to 30% mole AlN-containing composition but later decreases continuously for the 1500°C hot-pressed samples. The (cubic+tetragonal) zirconia content also decreases continuously after 1600°C hot pressing for all the compositions. The higher the hot-pressing temperature, the more ZrAlON(ZrN) phase forms. More than 80% volume of compositions with higher than 1.0 AlN/ZrO₂ molar ratio contains the ZrAlON(ZrN) phase after 1600°C hot pressing.

The relative amounts of tetragonal zirconia in the composites were determined from the area under the (400) peaks from the X-ray diffraction data. The amount of tetragonal zirconia is typically less than 30% volume. The tetragonal zirconia content of the composites increases more than 70% volume by the addition of Y₂O₃ to the starting powder mixtures. This is expected because Y₂O₃ addition is known to stabilize the tetragonal zirconia phase.¹² Increasing the tetragonal zirconia content is expected to improve the mechanical properties of the composites.

It was noted in earlier studies^{3,4} that ZrN phase formation occurs after reactions (1) and (2). This study suggests that in addition to ZrN formation, the ZrAlON phase also forms. The following observations support our hypothesis: (i) weight losses are negligible (less than 3% weight) during hot pressing, suggesting that oxygen is still present in the structure in large quantities, even after more than 80% volume ZrAlON(ZrN) peaks are observed; (ii) the relative amount of Al₂O₃ determined in the composites is not sufficiently high to accommodate the total oxygen content of the composites, which is between 18% and 24% weight depending on the composition used; (iii) the bulk density of the samples decreases not only with increasing ZrAlON(ZrN) content but also with increasing reaction temperature. Samples had less than 5% closed porosity since they were produced by hot pressing and did not show any water absorption during density measurements. If the reaction product was indeed the ZrN phase, the measured bulk densities would be expected to increase with an increasing ZrN amount, because the ZrN density (7.29 g cm⁻³) is much higher than that of any other phase observed among the reaction products, such as cubic zirconia (6.21 g cm⁻³) or alumina (3.96 g cm⁻³). There are no data available

in the literature about the density of the pure ZrAlON phase, so it is not possible to calculate the theoretical density of composites based on the volume fraction of the reaction products obtained. But, based on the bulk density data shown in Table 1 and X-ray diffraction data results shown in Fig. 2, the density of ZrAlON must be much lower than the density of the ZrN phase, since the composite bulk density decreases with increasing ZrAlON(ZrN) content as shown in Fig. 3.

Stoto *et al.*⁹ showed that the ZrAlON phase forms after the reaction, not only between ZrO₂ and AlN, but also between ZrN and Al₂O₃. Therefore, ZrAlON phase does not appear to be an intermediate phase in the reaction (3). No AlN/ZrO₂ molar ratio was defined in that study; thus, it is difficult to make any comparison with the quantitative results of our study. Ikeda *et al.*¹⁰ identified a new cubic form of the ZrN(O) phase after the reaction between ZrN and ZrO₂. However, Ikeda *et al.* also observed an alumina phase in their reaction system, suggesting contamination from

Table 1. Bulk density of composites hot pressed at 1500°C and 1600°C

AlN (% mole)	AlN/ZrO ₂	Bulk density (g cm ⁻³)	
		1500°C	1600°C
20	1/4	5.55	—
30	3/7	5.42	5.37
40	2/3	5.09	4.93
		5.03*	—
		5.03**	—
50	1/1	4.74	4.69
		4.69**	—
57	4/3	4.68	4.50
		4.32**	—
64	7/4	—	4.35

*Contains 2.5% mole Y₂O₃.

**Vacuum hot pressed.

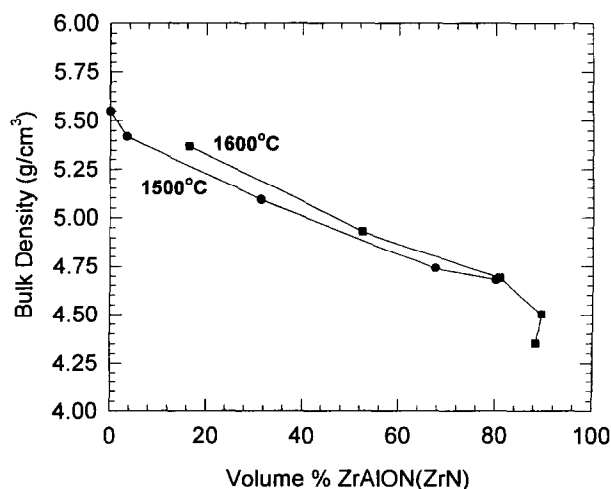


Fig. 3. Composite bulk density as a function of ZrAlON(ZrN) content and hot-pressing temperature.

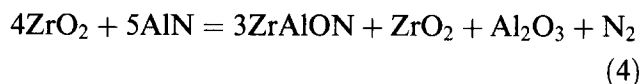
the ball milling step when alumina balls were used. The lattice constant of the new cubic ZrON ($a = 1.833$ nm) phase is very close to the lattice constant of the ZrAlON phase ($a = 1.834$ nm). Therefore, it appears that the presence of aluminum may stabilize the cubic ZrAlON structure. This is plausible, since AlN was claimed to stabilize cubic zirconia.⁴

The analytical transmission electron microscopy investigation of Stoto *et al.*⁹ showed that the ZrAlON phase is a superlattice of the ZrN phase. ZrAlON exhibits a face-centered cubic lattice with a measured cell parameter of 1.83 nm, which is four times larger than that of the ZrN lattice constant ($a_0 = 0.458$ nm). Therefore, the strongest diffraction lines of the ZrN and the ZrAlON phases overlap, making them difficult to identify by X-ray diffraction unless weak-intensity diffraction peaks less than 30° 2θ angles are determined to be present for the ZrAlON phase. In this study, those low-intensity diffraction peaks of the ZrAlON phase were present in all of the samples prepared. The ZrAlON phase is the major phase in composites with high-AlN-containing compositions and higher hot-pressing temperatures. Figure 4 shows a low-angle X-ray diffraction spectrum of the AlN:ZrO₂ composition after vacuum hot pressing at 1500°C for 1 h. Low-intensity ZrAlON peaks are marked on the spectrum.

The electrical resistance of the flexural test specimens was measured by using a two-point probe method. If the ZrN phase was present in the composites, the samples should display some conductance. However, all the samples showed very high electrical resistance (higher than 20 MΩ), indicating that the insulating ZrAlON phase formed instead of the conductive ZrN phase.

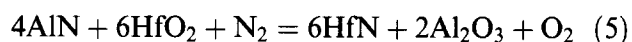
These results suggest that a solid-state displacement reaction in the ZrO₂-AlN system must be

occurring by reaction (4) below to yield the ZrAlON phase instead of ZrN. ZrO₂ was also included at the right side of the equation to indicate that the reaction is not fully completed under the conditions of this study.



The proposed reaction (4) is feasible not only under a nitrogen atmosphere but also under a vacuum, since ZrAlON and Al₂O₃ formation was observed for both conditions, in addition to the ZrO₂ phase. The relative intensity of one of the Al₂O₃ peaks in Fig. 4 (marked by the #) appears to be very high, suggesting a preferred orientation in the specimen or that more alumina may be forming under vacuum hot-pressing conditions. Bulk sample densities of the vacuum hot-pressed specimens were found to be slightly lower than the samples hot pressed under a nitrogen atmosphere. This result may suggest the presence of a lower density phase, most likely alumina, in the composite structure. However, it is not possible at this point to make any conclusive statement that more alumina can be formed under vacuum conditions.

Bayer and Mocellin³ claimed that the HfO₂-AlN system also displays a similar solid-state displacement reaction, but no data were presented to support their claim. One hot-pressing experiment was conducted in a 2AlN:3HfO₂ composition to investigate the feasibility of such a reaction under nitrogen atmosphere:



Reaction (5) is not possible according to thermodynamic calculations. The X-ray diffraction spectrum of the hot-pressed sample indicates that there was no reaction between the AlN and the HfO₂ after hot pressing at 1500°C under nitrogen gas, as thermodynamic calculations predict. The only phases present are the major orthorhombic and monoclinic forms of HfO₂ with AlN still present. The bulk density of the hot-pressed specimen was measured as 8.00 gcm⁻³, which is close to the theoretical density of hafnia. No further studies were conducted in the HfO₂-AlN system to evaluate its mechanical properties.

3.2 Characterization of composite properties

The measured flexural strengths and elastic moduli are shown in Table 2. The average strength appears to be decreasing with increasing AlN

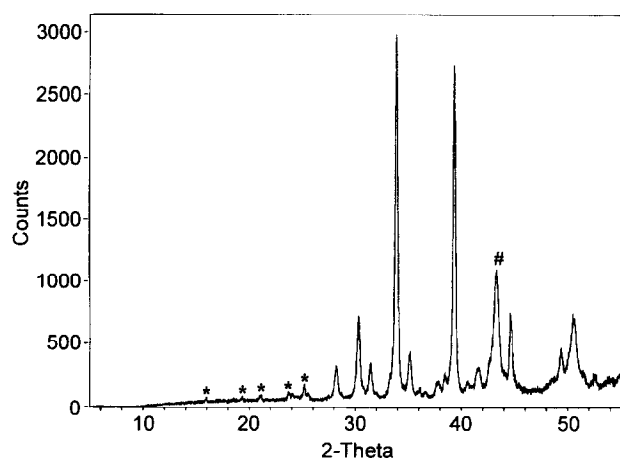


Fig. 4. X-ray diffraction spectrum of AlN:ZrO₂ composition after hot pressing under vacuum at 1500°C. [The marked peaks (*) are the low-intensity ZrAlON diffraction peaks.]

Table 2. Four-point flexural strength of ZrAlON composites

AlN (% mole)	AlN/ZrO ₂	σ_{4-pt} , SD (MPa)	E (GPa)
30	3/7	490.3 ± 43.19	272
40	2/3	383.0 ± 26.50 481.5 ± 42.59** 299.0 ± 56.70*	370 260 —
50	1/1	352.7 ± 67.74 414.1 ± 7.98**	354 241

*Contains 2.5% mole Y₂O₃.

**Vacuum hot pressed.

content in the samples hot pressed in a nitrogen environment. The samples hot pressed under vacuum conditions appear to be stronger than the samples hot pressed in a nitrogen environment. However, the number of specimens tested is not large enough to make a conclusive statement. The hardness of composites varied between 7 and 13 GPa (see Table 3).

The samples were fractured in a very brittle manner during the flexural testing, suggesting that the composites were brittle. In fact, it was very difficult to machine some of the high-AlN-containing samples for mechanical test specimens. Table 3 shows the results of the microindentation fracture toughness tests. As seen, the fracture toughness of the samples ranged between 3 and 5 MPa√m. In general, these results are comparable to the fracture toughness of single-phase ceramic materials, such as aluminum nitride and alumina. Low fracture toughness must be due not only to the brittleness of the ZrAlON phase but also to the lack of the presence of tetragonal zirconia in the composite micro-structure. The microindentation toughness appeared to increase above 7 MPa√m when 2.5% mole Y₂O₃ was added to the composite structure to stabilize the tetragonal phase.

Table 3. Microhardness and indentation fracture toughness of ZrAlON composites

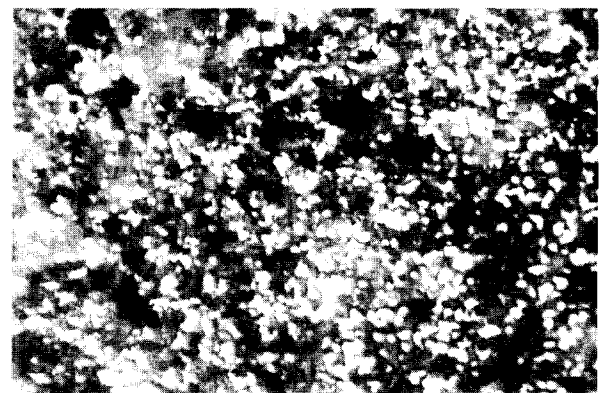
AlN (% mole)	Microhardness, SD (GPa)		K _{IC} (MPa·m ^{1/2})	
	1500°C	1600°C	1500°C	1600°C
20	12.45 ± 0.88	—	5.6	—
30	7.34 ± 0.31	13.61 ± 0.51	4.3	—
40	10.19 ± 0.91 11.27 ± 0.57*	12.44 ± 1.04 —	3.8** 7.2*	3.9 —
50	11.20 ± 0.45 8.18 ± 0.44**	11.52 ± 0.93 —	4.7 5.3**	4.5 —
57	10.21 ± 0.66 8.11 ± 0.82**	9.7 ± 0.72 —	3.9 —	3.2 —
64	—	12.4 ± 0.76	—	4.0

*Contains 2.5% mole Y₂O₃.

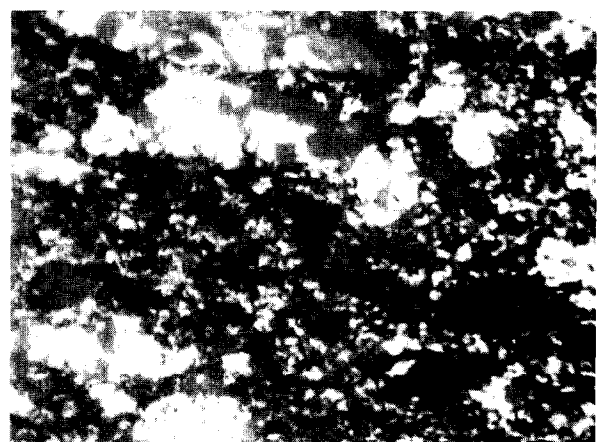
**Vacuum hot pressed.

Optical microscopy of the polished surfaces indicates that composite structures are dense and display a fine-grained microstructure, as shown in Fig. 5. Two different-colored phases are the major phases in each structure. The high-AlN-containing sample shows a larger amount of the light-colored phase. Since X-ray diffraction analysis showed that more ZrAlON was present in that particular composition, the light-colored phase must be the ZrAlON phase.

The friction and wear behavior of composites was investigated by ball wear tests. Friction coefficients were initially measured as 0.6 for all the compositions studied. But, as the test progressed, the average friction coefficient values ranged between 0.75 and 0.85. This result is the typical friction coefficient observed for steel rubbing against steel, suggesting that steel particles were entrapped on the composite's surface. With the exception of one sample, steel ball wear volume results were also comparable to each other regardless of the sample used. Steel ball wear rates against the composites were found to be less than $3 \times 10^{-5} \text{ mm}^3 \text{ N} \cdot \text{m}^{-1}$.



(a)



(b)

Fig. 5. Optical microscopy images from the polished surfaces of samples hot pressed at 1500°C under nitrogen gas (a) 3AlN:7ZrO₂; (b) 4AlN:3ZrO₂. (Scale bar 30 μm)

4 Conclusions

A solid-state displacement reaction between AlN and ZrO₂ results in ZrAlON phase formation in vacuum and nitrogen environments. The amount of ZrAlON formation is directly proportional to the AlN content used in the starting composition and to the reaction pressing temperature. AlN stabilizes the cubic + tetragonal ZrO₂ structure. The amounts of ZrAlON and (cubic + tetragonal) phase formation in composites are inversely proportional to each other. The amount of tetragonal ZrO₂ is less than 30% volume in composites. Additions of as small as 2.5% mole yttria increase the amount of tetragonal zirconia to more than 70% volume. The flexural strength of composites is comparable to that of alumina. An increase in the fracture toughness, up to 7 MPa√m, can be achieved with Y₂O₃ addition while the flexural strength stays at about 300 MPa. Finally, contrary to what is reported in the literature for AlN-HfO₂ system, no solid-state displacement reaction is observed when AlN:HfO₂ ratio is 2:3.

Acknowledgements

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References

1. Singh, M. and Lewis, D., *In Situ Composites: Science and Technology*. TMS Publication, Warrendale, PA, 1994.
2. Radhalsrishnan, R., Henager, C. H., Brimhall, J. L. and Bhaduri, S. B., Synthesis of Ti₃SiC₂/SiC and TiSi₂/SiC composites using displacement reactions in the Ti-Si-C system. *Scripta Materialia*, 1996, **34**, 1809-1814.
3. Bayer, G. and Mocellin, A., Displacement reaction sintering in the system ZrO₂-AlN. *Revue de Chimie Minerale*, 1986, **23**, 80.
4. Mukerji, J., Stabilization of cubic zirconia by aluminum nitride. *J. Amer. Ceram. Soc.*, 1989, **72**, 1567.
5. Mocellin, A. and Bayer, G., Chemical and microstructural investigations of high temperature interactions between AlN and TiO₂. *J. Mater. Sci.*, 1985, **20**, 3697.
6. Tuey, M., Savrun, E. and Chen, C. F., *Advanced Structural Inorganic Composites*, ed. P. Vincenzini. Elsevier, Amsterdam, 1991, p. 593.
7. Mukerji, J. and Biswas, S. K., Synthesis, properties and oxidation of alumina-titanium nitride composites. *J. Am. Ceram. Soc.*, 1990, **73**, 142.
8. Savrun, E. and Guinchi, G., Unpublished work, 1990.
9. Stoto, T., Doukhan, J.-C. and Mocellin, A., Analytical electron microscopy investigation of the AlN-ZrO₂ system: Identification of a quaternary Zr-Al-O-N phase. *J. Am. Ceram. Soc.*, 1989, **72**, 1453.
10. Ikeda, S., Yagi, T., Ishizawa, N., Mizutani, N. and Kato, M., A new face-centered cubic phase in the ZrO₂-ZrN system. *J. Sol. Sta. Chem.*, 1988, **73**, 52.
11. Anstis, G. R., Chantikul, P., Lawn, B. R. and Marshall, D. B., A critical evaluation of indentation techniques for measuring fracture toughness: I, Direct crack measurements. *J. Am. Ceram. Soc.*, 1981, **64**, 533.
12. Gupta, T. K., Lange, F. F. and Bechtold, J. H., Effect of stress-induced phase transformation on the properties of polycrystalline zirconia containing metastable tetragonal phase. *J. Mater. Sci.*, 1978, **13**, 1464.