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# Pressureless sintering of $B_4C$ whisker reinforced $Al_2O_3$ matrix composites

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$Al_2O_3$-$B_4C$ whisker composites have been successfully densified by pressureless sintering. Low oxygen partial pressures, below $10^{-10}$ atmospheres, were determined to be suitable for the composite densification, and the maximum densities were achieved at 1800 °C for 60 minutes. The $B_4C$ whiskers were screened classified into five size fractions and the effect of size and size distribution on the densification were studied. The small whiskers with a narrow size distribution ($-325 + 400$ mesh) yielded the highest density results. The maximum value of relative densities was 98%, 97%, 94% and 89% at 10, 20, 30 and 40 vol % $B_4C$ whiskers, respectively. Addition of $B_4C$ between 5 and 15 vol % proved to be a sintering aid to the alumina densification via mechanisms other than being a grain growth inhibitor. An increased fracture toughness up to 6.2 $MPa \cdot m^{1/2}$ was achieved in the composites containing 10–20 vol % $B_4C$ whiskers. *© 2000 Kluwer Academic Publishers*

## 1. Introduction

Alumina is one of the most widely used ceramics for its unique combination of strength, hardness, thermal stability, corrosion resistance and electrical insulation. However, the low fracture toughness is a well known impediment to its application as structural components. An effective improvement in the toughness has been achieved by incorporating a reinforcing phase, giving rise to alumina matrix composites [1–3]. The reinforcing phase can either be isolated particulates, platelets, or whiskers, or continuous fibers. Whiskers with a high aspect ratio tend to be the ideal inclusions for toughening alumina because these single crystals possess inherent perfection and hence higher strength [4]. To date, SiC whisker has been the most popular reinforcement for the alumina matrix. However, hot pressing or hot isostatic processing must normally be used to produce a dense composite microstructure [5–7].

Boron carbide is a light weight ceramic commercially available in whisker form, and has the necessary high strength (300–500 MPa) and Young's modulus (450 GPa) required to produce enhanced mechanical properties in alumina ceramics [4]. Furthermore, boron carbide has the highest hardness (30–38 GPa) of all materials, except diamond and cubic boron nitride, and the lowest density (2.51 $g/cm^3$) of all of the super hard materials [8]. The boron carbide whiskers used in this study have some unique properties. They have a different shape than traditional whiskers. They are much thicker with an appreciably lower aspect ratio, 30. This gives them special advantages with respect to the health and safety of the personnel exposed in the composite fabrication area. These whiskers cannot be inhaled [9] as can most other ceramic whisker reinforcements such as silicon carbide whiskers. Their higher aerodynamic equivalent diameter is in excess of the limit of alveolar deposition so that they do not damage the lungs as do other whiskers. Additionally it has been shown [10] that these boron carbide whiskers are not carcinogenic as are silicon carbide whiskers, asbestos and other related fibers. Based on these favorable properties, boron carbide whisker reinforced alumina matrix composite should be excellent light-weight structural material candidates with improved mechanical properties. The improved mechanical performances of $Al_2O_3$ with $B_4C$ whisker reinforcement has been demonstrated by Liu and Ownby [8]. A fracture toughness of 7.26 $MPa \cdot m^{1/2}$ was reported on hot pressed $Al_2O_3$-15 vol % $B_4C$ composite, which exceeds that of $Al_2O_3$-SiC composite at the same whisker loading. An improvement of flexural strength up to 670 MPa was further reported [4].

With respect to the well known cost and shape limitations associated with hot pressing, it is of great value to fabricate $Al_2O_3$-$B_4C$ composites by pressureless sintering. Jung and Kim [11] have achieved 97% of theoretical density for the $Al_2O_3$ matrix composite reinforced with 20 vol % $B_4C$ particulates, sintered at 1850 °C for 60 minutes. A maximum flexural strength of 550 MPa and hardness of 20.6 GPa were obtained. However, the composites exhibited only slightly increased fracture toughness (4 $MPa \cdot m^{1/2}$) which obviously is partially attributed to the equiaxed geometry of the inclusion phase. It is possible to achieve higher toughness on the $Al_2O_3$-$B_4C$ system by using whiskers instead of particulates. Of course, densification is the inevitable prerequisite for the toughening effect which is more difficult to achieve with non-equiaxed inclusions.

The present study demonstrates that $Al_2O_3$-$B_4C$ whisker composites can be sintered to high density comparable to that achieved by $Al_2O_3$-$B_4C$ particle

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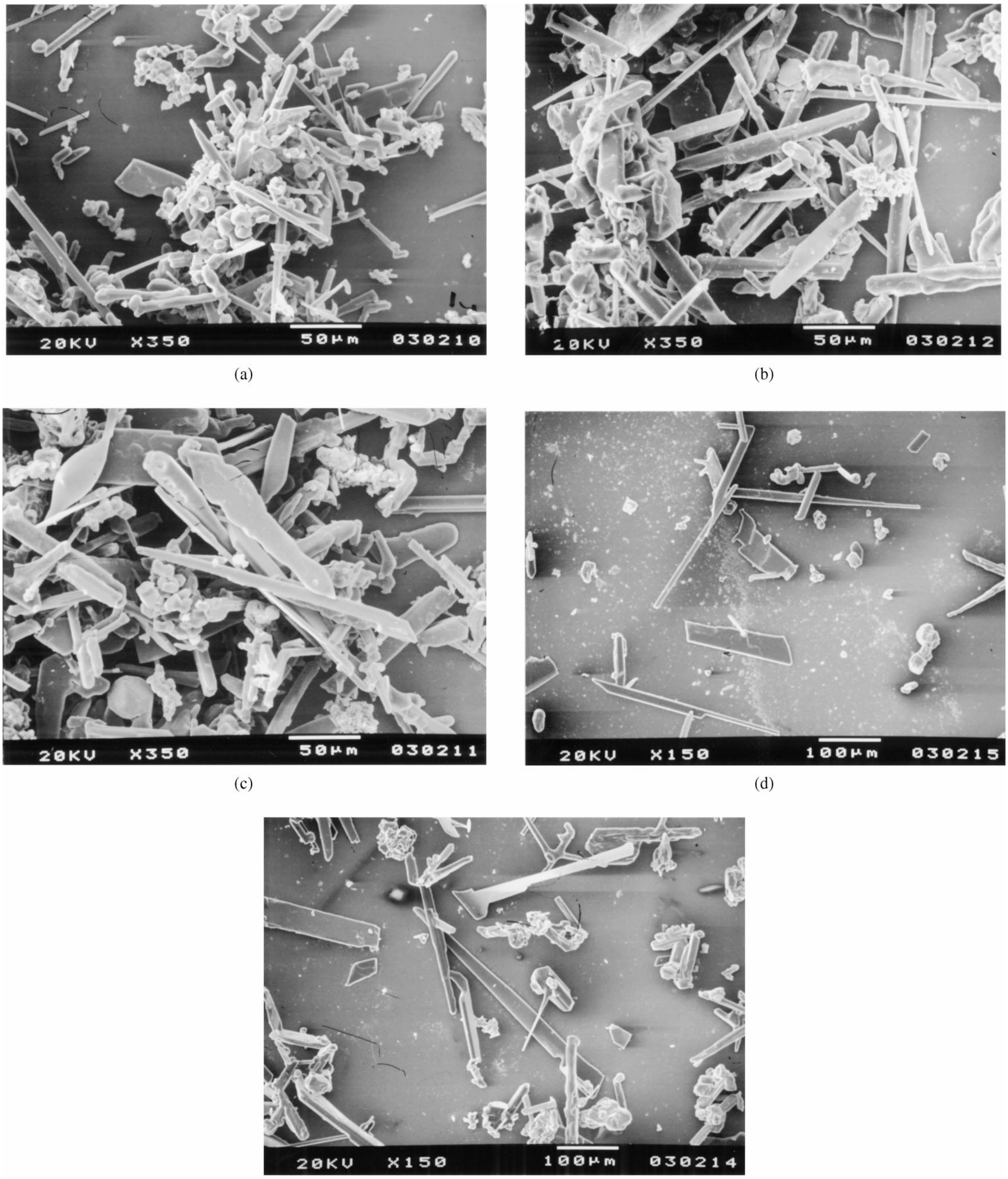
[*] Member, American Ceramic Society.



(a) (b) (c) (d) (e)

*Figure 1* Scanning electron micrograph of screen-classified boron carbide whiskers: (a) −400 mesh, (b) −325 + 400 mesh, (c) −230 + 325 mesh, (d) −200 + 230 mesh, (e) −170 + 200 mesh.

composites. The densification behavior of the composites as a function of sintering atmosphere, oxygen partial pressure, temperature and whisker size was investigated. The fracture toughness of the composites was also measured and discussed.

## 2. Experimental

The matrix powders used in the experiments were $\alpha Al_2O_3$ (Ceralox APA-0.5, purity 99.97%, MgO 291 ppm) with an average particle diameter of 0.2 $\mu$m. Boron carbide single crystal whiskers from Third Millennium Technologies, Inc.[*] were used as the reinforcement material. The Horiba CAPA-700 Particle Size Distribution Analyzer determined that most of the whiskers had particle sizes ranging from 10 to 200 $\mu$m. Scanning electron microscopy, SEM (JEOL J & M-T330A) revealed that the as-received whiskers contained many equiaxed particles or "shot." The whiskers had aspect ratios of 30 and the length varied from 20 $\mu$m to 400 $\mu$m.

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[*] These whiskers are now available at Millennium Materials, Inc., Knoxville TN.

The unusual shape and size of these whiskers made it possible to screen classify them into five different size fractions: −400 mesh, −325 + 400 mesh, −25 mesh, −200 + 230 mesh and −170 + 200 mesh. The particle sizes and shapes of these classified whiskers were characterized by means of SEM and are shown in Fig. 1.

Whiskers at each size fraction were ultrasonically dispersed in distilled water for 30 minutes to break up agglomerates. Mixing of the powders was accomplished by adding alumina powder while continuing the ultrasonic treatment for another 30 minutes. The mixtures with various percents of $B_4C$ whiskers were ball mixed for 2 hours using alumina balls in a plastic jar. The size of the whiskers was not changed by this mixing process. The resulting slurries were dried on a hot plate with magnetic stirring to prevent settling. The dried mixtures were then broken up to pass a 40 mesh sieve. Finally the specimens were uniaxially pressed into rods 13 mm in diameter by 20 mm long under 100 MPa pressure, and then cold isostatically pressed at 270 MPa. The compacted samples had green densities ranging from 60 to 65% of theoretical. Pressureless sintering was performed at 1700 to 1850 °C in either an alumina tube furnace with controlled atmospheres or a graphite tube furnace using helium as the protective atmosphere.

The sintered specimens were characterized by density, phase content, microstructure and fracture toughness. The densities were measured by the Archimedes method. The microstructure was examined by SEM, and the phase content was identified by X-ray diffraction (XRD). Fracture toughness of the composites was determined by the Chevron-Notched Short Bar (CNSB) method [12], using a Terra Tek Systems Model 4200 Fractometer.

## 3. Results and discussion

### 3.1. Sintering atmosphere

Boron carbide is highly susceptible to oxidation at elevated temperature. Low oxygen partial pressure must be maintained to avoid oxidation of the inclusion phase. For the alumina tube furnace, research grade nitrogen, helium or $CO/CO_2$ mixtures at a ratio of 100 was used as the sintering gas. For the graphite furnace, helium was used. Fig. 2 compares the relative density of the $Al_2O_3$-$B_4C$ whisker (−400 mesh) composites sintered in these atmospheres at 1700 °C for 1 hour. The density of the composites decreased with increasing volume fraction of $B_4C$ whiskers for each sintering atmosphere. The density results indicate that $Al_2O_3$-$B_4C$ whisker composites have poor densification behavior at 1700 °C, even at the low whisker loading (5 vol %).

The variation of density results with sintering gases as shown in Fig. 2 indicates that the densification development of $Al_2O_3$-$B_4C$ composites is strongly atmosphere-dependent. The specimens sintered at oxygen partial pressures less than $10^{-10}$ atmospheres achieved the highest density whether in $CO/CO_2$ in the alumina tube furnace or in the graphite furnace with helium as the protective atmosphere. Again the oxygen partial pressure was greatly reduced by the presence of the carbon phase. Similar density results between the composites sintered in $CO/CO_2$ in the alumina tube and in helium in the graphite furnace establish that low oxygen partial pressure atmospheres are suitable the pressureless sintering of $Al_2O_3$-$B_4C$ composites.

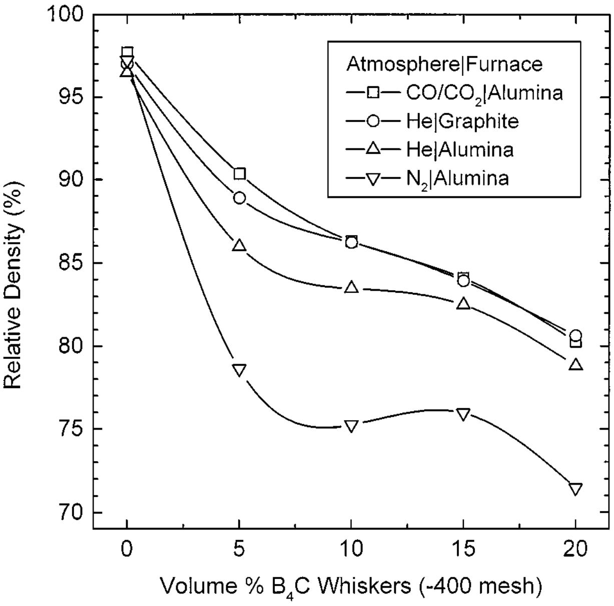


*Figure 2* Relative densities of $Al_2O_3$-$B_4C$ composites sintered at 1700 °C in different atmospheres.

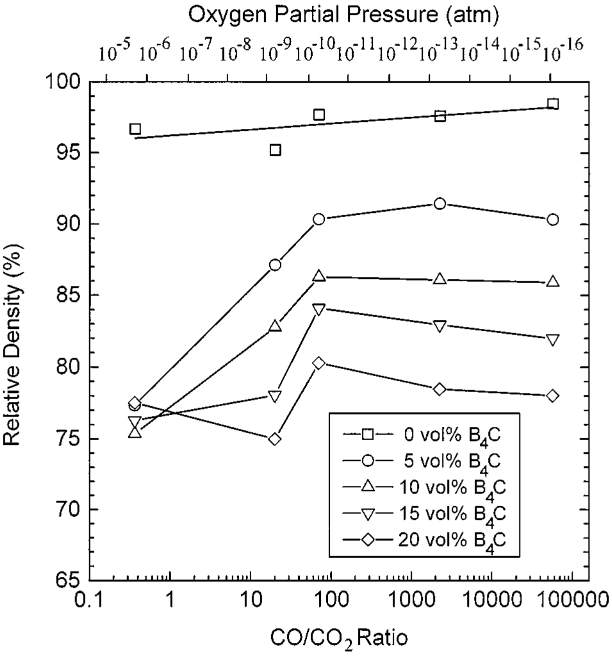


*Figure 3* Relative densities of $Al_2O_3$-$B_4C$ composites as a function of oxygen partial pressures sintered in the alumina tube furnace at 1700 °C for 1 hour.

Fig. 3 shows the relative density of $Al_2O_3$-$B_4C$ whisker (400 mesh) composites sintered at 1700 °C for 1 hour in various $CO/CO_2$ mixtures. At 1700 °C, increasing the $CO/CO_2$ ratio from 0.1 to $10^5$, correspondingly decreases the oxygen partial pressure from $10^{-5}$ to $10^{-16}$ atm. Poor densification was observed at relatively high partial pressures ($10^{-5}$ to $10^{-9}$ atm). The poor density results and the white coloration on the specimens sintered at $5 \times 10^{-6}$ atm indicated oxidation of the $B_4C$ phase had occurred, which was gradually eliminated by reducing the oxygen partial pressure. As a result, the relative densities of sintered composites steadily increased with the $CO/CO_2$ ratio until it reached 100. The stable density results obtained at the low oxygen partial pressure region ($10^{-10}$ to $10^{-16}$ atm) suggest no effect of oxygen partial pressure on the densification of $Al_2O_3$-$B_4C$ composites in this range. For maximum densification during sintering, a $CO/CO_2$ ratio higher than 100 at 1700 °C was required, i.e. an oxygen partial pressure lower than $10^{-10}$ atm which could also be obtained in a graphite furnace with a helium atmos- phere.

## 3.2. Sintering temperature and time

The density results obtained at 1700 °C as shown in Fig. 2 are not high enough for the proper mechanical application of $Al_2O_3$-$B_4C$ composites. Further increase in density requires higher temperatures. The study of sintering temperature was performed in the graphite tube furnace which allows higher temperature and faster heating rate. The composites with 5 to 20 vol % $B_4C$ whiskers (−400 mesh) were sintered at 1700 to 1850 °C for 1 hour at a heating rate of 15 °C/min in helium atmosphere, and their density results were plotted in Fig. 4. The relative densities increase significantly with the increasing temperature up to 1800 °C where all $Al_2O_3$-$B_4C$ composites were sintered to >94% of theoretical density.

Another observed effect in Fig. 4 is that the densities were reduced with the increasing temperature above 1800 °C, except for the composite with 20% $B_4C$ loading. At 1850 °C, the highest density was obtained from the specimen containing 20 vol % whiskers, while the lowest density came from the one with 5 vol % whiskers. This reverse trend may be attributed to abnormal grain growth at elevated temperature, which leads to higher porosity trapped in the large grains. Because very fine $B_4C$ particles may be present in the −400 mesh size fraction, the grain growth rate may be effectively reduced by the grain-boundary pining effect as shown by Jung and Kim [11]. For pressureless sintering of $Al_2O_3$-$B_4C$ composites with loadings 15 vol %, the optimum temperature of 1800 °C is where the densification rate and grain growth rate are best compromised.

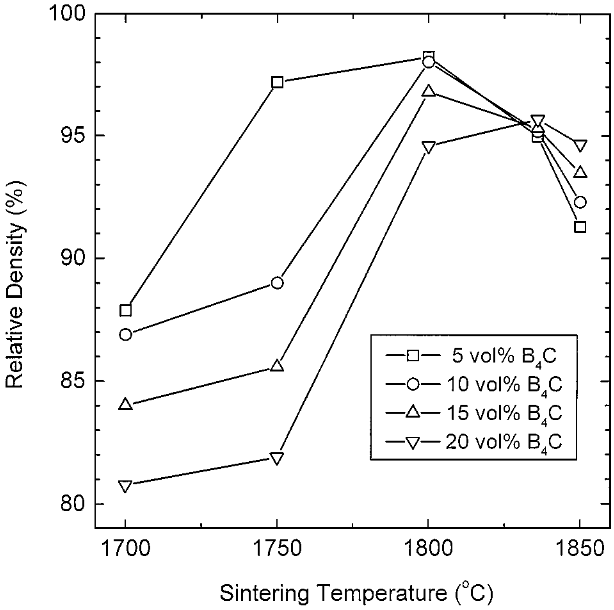


*Figure 4* Effect of sintering temperature on the relative density of $Al_2O_3$-$B_4C$ composites.

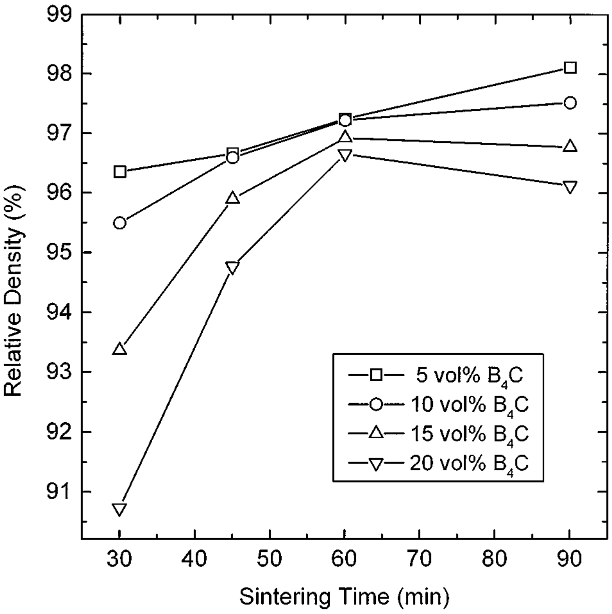


*Figure 5* Relative density of $Al_2O_3$-$B_4C$ composites as a function of sintering time at 1800 °C.

The relative densities of composites containing 5 to 20 vol % whiskers (400 mesh) as a function of sintering time at 1800 °C are plotted in Fig. 5. At that temperature, the composites needed about 60 minutes to achieve densification, especially for those specimens with higher whisker loadings (15 & 20 vol %). Further increasing in sintering time up to 90 minutes yielded no improvement in density, except for the 5 vol % loading. Thus, the sintering process for $Al_2O_3$-$B_4C$ composites was optimized at 1800 °C for 60 minutes in a graphite tube furnace.

## 3.3. $B_4C$ whisker size

The sintered densities of $Al_2O_3$-$B_4C$ composites at 1800 °C for 1 hour as a function of whisker content at five size fractions are compared in Fig. 6. The densities of the composites decreased with increasing volume fraction of $B_4C$ for each size fraction. However, all of the specimens were sintered to higher than 94% of theoretical density. In general, those fractions with fine inclusion size (−400 mesh, 325 + 400 mesh, 230 + 325 mesh) exhibited better density results than those more coarse inclusions (170 + 200 mesh, 200 + 230 mesh). It is well known that a homogenous packing is easier to be achieved between particles that have similar sizes and densities. In the present system, however, $B_4C$ whiskers are a hundred to a thousand times larger than the $Al_2O_3$ powder particles. Green body homogeneity decreases with an increase in whisker size. As a result, the composites reinforced with coarse whiskers exhibited lower sintered densities.

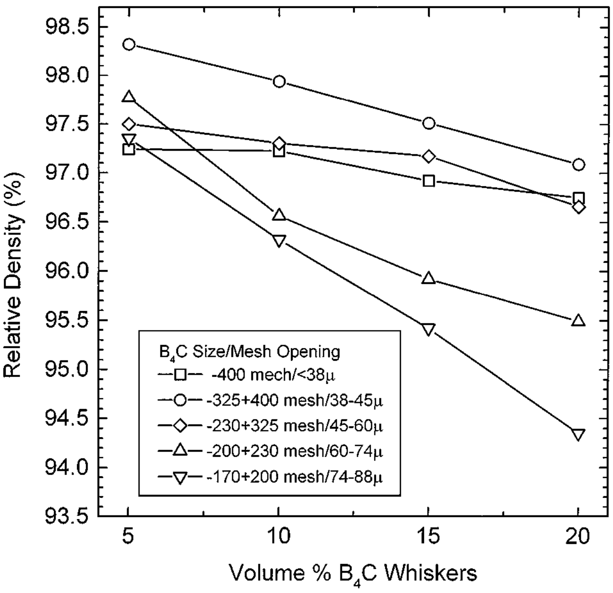


*Figure 6* Variation of relative density with volume % $B_4C$ at different size fractions.

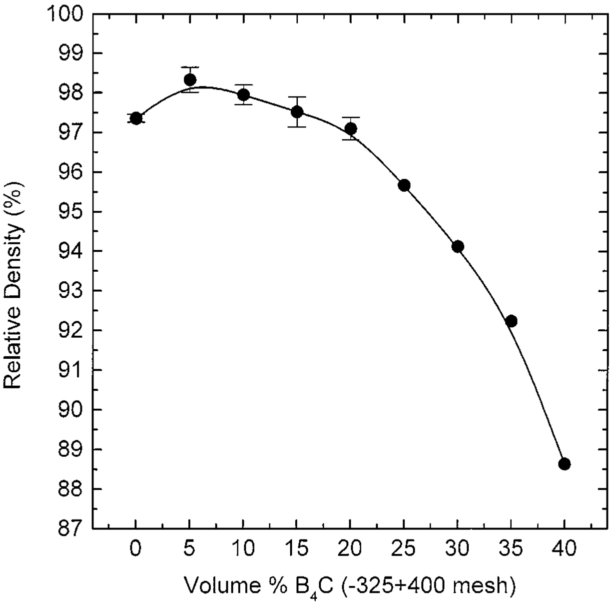


*Figure 7* Sintered density of $Al_2O_3$-$B_4C$ composites as a function of volume % $B_4C$ whiskers.

Another observed effect in Fig. 6 is that the composites containing a small, narrow size distribution (−325 + 400 mesh) yielded higher densities than those with wider distribution (−400 mesh and 230 + 325 mesh) or larger size. This agrees with the findings of previous studies involving the sintering of $Al_2O_3$-$TiB_2$ composites [13].

## 3.4. Densification

Because of the superior sinterability of the composites with the $B_4C$ size fraction of −325 + 400 mesh, composites containing 0 to 40 vol % whiskers at this size range were sintered at 1800 °C for 1 hour, and their density results were plotted in Fig. 7. The relative densities increased with whisker addition from 97% (without $B_4C$) to 98% (5 to 15 vol % $B_4C$) and remained at 89% for 40 vol % whisker loading. Compared to the $Al_2O_3$-$B_4C$ particle composites sintered at 1850 °C by Jung and Kim [11], the present $Al_2O_3$-$B_4C$ whisker composites achieved higher densities, although they were sintered at lower temperature. The density results from both studies suggested that small additions of boron carbide act as a sintering aid promoting densification. Jung and Kim [11] attributed this improved densification to the grain-boundary pinning effect of $B_4C$ particles which had an average diameter of 1 $\mu$m. However, $B_4C$ whiskers used in the present investigation had a mean size of 40 $\mu$m which were too large to prevent grains from growing. The microstructure examination showed no difference in grain size between specimens with and without whiskers. Since small boron carbide whisker additions increased the density of the alumina matrix beyond its density without additions while leaving the grain size unchanged it can be concluded that they act as a sintering aid to alumina densification via a mechanism other than being grain-growth inhibitors.

## 3.5. Characterization

Fig. 8 exhibits the X-ray diffraction patterns of $Al_2O_3$-20 vol % $B_4C$ whisker composites sintered at 1800 °C. All detectable diffraction peaks correspond to those of either $Al_2O_3$ or $B_4C$, except that at 26.7 which indicates the existence of a third phase. In the B-C-Al and $B_4C$-Al cermet systems, several reaction products such as $AlB_2$, $Al_4C_3$, $AlB_{12}C_2$ and $AlB_{24}C_4$ have been detected by XRD [14]. However, none of them matches the X-ray pattern of Fig. 8, which verifies the lack of reaction between the $Al_2O_3$ and $B_4C$ phase. Further examination revealed that the peak at 26.7 belongs to graphite which resulted from the high temperature whisker manufacturing process. It is speculated that the graphite may help the densification of the $Al_2O_3$-$B_4C$ composites by reducing the friction between the matrix and the whiskers although this mechanism is not clearly understood.

Fig. 9 shows SEM fracture surfaces of the $Al_2O_3$-$B_4C$ ceramics containing 0–20 vol % whiskers (325 + 400 mesh), sintered at 1800 °C for 60 minutes in the graphite tube furnace. The alumina specimen has an average grain size of about 30 $\mu$m which is similar to that of the alumina sample sintered at 1850 °C by Jung and Kim [11]. With the addition of 5 to 20 vol % $B_4C$ whiskers, no change in grain size was observed in the composites. The whiskers were too big to prevent grain growth. In general, the $B_4C$ whiskers were uniformly distributed in the alumina matrix, and their aspect ratios were unchanged by the mill mixing in the fabrication process.

## 3.6. Fracture toughness

A plot of fracture toughness as a function of volume % whiskers of the size fraction −325 + 400 mesh using the CNSB method is given in Fig. 10. With increased additions of $B_4C$, the fracture toughness increased rapidly and then leveled off at 6.2 $MPa \cdot m^{1/2}$. The great improvement in toughness at small whisker loadings (5 & 10 vol %) was associated with the $B_4C$ reinforcements. $B_4C$ whisker loadings higher than 10% did not further

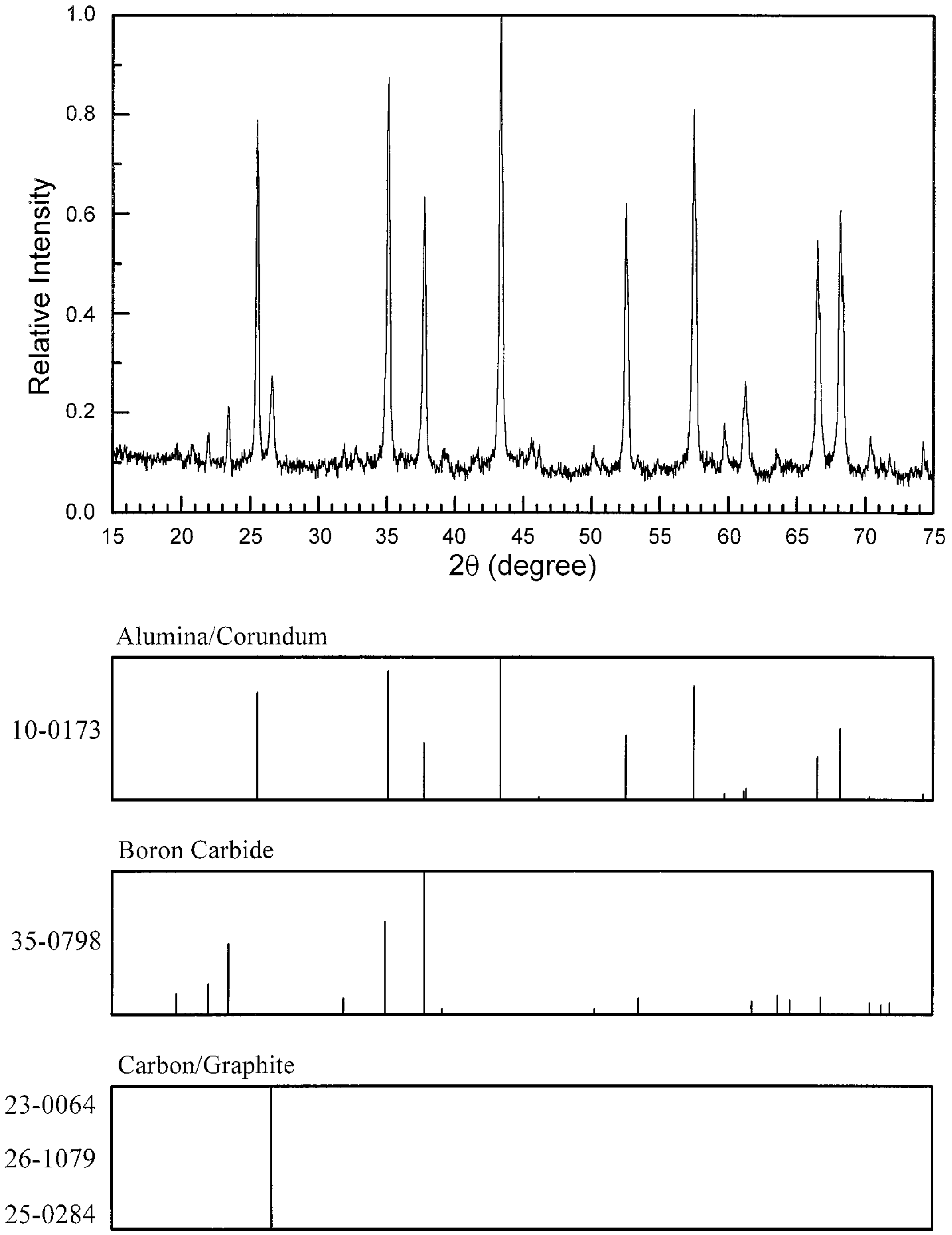
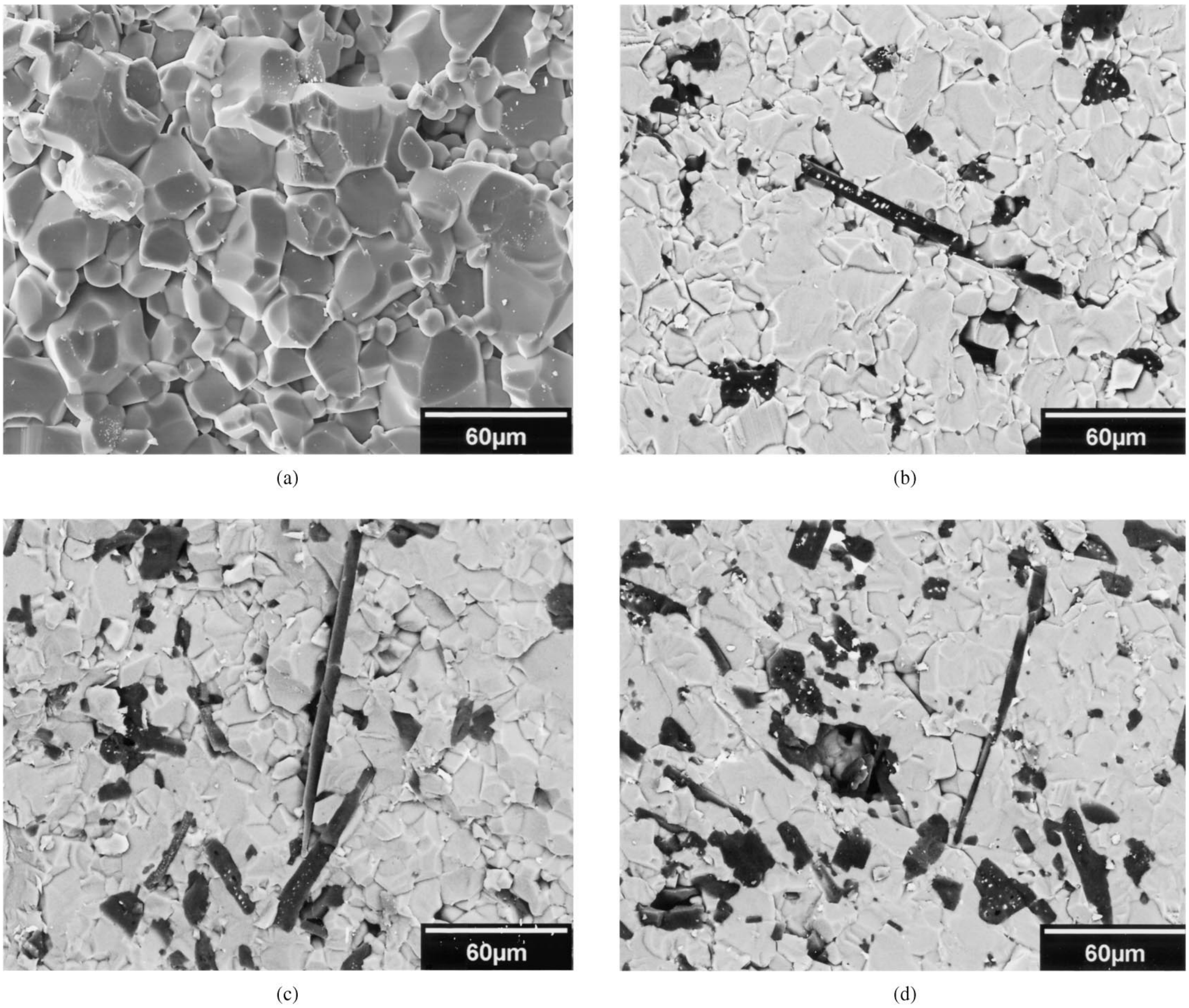


*Figure 8* X-ray diffraction pattern of an $Al_2O_3$-20 vol % $B_4C$ composite sintered at 1800 °C.

increase the fracture toughness because of the density drop shown in Fig. 7. In general, the $B_4C$ whisker composites are more tough than the $Al_2O_3$-$B_4C$ particle composites, where a maximum toughness of 4 $MPa \cdot m^{1/2}$ was reported [11]. The improved toughening effect in the present study is a result of the more dense microstructure, higher aspect ratio of inclusions and the lower sintering temperature which produced weaker bonding between the matrix and the second phase. The more dense microstructure is a result of the experimental procedure and the processing environment which produced high green densities with uniform inclusion dispersions.

Comparison of these pressureless sintered composite fracture toughness values with those obtained previously by hot pressing [8] should be made. At 5 vol % whisker loading the fracture toughness was the same, just above 5.5 $MPa \cdot m^{1/2}$. At higher loadings the densities in the present study gradually decreased while the hot-pressed composites remained >98% of theoretical. The maximum fracture toughness by pressureless sintering of 6.2 $MPa \cdot m^{1/2}$ was achieved at only 10 vol % loading and did not drop as long as the density remained above 97%. The hot-pressed composites reached a maximum of 7.5 $MPa \cdot m^{1/2}$ at 15 vol % loading [8] and remained above 7.0 $MPa \cdot m^{1/2}$ up to 30 vol % loading because the density did not drop off.

The Modulus-of-Rupture, MOR, flexural strength of these composites did not increase over that of the matrix



(a) (b) (c) (d)

*Figure 9* Scanning electron micrographs of $Al_2O_3$-$B_4C$ ceramics sintered at 1800 °C for 1 h with (a) 0, in the secondary electron mode, and (b) 5, (c) 10, and (d) 20 vol % $B_4C$, in the back scattered mode.

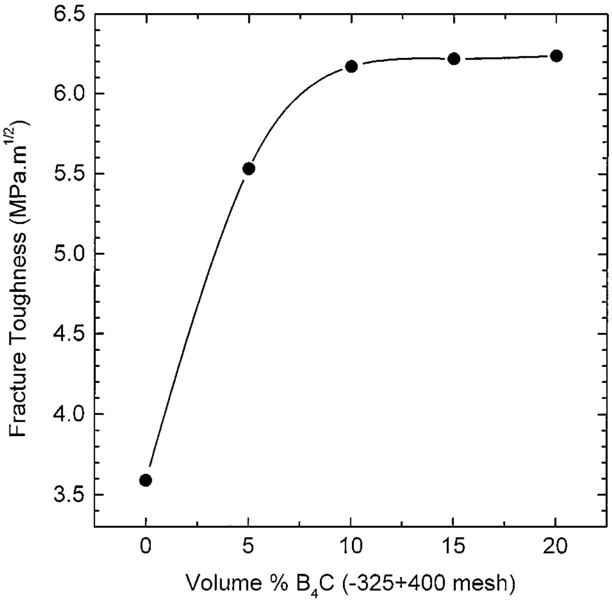


*Figure 10* Variation of CNSB fracture toughness with volume % $B_4C$ for sintered $Al_2O_3$-$B_4C$ composites.

alone. MORs for composites with 15 vol % whiskers overlapped those for alumina without additions. The mean MOR for 15 vol % composites was 210 MPa while for alumina was 240 MPa.

## 4. Conclusions

Boron carbide whisker reinforced alumina matrix composites have been pressureless sintered to high density, avoiding the cost and size limitations of hot pressing. Dense composite specimens were produced at 1800 °C for 60 minutes, sintered in low oxygen partial pressure in a graphite furnace. The composites containing relatively small whiskers with a narrow size distribution ($-325 + 400$ mesh) were determined to yield better densification results. The maximum value of relative densities was 98%, 97%, 94% and 89% at 10, 20, 30 and 40 vol % $B_4C$ whiskers, respectively. Additions of $B_4C$ proved to be a sintering aid to the densification via an unknown mechanism. An increased fracture toughness up to 6.2 $MPa \cdot m^{1/2}$ was achieved in the composites containing 10–20 vol % $B_4C$ whiskers.

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