JOURNAL OF MATERIALS SCIENCE 21 (1986) 1448–1456

Sintering behaviour and properties of SiCAlON ceramics

JOW-LAY HUANG, ANDREW C. HURFORD, RAYMOND A. CUTLER
Ceramatec Inc, 163 West 1700 South, Salt Lake City, Utah 84115, USA
ANIL V. VIRKAR
Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA

Silicon carbide (SiC), aluminium oxycarbide (Al_2OC), and aluminium nitride (AlN) all have the same wurtzite crystal structure and can be processed so as to form SiCAlON, an acronym for the solid solution. This paper describes processing of SiC–Al_2OC ceramics by pressureless reactive sintering and gives mechanical property data on the same. Experiments showed that densification occurred by a liquid-phase sintering mechanism. Both alpha and beta SiC up to a particle size of 5 μm were used to form the solid solution, boron additions were not necessary to promote densification, and densities greater than 97% of the theoretical were achieved by pressureless sintering. SiC–Al_2OC ceramics, containing minor amounts of AlN, were fabricated from conventional raw materials. Phase identification by X-ray diffraction and metallography showed that the materials consisted of two phases: SiCAlON and SiC. Mechanical property data were obtained on pressureless sintered and hot-pressed materials. Hot-pressed materials had room-temperature strengths in excess of 600 MPa, hardness greater than 25 GPa, and fracture toughness greater than 4 MPa $m^{-1/2}$. Pressureless sintered bars had bend strengths in excess of 300 MPa.

1. Introduction

Recent advances in the synthesis, fabrication, and densification of silicon-based ceramics make them attractive candidates (as compared to oxide-based ceramics) for low-temperature applications requiring improved wear or chemical resistance. The high-temperature oxidation resistance and strength retention of SiC and Si_3N_4 have made them leading candidates for heat engines and other structural applications. Prochazka's [1] sintering of beta-SiC followed by the densification of alpha-SiC [2], both using boron and carbon additions, have made the mass production of high-temperature wear-resistant ceramics having complex shapes possible. Boecker *et al.* [3] showed that aluminium (or aluminium and carbon) additions can be used to pressureless sinter SiC. Recent work by Tanaka *et al.* [4] confirmed the earlier finding of Boecker *et al.* and demonstrated that the aluminium and boron additions result in fine-grained ceramics with strength retention to 1600° C. The pressureless sintering of SiC by boron and carbon additions, and aluminium and carbon (or aluminium, boron and carbon) additions, require submicrometre SiC powders (surface areas greater than $10\,m^2\,g^{-1}$). A method to pressureless sinter relatively coarse (1 to 5 μm) SiC (surface areas less than $2\,m^2\,g^{-1}$) would decrease the processing costs, an important consideration for the mass production of silicon-based ceramics.

Oyama and Kamigaito [5] and Jack [6] discovered that aluminium and oxygen can replace silicon and nitrogen in the silicon nitride lattice. This family of ceramics is commonly referred to as "SiAlON" ceramics, the letters in the acronym are taken from the chemical abbreviation for the elements in the solid solution (i.e. silicon, aluminium, oxygen and nitrogen). SiAlON ceramics, although introduced much later than SiC and Si_3N_4, are being used as cutting tools and wear parts, and are the most prevalent silicon-based ceramics used today. The combination of good physical properties and ease of processing (good sinterability due to the liquid phase) is the main reason SiAlON ceramics have been commercialized.

Erwin [7] found that a solid solution between SiC and AlN was possible when processing occurred above 1800° C. Cutler and Miller [8] reported that a complete solid solution exists between alpha-phase SiC (2H polytype), AlN, and Al_2OC. This family of new materials was named using the acronym SiCAlON [9], in analogy to the SiAlON system. SiC, AlN and Al_2OC all exhibit the same hexagonal wurtzite structure and have similar lattice parameters.

Subsequent studies [10–13] were directed at SiC–AlN solid solutions. Rafaniello and co-workers [10–12] found that properties could be engineered by varying the composition. Microhardness, thermal expansion and Young's modulus were found to vary linearly with changes in composition. The creep resistance and fracture toughness were enhanced by additions of AlN to SiC. Room-temperature thermal conductivity decreased, as predicted, due to the formation of a solid solution. Experiments showed that a complete solid solution exists at 2100° C between 5 and 100 wt % AlN.

0022–2461/86 $03.00 + .12

TABLE I Raw materials characterization

Composition	Manufacturer	Trade name	Surface area ($m^2 g^{-1}$)	Purity (%)
Alpha-SiC	Carborundum	1500 grit	0.6	> 99
Alpha-SiC	Starck	A-10	13–17	> 98
Boron-doped alpha-SiC	Starck	AD-10	13–17	98
Beta-SiC	Starck	B-10	13–17	> 98
Boron-doped beta SiC	Starck	BD-10	13-17	98
Beta-SiC	Ibiden	Betarundum	16	> 99
Al_2O_3	Reynolds	HP-DBM	6–8	99.95
Al_2O_3	Baikowski	CR-30	30	99.99
Al_4C_3	Cerac	A-1010	– 325 mesh	99
Al	Cerac	1415	1 to 5 μm	99.5
C	Cabot	Mogul L	–	–
C	Gulf	Acetylene Black	64	99.5

Ruh and Zangvil [13] demonstrated that SiCAlON could be made by reacting commercial powders instead of the intimate mixture of submicrometre powders used in the work at the University of Utah [8–12].

The major limitation of work in the SiC–AlN system was that attempts to pressureless sinter the composites were unsuccessful and processing was expensive, requiring hot pressing. Recent work by Lessing *et al.* [14] has shown that it is possible to sinter SiC–Al_2OC ceramics to closed porosity without applied pressure. The purpose of this paper is to report on properties of SiCAlON ceramics which can be processed by pressureless sintering. It will be shown that densification occurs by a liquid-phase sintering mechanism, aided by an eutectic between Al_2O_3 and Al_4O_4C, which is also believed to be responsible for the sintering of SiC with minor additions of Al and C.

2. Experimental procedures

The raw materials used to make SiCAlON ceramics are listed in Table I with nomial properties as supplied by manufacturers. Homogeneous powders were prepared by ball milling the individual constituents in a polyethylene mill for 8 h using Al_2O_3 media in isopropanol or by vibratory milling for 15 h. The powders were dried in air and screened – 40 mesh. Disk or bar-shaped specimens used for sintering studies were formed by uniaxially pressing at 35 MPa, followed by isostatic pressing at 200 MPa. Sintering experiments were performed in a contained environment [15] within a resistance-heated graphite heating element furnace at temperatures between 1800 and 2150° C under $1\,l\,min^{-1}$ N_2 gas. Hot pressing was performed at temperatures between 1800 and 2000° C at pressures of 35 MPa under nitrogen gas.

X-ray diffraction (XRD) was performed using a diffractometer with Cu*Kα* radiation. The density of sintered samples was determined using water displacement. Four-point bend tests were performed on a universal testing machine (Model 1123, Instron Corp, Canton, Massachusetts, USA) with an inner span of 9.5 mm and an outer span of 31.8 mm at a crosshead speed of $0.5\,mm\,min^{-1}$. Sintered and hot-pressed bar dimensions were approximately 4 mm × 10 mm × 50 mm and 5 mm × 5 mm × 40 mm, respectively. All bars were diamond ground to a 30 μm finish before testing. Broken test bars were polished to a 1 μm diamond finish and Vicker's hardness measurements were made at loads of 50 to 100 N using a 136° diamond pyramid indenter. Indentation toughness measurements were made based on an equation proposed by Anstis *et al.* [16]. Grain size was determined by SEM on fractured surfaces or after etching polished specimens in boiling Murakami's etch for 25 min.

3. Results and discussion

3.1. Sintering mechanism

Initial experimentation was directed at making Al_2OC and reacting the aluminium oxycarbide with SiC. Two approaches for making Al_2OC were tried:

$$4Al + 3C + Al_2O_3 \rightarrow 3Al_2OC \qquad (1)$$

$$Al_4C_3 + Al_2O_3 \rightarrow 3Al_2OC \qquad (2)$$

Both reaction paths were investigated by sintering precompacted disks at temperatures between 1800 and 1950° C in argon. There was no shrinkage at temperatures up to 1840° C, but significant shrinkage (10%) and densification occurred between 1850 and 1875° C, in good agreement with eutectic temperatures reported by Foster *et al.* (1840° C) [17], Lihrmann *et al.* (1840° C) [18, 19], and Sandberg (1905° C) [20] for the Al_2O_3–Al_4C_3 pseudobinary phase diagram. Although there are differences in the phase diagrams (i.e. Lihrmann *et al.* report that Al_2OC decomposes to Al_4O_4C and Al_4C_3 below 1715° C under equilibrium conditions, whereas no Al_4O_4C was found upon rapid cooling, while Sandberg found no Al_2OC) the eutectic is known to occur at 10 to 12 mol % Al_4C_3. On the basis of the Al_2O_3–Al_4C_3 pseudobinary, the presence of three phases as revealed by XRD patterns, suggests equilibrium had not been established. Sintering for short times (10 min) promoted the formation of Al_4O_4C, Al_2OC and Al_4C_3. Al_4O_4C and Al_2OC were observed at intermediate times, and Al_4C_3 was the only phase seen at long sintering holds (60 min), indicating that the highly reducing environment of the furnace carbothermally reduces Al_2O_3.

Sandberg [20] claimed that Al_2OC is not a stable phase in the pseudobinary and was only seen by

Foster *et al.* [17] due to a leak in the furnace allowing AlN to stabilize the Al_2OC–AlN solid solution. Although it will be shown that AlN, SiC, and other isomorphous compounds stabilize the formation of Al_2OC, the present data clearly show that both oxycarbides exist when heated in argon (nitrogen content was less than 0.1%) in agreement with the data of Lihrmann [18]. Cox and Pidgeon [21] claimed that Al_2OC formation is not part of the Al_2O_3 reduction process. Al_2OC peaks in XRD patterns were stronger than Al_4C_3 at short times showing that the carbothermal reduction of Al_2O_3 occurs as suggested below:

$$2Al_2O_3 + 3C \rightleftharpoons Al_4O_4C + 2CO\uparrow \qquad (3)$$

$$Al_4O_4C + 3C \rightleftharpoons 2Al_2OC + 2CO\uparrow \qquad (4)$$

$$\underline{2Al_2OC + 3C \rightleftharpoons Al_4C_3 + 2CO\uparrow} \qquad (5)$$

$$2Al_2O_3 + 9C \rightleftharpoons Al_4C_3 + 6CO\uparrow \qquad (6)$$

It can therefore be seen that Al_4O_4C and Al_2OC will exist over a given range of CO partial pressures.

The most important result of the above experimentation was the confirmation of a liquid phase in the Al–O–C ternary system. Thus, the sintering which occurs when SiC or AlN are present, as observed by Lessing *et al.* [14], most likely occurs as a result of the liquid phase. Additionally, it was observed that Al_2OC is formed much more readily in a nitrogen environment than in argon (presumably due to the stabilization of Al_2OC by AlN as reported by Sandberg [20] and Lihrmann [18]), and all subsequent experiments were performed in nitrogen.

TABLE II Compositions used in sintering studies

Code	Composition (wt %)			% SiC in SiC Al_2OC (mol %)
	SiC	Al_2O_3	Al_4C_3	
A	100.0	0.0	0.0	100.0
B	81.5	7.7	10.8	90.0
C	66.1	14.0	19.9	80.0
D	50.7	19.7	29.6	70.0
E	42.3	23.9	33.8	60.0
F	32.8	27.9	39.3	50.0

SiCAlON ceramics were synthesized (during the sintering process) using commercial sources of raw materials, with Al_2O_3 being the primary source of oxygen for the solid solution as shown in Reactions 7 and 8 below:

$$x(SiC) + z(4Al + Al_2O_3 + 3C) \rightarrow xSiC \cdot 3z(Al_2OC) \qquad (7)$$

$$x(SiC) + z(Al_2O_3 + Al_4C_3) \rightarrow xSiC \cdot 3z(Al_2OC) \qquad (8)$$

In order to demonstrate that the eutectic in the Al_2O_3–Al_4C_3 pseudobinary phase diagram is responsible for liquid-phase sintering, a variety of compositions ranging between 50 and 100 mol % SiC were prepared based on Reaction 8, with nominal compositions as shown in Table II. The samples reacted with

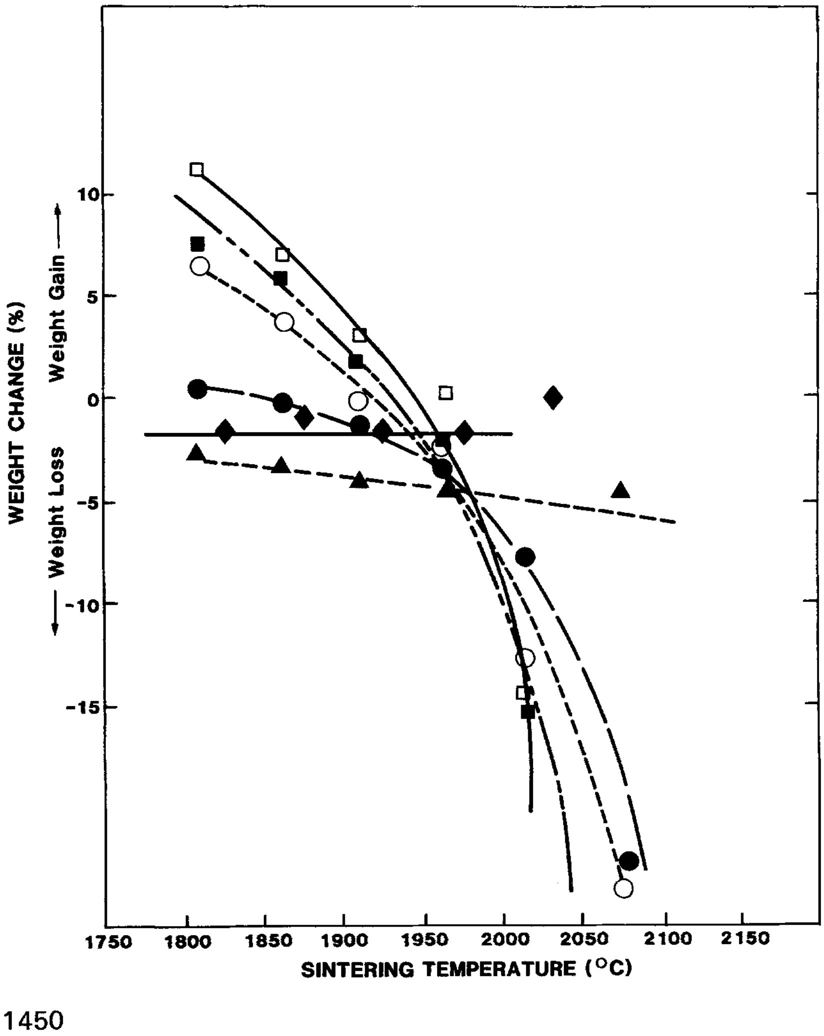

Figure 1 Weight change as a function of temperature for SiCAlON with varying amounts of Al_2OC. □, 50 mol % SiC; ■, 60 mol % SiC; ○, 70 mol SiC; ● 80 mol % SiC; ▲, 90 mol % SiC; ♦, 100 mol % SiC.

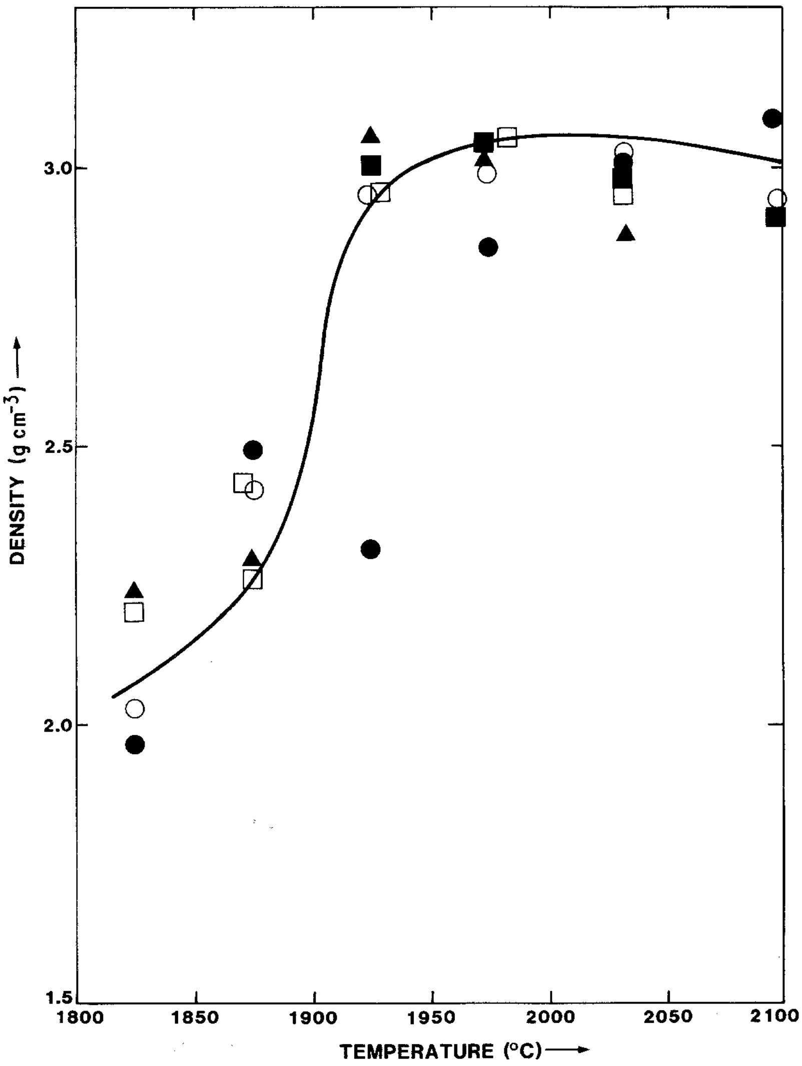

Figure 2 Densification of SiCAlON ceramics as a function of sintering temperature. Note rapid densification between 1850 and 1950° C. ●, 90 mol % SiC; ○, 80 mol % SiC; ■, 70 mol % SiC; □, 60 mol % SiC; ▲, 50 mol % SiC.

the graphite container [15] and resulted in a significant weight gain during heating, followed by weight loss which increased with temperature above 1800° C (see Fig. 1) due to the carbothermal reduction of alumina and presumably due to a high vapour pressure of the liquid phase. Research in progress will show whether it is possible to control stoichiometry by controlling the partial pressure of CO.

Table III shows that significant shrinkage and densification occurred for all samples forming the solid solution (note that SiC can be densified by various dopant additions as discussed above). Rapid densification occurred between 1850 and 1950° C, as predicted by the eutectic temperature for compositions which formed the solid solution (see Fig. 2).

When the same compositions were sintered under identical conditions, except without containment in a graphite crucible [15], minimal shrinkage and no densification occurred, while weight losses of greater than 30% were recorded. The graphite crucible therefore limits decomposition and promotes the sintering.

TABLE III Sintering conditions and densification of SiCAlON ceramics

Code	Sintering conditions		Shrinkage (%)	Density (g cm^{-3})
	Temp. (° C)	Time at temp. (min)		
B	1925	60	14.8	3.12
C	2050	5	14.2	3.15
D	2050	5	14.2	3.15
E	2050	5	16.3	3.14
F	1925	60	13.0	3.07

With the presence of a significant amount of liquid phase, one should not be limited to submicrometre powders in order to promote sintering. Fig. 3 shows that this is indeed the case as 1500 grit SiC incorporated into Reaction 8 sinters readily aided by the liquid phase, whereas boron (or boron and carbon additions) do not promote densification of larger particles. This result also strongly suggests that the pressurelesss sintering of submicrometre SiC aided by small additions of aluminium and carbon (or aluminium, carbon and boron) [3, 4] is not due to an alumina–calcia–silicate liquid phase as suggested by Lange [22], but is rather due to the aluminium oxycarbide eutectic liquid which reacts with SiC to form SiCAlON. Recent results by Sherman [23], using Auger spectroscopy, showed that the grain-boundary phase of hot-pressed SiC containing aluminium additions consisted of silicon, carbon, aluminium, oxygen, nitrogen and calcium. The absence of SiO_2 from the grain-boundary phase showed that it was not a silicate [23], and the present work gives strong support for the formation of SiCAlON.

Experimentation with a variety of powders showed

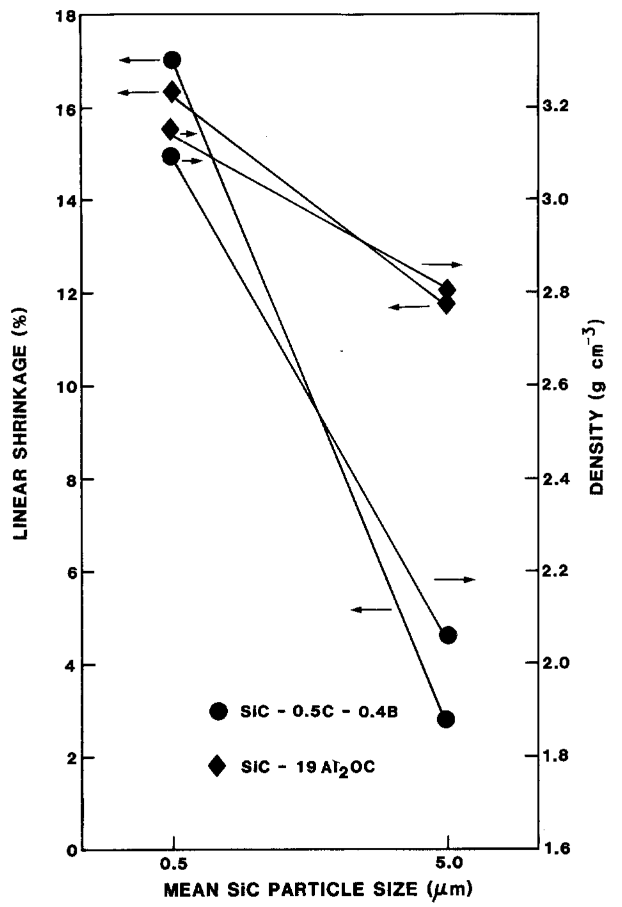

Figure 3 Effect of SiC particle size on densification of SiC–10 mol % Al_2OC and SiC containing boron and carbon as sintering aids. Note that liquid phase in SiCAlON ceramics aid sintering of larger particles.

that pressureless sintering to greater than 97% theoretical is possible using either alpha- or beta-SiC. Densification occurs without boron or carbon additions although boron additions influence the formation of 4H polytype over 6H polytype when starting with alpha-SiC. Samples made via reactions 7 and 8 sintered in an identical manner with similar microstructures.

As opposed to the earlier work [14] which showed that single-phase materials could be made by starting with ultra-fine SiC (made by the carbothermal reduction of silica), two distinct phases, SiCAlON solid solution and SiC, were observed by XRD in the majority of samples when commercially available SiC was used. SiC remains cubic (beta polytype) after sintering at 2050° C for 1 h. If alpha-SiC is used as a starting material, densification occurs and alpha peaks (primarily 4H) are observed in addition to the solid solution peaks. In some cases, three phases were evident in the microstructures, which are believed to be SiC, Si-rich SiCAlON, and Al-rich SiCAlON. Work to characterize the chemistry of each phase is in progress. The alternative of providing oxygen in the form of silica has been reported elsewhere [24]. SiC and AlN stabilize the solid solution, as no Al_2O_3, Al_4O_4C, Al_2OC, or Al_4C_3 were observed in X-ray diffraction patterns.

3.2. Mechanical properties

Four-point bend strength, hardness, and fracture toughness were the response variables used to assess the room-temperature performance of SiCAlON ceramics. Fig. 4 shows bend strength data for pressureless

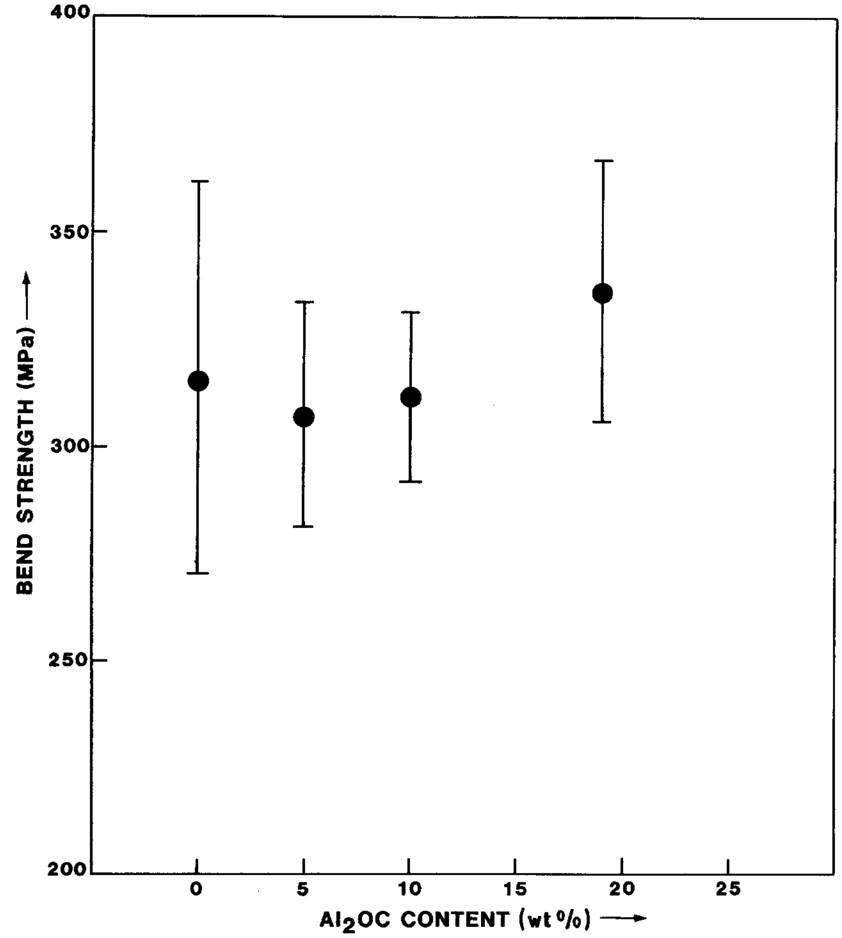

Figure 4 Bend strength of pressureless sintered SiCAlON as a function of Al_2OC content.

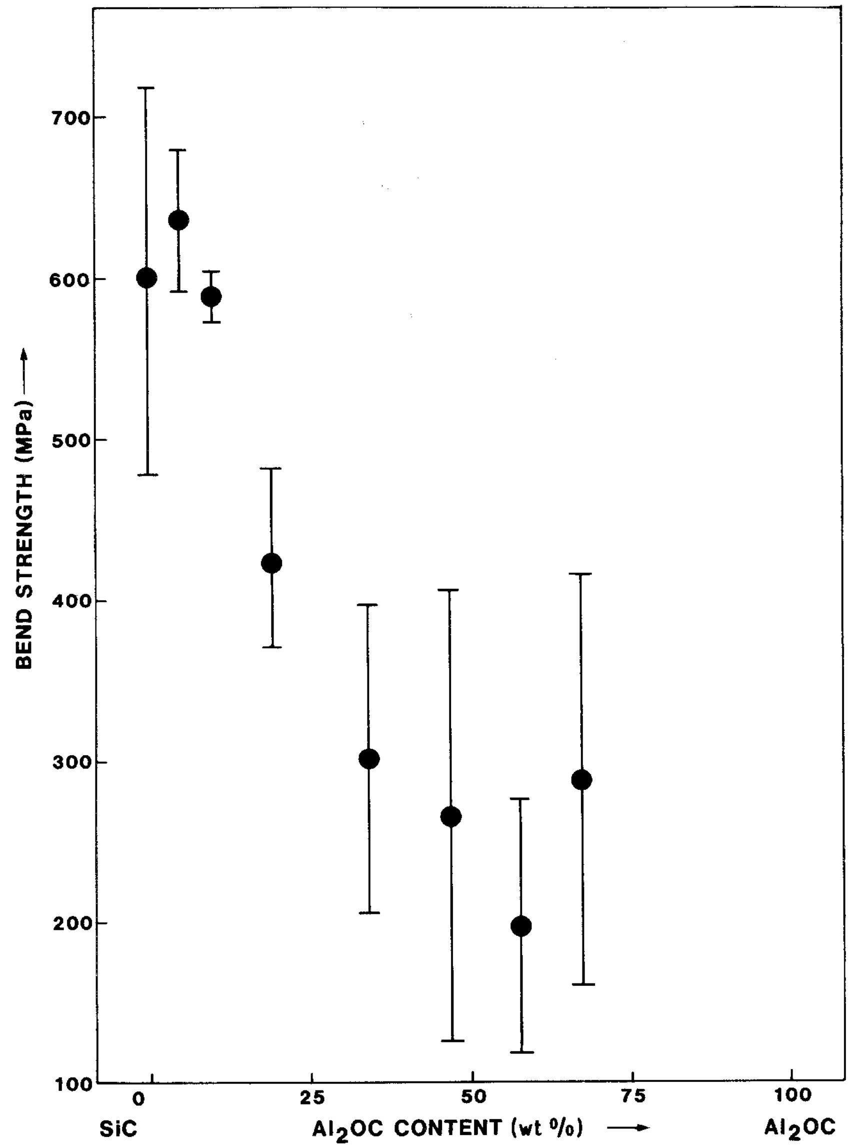

Figure 5 Bend strength of hot-pressed SiCAlON as a function of Al_2OC content. Note that compositions with greater than 10% Al_2OC contained free carbon, which may have contributed to low strength.

sintered bars made by Reaction 8 using undoped beta-silicon carbide powder in comparison to data on commercially available alpha-SiC (doped with boron and carbon) tested in the same manner. Even at relatively low Al_2OC contents (i.e. small volume fractions of the liquid phase), densification occurred. Strengths were independent of Al_2OC content, although it is believed that through improved processing much higher strengths can be achieved by eliminating large voids. As mentioned previously, no densification occurred when the undoped SiC submicrometre powder used in these compositions was heated to 2100° C.

In order to determine what ultimate properties might be achieved by improved processing to eliminate large flaws, hot pressing or hot isostatic pressing can be used to increase the density and close large voids. Strength data for hot-pressed SiCAlON materials are shown in Fig. 5 along with hot pressed SiC containing 0.5 wt % boron and carbon. Hot pressed samples with Al_2OC content greater than 10 wt % contained some Al_2O_3 and carbon. The decrease in strength with increasing Al_2OC may be due to free carbon. By contrast, in the case of sintered SiCAlON samples, the strength was independent of Al_2OC content. It thus appears that if decomposition of Al_2OC to Al_2O_3 and carbon can be prevented and large flaws are eliminated, SiCAlON ceramics should exhibit strengths comparable to monolithic SiC. Since proper compositional or atmospheric control will eliminate deleterious phases, such as carbon, work in progress will further investigate mechanical properties over a broad range of stoichiometry.

Scanning electron microscopy (SEM) was used to examine fracture origins in hot-pressed bars. Invariably, fracture initiated from voids located a short distance below the tensile surface, as shown in Fig. 6 for SiC–10 wt % Al_2OC bars. Higher magnification showed that the voids contained plate-like grains as large as 5 to 15 μm (see Fig. 7). Cursory attempts to identify impurities within the voids by energy dispersive spectroscopy (EDS) were not successful. It is possible that the voids were caused by CO evolution during the alumina reduction and the plate-like grains grew by the solution-precipitation of SiC due to the presence of the liquid as SiCAlON was formed. It is important to note that the grain size away from the voids is very fine (less than 1 μm) and uniform, which is in accordance with the findings of other investigators using aluminium as a sintering aid [3, 4] and the previous findings of Rafaniello *et al.* [10–12] in the SiC–AlN system. The plate-like grains in Fig. 7 are an

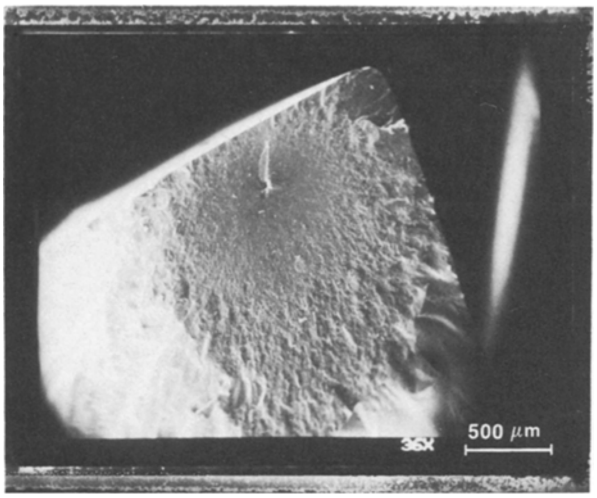

Figure 6 Fracture surface of hot-pressed SiC–10 wt % Al_2OC showing failure from internal void.

order of magnitude smaller than the exaggerated alpha grains often seen in commercial SiC. Intergrannular, transgranular, and mixed mode fracture were observed on fractured samples. It is clear that more detailed characterization of samples is required. Higher magnification transmission electron microscopy is in progress to investigate grain boundaries and phase homogeneity.

Hardness of hot-pressed composites ranged between 18.5 and 15.0 GPa, as shown in Table IV, whereas sintered alpha-SiC, with a density of 97.5% theoretical, had a hardness of 23.3 GPa. As stated earlier, hardness is one of the variables which can be engineered by controlling the composition of SiCAlON ceramics, since SiC is harder than Al_2OC or AlN. Fig. 8 shows fracture toughness data as a function of Al_2OC content. The large error bars are indicative of the problems of determining the toughness using indentation techniques. As expected, there was no significant difference between hot-pressed and sintered samples having the same composition. The significant aspect of Fig. 8 is that it appears that the fracture toughness of SiCAlON ceramics is considerably higher than SiC, which is in agreement with the work of Rafaniello *et al.* [10–12]. Owing to the large error bands for the data in Fig. 8, bulk fracture toughness measurements will be made in subsequent studies. Preliminary microstructures for SiC-rich SiCAlON ceramics, as shown in Fig. 9, were very typical of SiC made with small aluminium additions [3, 4], although the toughness is considerably higher. A pressureless sintered SiC-based ceramic with toughness values comparable to Si_3N_4 would find use in a wide range of applications. As is evident in Table IV, the processing of SiCAlON is sensitive to temperature for the reasons explained earlier and there is little reason to believe that ultimate properties have been obtained.

The excellent room-temperature properties obtained in the present study and the previous results for SiC–AlN ceramics showing good high-temperature properties indicate that SiCAlON ceramics are promising engineering materials. Additionally, recent work [4] with much smaller aluminium, boron and carbon additions shows excellent strength retention to 1600° C. SiC has excellent high-temperature properties and it follows that the SiCAlON–SiC composite formed upon sintering should exhibit good properties if the solid solution has desirable physical propeties. Since the amount of SiC can be controlled by controlling the starting SiC particle size, one should be able to control thermal conductivity by particle size variation.

4. Conclusions

The research demonstrated that SiCAlON ceramics have good room temperature properties. Hot-pressed bars had strengths in excess of 600 MPa, hardness greater than 25 GPa, and fracture toughness greater than 4 MPa $m^{-1/2}$.

A variety of experiments showed that SiC–Al_2OC ceramics sinter via a liquid phase produced by a eutectic in the Al_2O_3–Al_4C_3 pseudobinary phase diagram. Liquid-phase sintering of SiC–Al_2OC resulted in specimens sintered to greater than 97% theoretical density with bend strengths in excess of 300 MPa. Coarse-grained SiC powder, up to a particle size of

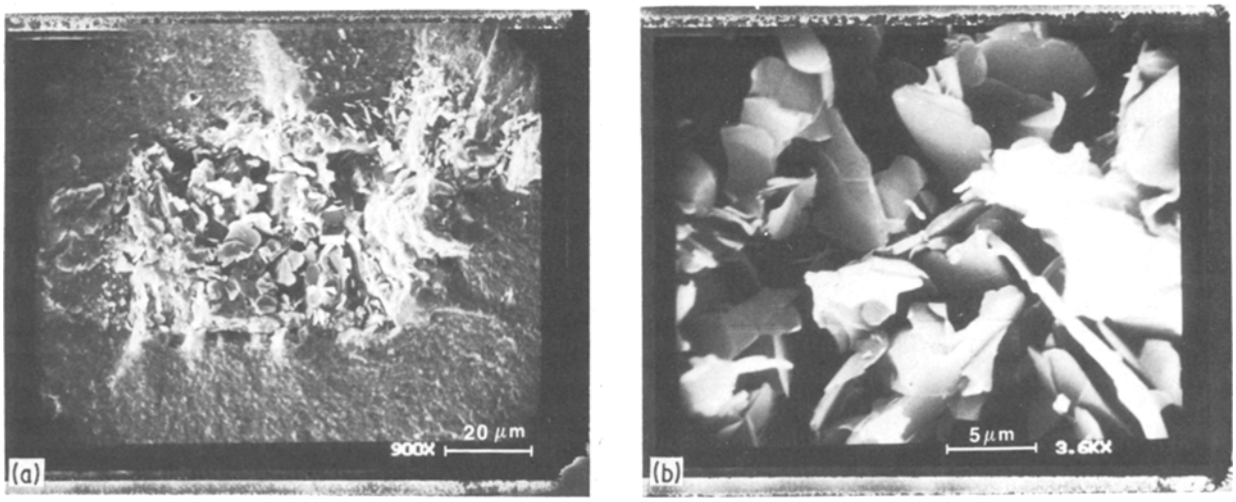

Figure 7 Scanning electron micrograph of internal fracture initiation site from Fig. 6. (1) Void with 5 to 15 μm grains surrounded by fine-grained matrix. (b) tabular grains within the void.

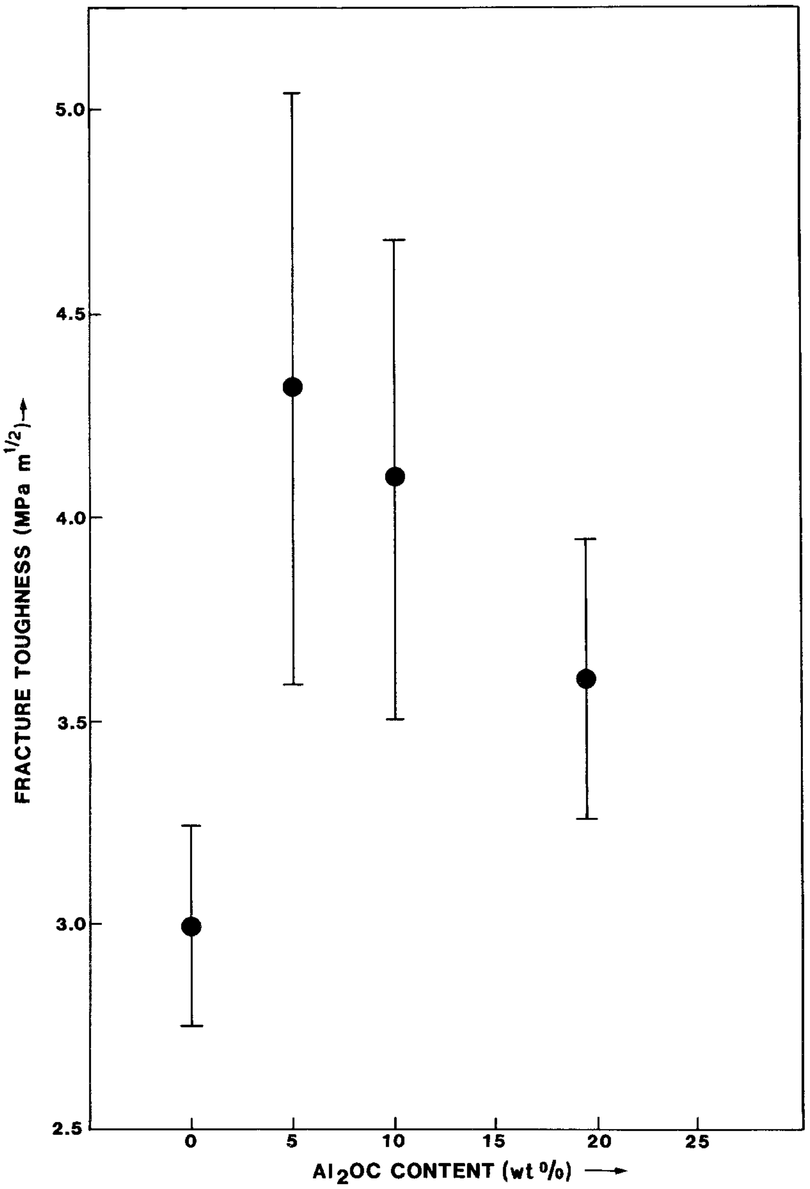

Figure 8 Fracture toughness of SiCAlON ceramics as a function of Al_2OC content, determined by indentation [16].

5 μm, can be sintered without boron and carbon additions due to the presence of a transient liquid phase.

SiC and AlN stabilize Al_2OC, allowing the formation of SiCAlON. X-ray diffraction showed that SiCAlON and SiC phases occur upon sintering commercial powders at temperatures below 2100° C. Both alpha- and beta-SiC can be used as starting materials for the formation of the solid solution. Samples which appear to be single-phase based on XRD, contained two phases, presumably silicon-rich and aluminium-rich solid solutions. Both Al_2O_3 and SiO_2 can be used as oxygen sources to form the solid solution.

Substantial variations in microstructure were seen in SiCAlON ceramics. The sintered materials are generally fine grained, but larger (5 to 15 μm) grains

TABLE IV Physical properties of SiCAlON ceramics

Composition*			Processing Temp. (° C)	Density (g cm^{-3})	σ† (MPa)	H‡ (GPa)	K_{Ic} (MPa m$^{1/2}$)
SiC	Al_2O_3	Al_4C_3					
90.0	4.1§	5.9	1830	3.19	520 ± 90	20.5	4.1
90.0	4.1§	5.9	1950	3.15	290 ± 15	20.3	4.0
90.0	4.1¶	5.9	1830	3.16	542 ± 26	25.0	2.3
90.0	4.1¶	5.9	1950	3.07	295 ± 51	–‖	–‖
95.0	2.1§	2.9	1830	3.16	636 ± 41	21.4	4.3

*Starting composition before hot pressing (wt %).

†Four-point bend stength.

‡Hardness.

§Baikowski grade CR-30.

¶Reynold's grade HP-DBM.

‖No data obtained.

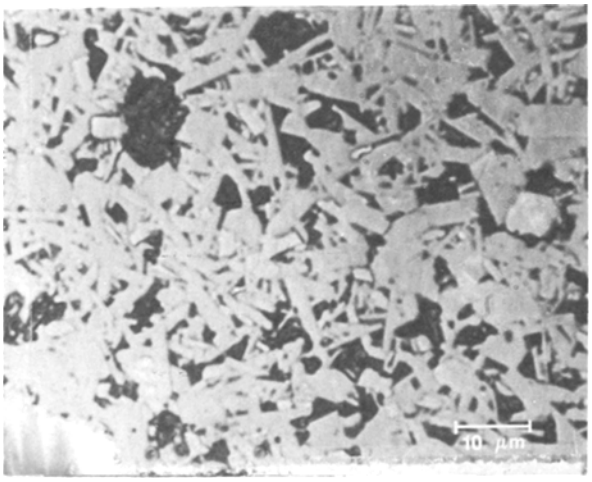

Figure 9 Microstructure of etched SiC–5 wt % Al_2OC hot pressed at 1840° C for 5 min.

were observed at fracture initiation sites. Both equiaxed and tabular grains were seen on etched surfaces depending on the sintering conditions.

Acknowledgements

This work was supported by the US Department of Energy under Contract no. DE-AC03-84ER80191. Discussions with Dr J. M. Lihrmann of Massachusetts Institute of Technology, and D. W. Richerson and Dr P. A. Lessing of Ceramatec are appreciated. The assistance of Y. Pan of Ceramatec is acknowledged.

References

1. S. PROCHAZKA, in "Ceramics for High Performance Applications" edited by J. J. Burke, A. E. Gorum and R. M. Katz (Brook Hill, Massachusetts, 1975) p. 239.
2. J. A. COPPOLA, L. N. HAILEY and C. N. McMURTRY, US Patent 4 124 667, 7 November (1978).
3. W. BOECKER, H. LANDFERMANN and H. HAUSNER, *Powder Met. Int.* **11** (1979) 83.
4. H. TANAKA, Y. INOMATA, K. HARA and H. HASEGAWA, *J. Mater. Sci. Lett.* **4** (1985) 315.
5. Y. OYAMA and O. KAMIGAITO, *Jpn. J. Appl. Phys.* **10** (1971) 1937.
6. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
7. G. ERWIN Jr, US Patent 3 492 153, 27 January (1970).
8. I. B. CUTLER and P. D. MILLER, US Patent 4 141 740, 27 February (1979).
9. I. B. CUTLER, P. D. MILLER, W. RAFANIELLO, H. K. PARK, D. P. THOMPSON and K. H. JACK, *Nature* **275** (1978) 434.
10. W. RAFANIELLO, K. CHO and A. VIRKAR, *J. Mater. Sci.* **16** (1981) 3479.
11. W. RAFANIELLO, M. R. PLICHTA and A. V. VIRKAR, *J. Amer. Ceram. Soc.* **66** (1983) 772.
12. W. RAFANIELLO, PhD dissertation, University of Utah (1984).
13. R. RUH and A. ZANGVIL, *J. Amer. Ceram. Soc.* **65** (1982) 261.
14. P. A. LESSING, A. V. VIRKAR and K. CHO, Fabrication of SiCAlON Ceramics, Ceramatec Report 4283001 (1983).
15. R. A. CUTLER and A. V. VIRKAR, unpublished research.
16. G. R. ANSTIS, P. CHANTIKUL, B. R. LAWN and D. B. MARSHALL, *J. Amer. Ceram. Soc.* **64** (1981) 533.
17. L. M. FOSTER, G. LONG and M. S. HUNTER, *ibid.* **39** (1956) 1.
18. J. M. LIHRMANN, PhD dissertation, Universite Louis Pasteur (1982).
19. Y. LARRERE, B. WILLER, J. M. LIHRMANN and M. DAIRE, *Rev. Int. Hautes Temp. Refract. Fr.* **21** (1984) 3.
20. B. SANDBERG, PhD dissertation, University of Trondheim (1981).
21. J. H. COX and E. M. PIDGEON, *Can. J. Chem.* **41** (1963) 671.
22. F. F. LANGE, *J. Mater. Sci.* **10** (1975) 314.
23. R. SHERMAN, *J. Amer. Ceram. Soc.* **68** (1985) C7.
24. R. A. CUTLER, J. L. HUANG, and A. C. HURFORD, Ceramatec Report 85027001 (1985).

Received 28 August
and accepted 4 October 1985