JOURNAL OF MATERIALS SCIENCE 19 (1984) 1307–1313

# Sinterability, strength and oxidation of alpha silicon carbide powders

SUNIL DUTTA
*NASA Lewis Research Center, Cleveland, Ohio 44135, USA*

Pressureless sintering of commercially available α-SiC powders was investigated at temperatures between 1900 and 2150° C for times of 10 to 240 min under one atmosphere of argon pressure. Alpha-SiC powder containing boron and carbon sintering aids was sinterable at 2150° C for a period of 30 min to a high final density greater than 96 per cent of theoretical. In contrast, a final density only about 80 per cent of theoretical was achieved in α-SiC powder containing aluminium and carbon sintering aids. Room temperature and high temperature (1370° C) flexure strength and oxidation resistance were determined on sintered high density (> 96% of theoretical) α-SiC (boron, carbon) material. Both the strength and the oxidation resistance were found to be equivalent and comparable to those of Carborundum Company sintered α-SiC, which is representative of the current state-of-the-art material.

## 1. Introduction

Pressureless sintering of silicon carbide and silicon nitride is an attractive densification process for producing components from the point of view of cost, volume production, and ability to reproduce complex shapes. However, for sintering to full density, sintering aids are required, which often form a glassy phase at the grain boundaries. In silicon nitride, the glassy phase is responsible for strength loss at high temperature [1, 2]. In silicon carbide, however, very minor strength loss occurs at high temperature [3, 4]. The good strength retention of silicon carbide at high temperature, good oxidation resistance, and the recent improvements in pressureless sintered silicon carbide has increased interest in silicon carbide ceramics. The pressureless sintering of β-SiC was reported by Prochazka [5] at General Electric (GE) several years ago. Recently, the pressureless sintering of α-SiC was reported by Carborundum Company [6]. However, the GE and Carborundum SiC powders are not available commercially. Therefore, the purpose of the present study was to determine the sinterability, strength, and oxidation behaviour of commercially available submicrometre α-SiC powders, and to evaluate their potential for high temperature structural applications.

## 2. Experimental procedure

Three types of α-SiC powder* were employed in this sintering study; Type 1 powder had no pre-mixed sintering aids; Type 2 powder had pre-mixed boron and carbon sintering aids; and Type 3 powder had pre-mixed aluminium and carbon sintering aids.

Prior to sintering, all three powders were cold pressed isostatically at 483 MPa into rectangular bars of 3.5 mm by 7.9 mm by 38.0 mm. The sintering was performed in an Astro furnace at temperatures from 1900 to 2150° C for 10 to 240 min under an argon pressure of one atmosphere.

Sintered specimens were machined into test bars (2.54 cm by 0.64 cm by 0.32 cm) and the surfaces were ground with a 400 grit fine diamond wheel to final surface finish of 8 r.m.s. Density was measured on both as-sintered and machined test bars by the pycnometric method. Microstructural characterization was made by scanning electron microscopy, while phase identification was performed by an X-ray diffraction technique.

Flexural strength tests were conducted by four-

---

*Herman C. Starck, West Berlin, West Germany.

0022–2461/84 $03.00 + .12

TABLE I Analysis of as-received α-SiC powders

| Element | Impurity analysis (p.p.m.) | | |
|---|---|---|---|
| | Type 1<br>α-SiC (100%) | Type 2<br>α-SiC (B, C) | Type 3<br>α-SiC (Al, C) |
| Al | 50 | 140 | 1.2* |
| Ca | 70 | 40 | 20 |
| Fe | 10 | 10 | 40 |
| Ti | 20 | 30 | 50 |
| V | 20 | 20 | 40 |
| B | – | 0.60* | – |
| Free C | 1.66* | 7.31* | 6.10* |
| Surface area (BET) (m$^2$/g$^{-1}$) | 31.47 | 4.19 | 11.38 |

*wt per cent.

point loading with 0.95 cm top and 1.87 cm bottom spans. Testing was conducted at room temperature, 1200 and 1370° C in air, with a cross-head speed of 0.05 cm min$^{-1}$. Fracture surfaces of selected test specimens were examined using scanning electron microscopy.

Oxidation tests were conducted on machined bars of dimensions 2.54 cm by 0.64 cm by 0.32 cm. Test bars were placed on a sintered α-SiC block which was then placed into a pre-heated furnace. The oxidation was continued for a total of 200 h at 1350° C with weight change data recorded at 20 h intervals. Characterization of the oxide scales was performed by X-ray diffraction.

## 3. Results and discussion

### 3.1. Powder characterization

Analyses of the three types of "as-received" α-SiC powders are shown in Table I. All three powders are chemically pure without any major impurities. In Type 2 α-SiC powder, boron and carbon were added deliberately as sintering aids, while aluminium and carbon were added as sintering aids in Type 3 powder. The oxygen contents of the "as-received" powders (Type 1, Type 2 and Type 3 powders) were estimated from an analysis to be 0.375 per cent, 1.14 per cent and 1.04 per cent, respectively. In all three types of powder, only α-SiC phase consisting of 6 H and 4 H polytypes was identified by X-ray diffraction.

The morphologies of the three powders are shown in Fig. 1. Type 1 α-SiC powder (≃ 100%

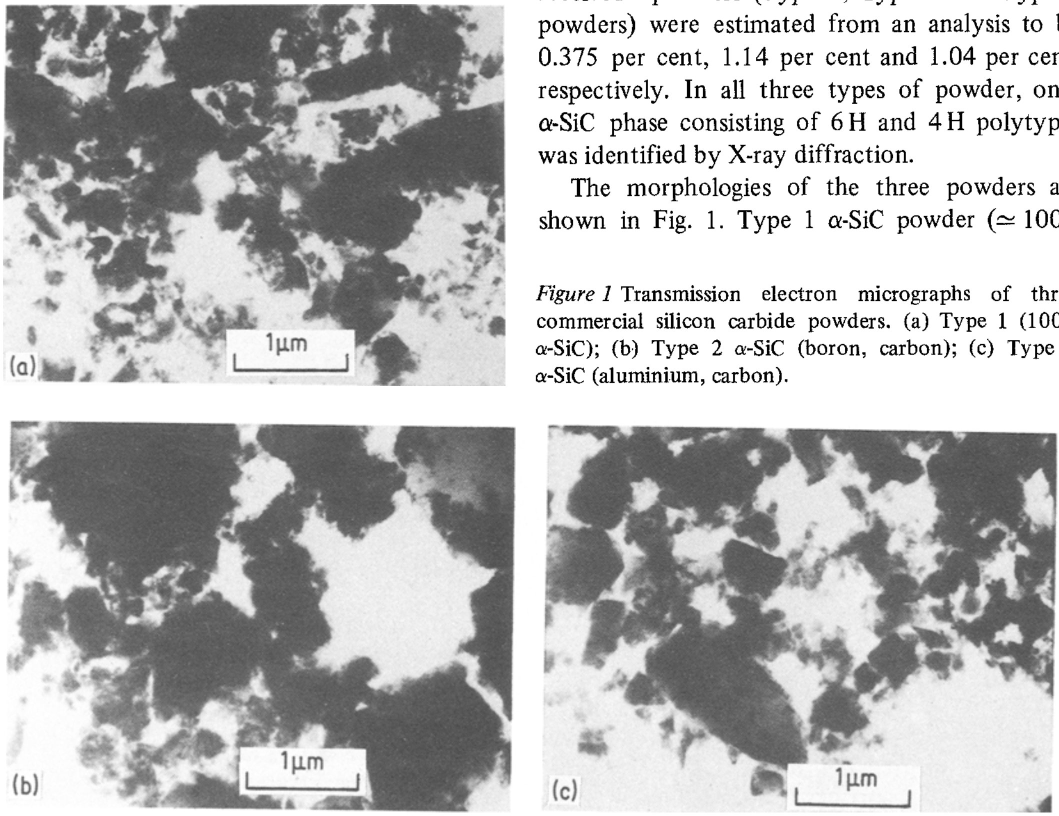


*Figure 1* Transmission electron micrographs of three commercial silicon carbide powders. (a) Type 1 (100% α-SiC); (b) Type 2 α-SiC (boron, carbon); (c) Type 3 α-SiC (aluminium, carbon).

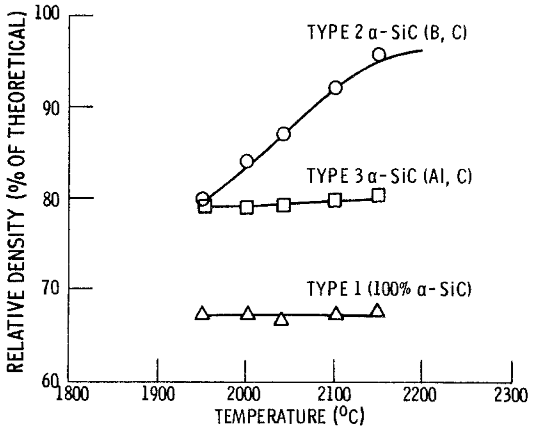


*Figure 2* Relative density of three types of Starck α-SiC powder sintered for 30 minutes at different temperatures.

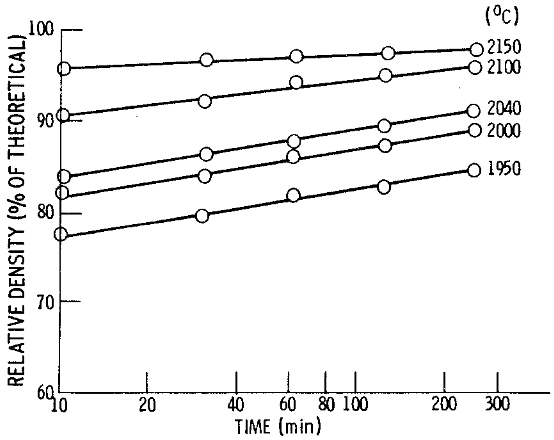


*Figure 3* Isothermal densification of Starck α-SiC powder (boron, carbon) as a function of time.

α-SiC) particles are generally flaky with agglomerates composed of fine particles. Some particles are generally discrete and appear to be angular in shape. In contrast, Type 2 α-SiC (boron, carbon) powder shows excessively agglomerated particles with diameters ranging from 0.02 to 10.0 μm. The morphology of Type 3 α-SiC (aluminium, carbon) powder appears to be somewhat inbetween Type 1 and Type 2 powders with particle diameters ranging from 0.02 to 10.0 μm.

## 3.2. Densification

Fig. 2 shows the densification behaviour of the three types of α-SiC powder pressureless-sintered at different temperatures for a period of 30 min. Type 1 powder containing no sintering aids, sintered only to a final density of about 67 per cent of theoretical.* In contrast, Type 2 powder containing boron and carbon sintering aids sintered to a high final density of greater than 96 per cent of theoretical, while Type 3 powder containing aluminium and carbon sintering aids sintered only to a final density of about 80 per cent of theoretical.

The excellent sinterability of SiC powder containing boron and carbon sintering aids was reported earlier by Prochazka [5] and Coppola *et al.* [6]. Prochazka further reported that aluminium and carbon sintering aids, although they allowed densification of about 80 per cent of theoretical, did not result in high final density unless boron was also present in the powder. According to Prochazka, boron segregates in the grain boundaries and reduces grain boundary energy ($\gamma_{GB}$), whereas carbon deoxidizes the SiC particle surfaces and increases the surface energy ($\gamma_{SV}$). Thus the ratio of $\gamma_{GB}/\gamma_{SV}$ decreases and permits densification during sintering [5]. Greskovich and Rosolowski [7] concluded that sintering aids such as boron impede matter transport by surface diffusion, and, therefore, inhibit grain growth at temperatures less than 1500° C but permit densification at higher temperatures. Because of poor sinterability of Type 1 and Type 3 powders, further sinterability study was pursued only with Type 2 α-SiC powder containing boron and carbon sintering aids.

The compacts of Type 2 powder were sintered at various temperature between 1950° C and 2150° C for 10 to 240 min. The isothermal densification is plotted in Fig. 3 as per cent relative density against log time. A density of greater than 96 per cent of theoretical density was attained after sintering for 30 min at 2150° C. With longer sintering time of 60 min, a final density of about 97 per cent of theoretical was achieved. The results suggest that sintering times of 30 to 60 min seem to be adequate at 2150° C to achieve a final density greater than 96 per cent of theoretical for the Type 2 α-SiC powder.

## 3.3. Microstructure characterization

Microstructural examinations were made of the fracture surfaces of samples sintered for 30 min at temperatures of 1950, 2040, 2100 and 2150° C. These are shown in Fig. 4. Samples sintered at

---

*Theoretical density of α-SiC is 3.208 g cm$^{-3}$.

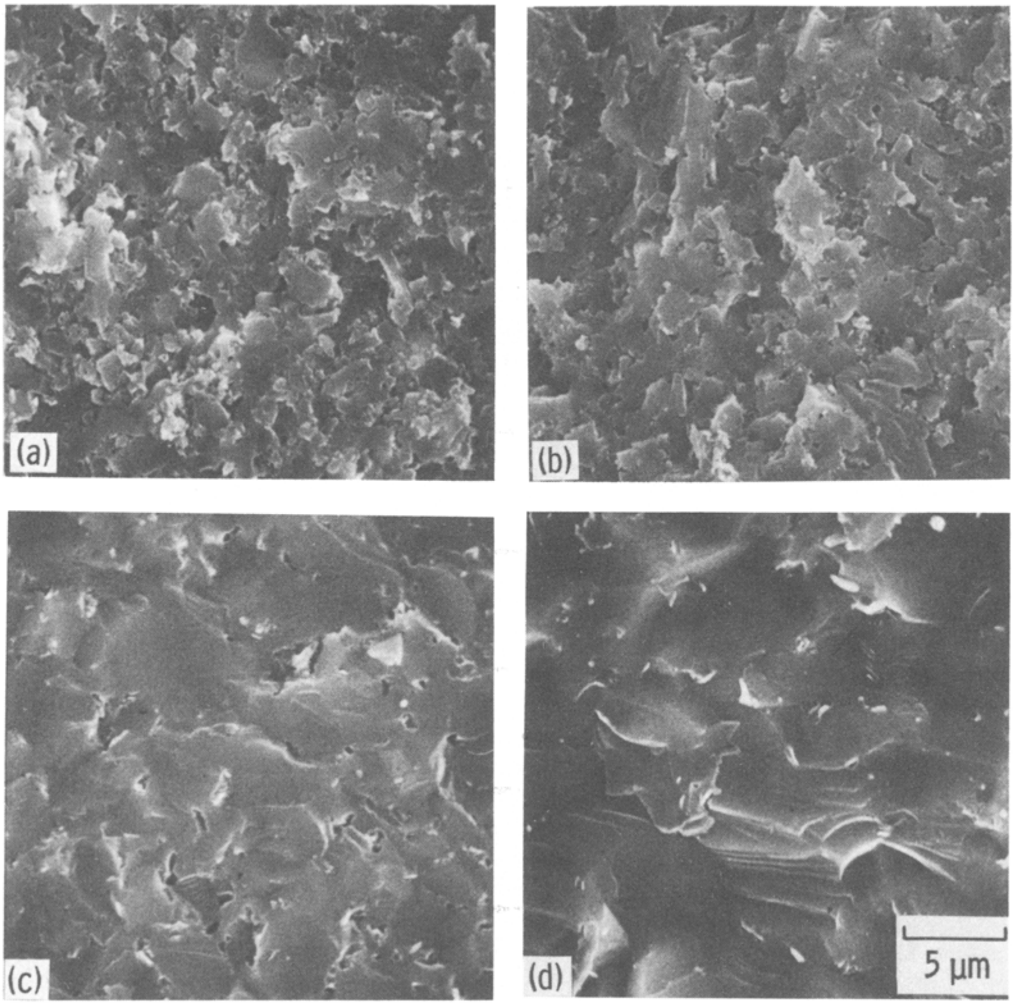


*Figure 4* Fracture surfaces of Starck α-SiC (boron, carbon) samples sintered for 30 minutes at different temperatures: (a) 1950° C, 79.5% dense; (b) 2040° C, 86% dense; (c) 2100° C, 92% dense; (d) 2150° C, 96% dense.

1950 and 2040° C exhibited grain structures with a large degree of porosity (Figs. 4a and b). In comparison, fracture surfaces of samples sintered at 2100 and 2150° C (Figs. 4c and d) consistently indicated lower porosity, i.e. typical of high density structures associated with more complete sintering. Fig. 4 also shows an increase in grain size with higher sintering temperatures.

A light photomicrograph of sintered α-SiC (boron, carbon) having a final density of more than 96 per cent is shown in Fig. 5. The photomicrograph shows well sintered, relatively pore-free material, with an essentially single phase matrix. The sintered material had a large population of equiaxed grains between 1.0 and 10.0 µm diameter, and a small population of elongated grains

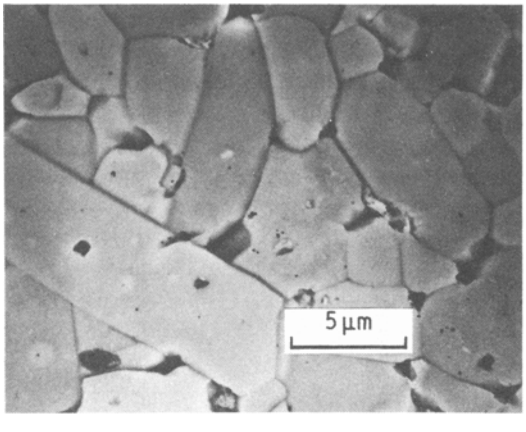


*Figure 5* Polished and etched surface of Starck α-SiC (boron, carbon) sintered for 30 minutes at 2150° C.

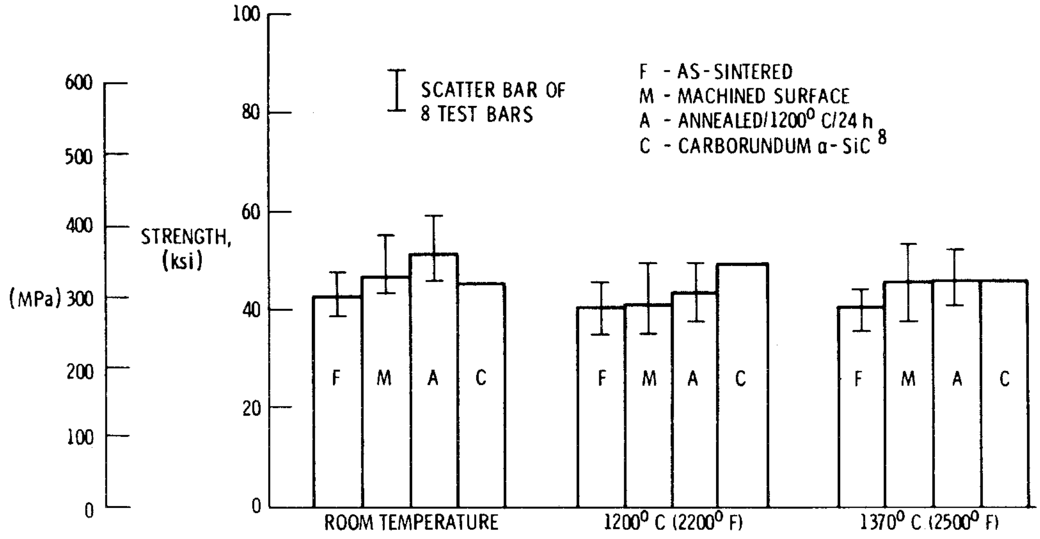


*Figure 6* Four-point flexure strength of α-SiC (boron, carbon) at different temperatures.

1.0 to 17.0 μm in length and 0.3 to 0.75 μm in width with aspect ratios varying between 1 : 2 and 1 : 4. X-ray diffraction analysis indicated α-SiC to be the only phase in the sintered material.

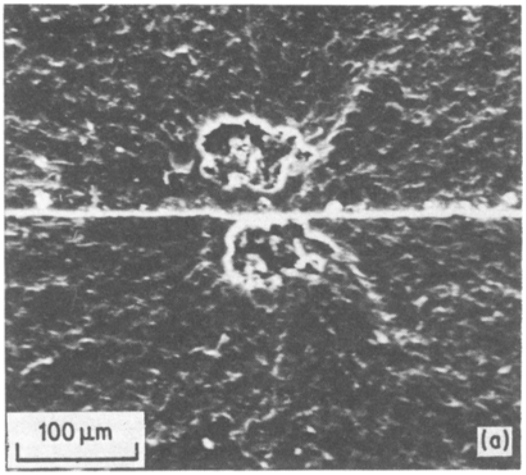
## 3.4. Flexure strength

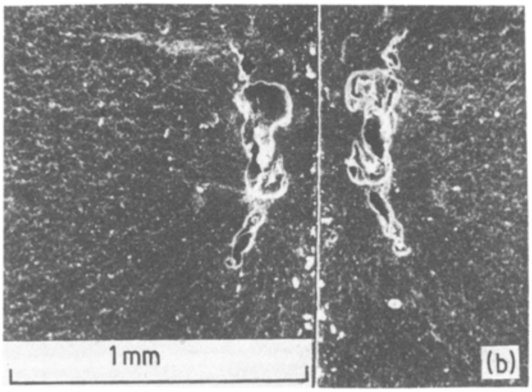
Flexure strength was determined on sintered α-SiC (boron, carbon) bars having densities more than 96 per cent of theoretical. Strength was determined on a total of eight test bars at each temperature (room temperature, 1200° C and 1370° C). Fig. 6 shows the strength values of α-SiC (boron, carbon) bars having various different surfaces. Average room temperature strengths were 297 MPa (43 k.s.i.) for the as-sintered surface, 329 MPa (47.7 k.s.i.) for the machined surface, and 363 MPa (52.7 k.s.i.) for the machined and heat-treated surface. At 1200° C, average strengths were 287 MPa (44.1 k.s.i.) for the heat-treated surfaces. At 1370° C, average strengths were 287 MPa (41.6 k.s.i.) for the as-sintered surfaces, and 323 MPa (47 k.s.i.) for both machined and machined and heat-treated surfaces. The strength data at both room temperature and high temperature for as-sintered, machined, and machined and heat-treated bars, are within the scatter range of one another, thus indicating that surface condition had no conclusive effect. The data also indicated that sintered α-SiC retains its room temperature strength at high temperatures in air. This strength retention is extremely important in high temperature applications of structural ceramic materials.

Flexure strength of the test bars made from the Type 2 α-SiC (boron, carbon) powder was compared with the strength of α-SiC produced by the Carborundum Company [8]. Sintered density of the Carborundum α-SiC was 97 per cent of theoretical. The average grain size range and maximum grain diameter were 2 to 8 μm and 15 μm, respectively [9]. Both density and grain size data were equivalent to that of Type 2 α-SiC (boron, carbon). As shown in Fig. 6, room temperature and 1370° C (2500° F) strengths were equivalent to those of the material produced by Carborundum, while strength at 1200° C (2200° F) may be somewhat less than the strength of the material produced by Carborundum.

## 3.5. Fracture

Fracture origin analysis of sintered α-SiC (boron, carbon) was performed on both as-sintered and machined test bars using scanning electron microscopy. Figs. 7a and b show the fracture origins of machined bars broken at room temperature having strengths of (a) 350 MPa (50.9 k.s.i.) and (b) 298 MPa (43.2 k.s.i.), respectively. These photographs represent matching fracture halves in the vicinity of the fracture origins. The failures in both test bars (a and b) are from single isolated voids of 100 μm or greater in size. The failure from a single isolated void was also observed in as-sintered surface bars. For example, Fig. 7c shows room temperature fracture of an as-sintered bar having strength of 331 MPa (48 k.s.i.). The failure was caused by a large void near the surface.





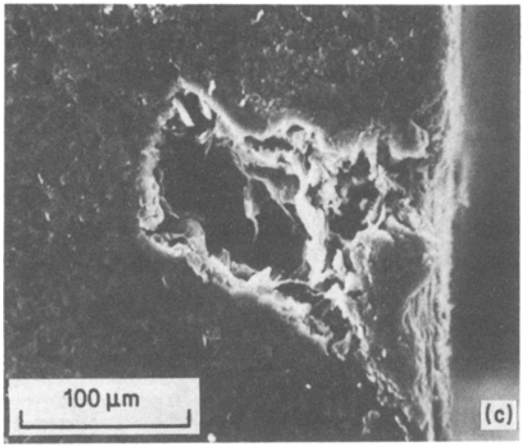


*Figure 7* SEM room temperature fracture of sintered α-SiC (boron, carbon) showing failures from single isolated pores. (a) Machined surface 350 MPa (50.9 k.s.i.); (b) machined surface 298 MPa (43.2 k.s.i.); (c) as-sintered surface 331 MPa (48 k.s.i.).

Although a large proportion of failures of test bars in this study were from large single irregular voids, a small number of bars failed as a result of flaws which appeared to be low density regions associated with agglomerates. This is shown in Fig. 8. The results suggest that in order to improve strength and reliability in sintered α-SiC material, removal of these processing defects is absolutely essential.

## 3.6. Oxidation

Oxidation tests were conducted simultaneously on both Type 2 α-SiC (boron, carbon) and α-SiC produced by Carborundum Company. Only one bar of each material was oxidized. A plot of weight change against time shown in Fig. 9 indicates a low total weight change up to 200 h at 1370° C for both materials. However, a comparatively lower weight change in α-SiC (boron, carbon) was observed. The oxide scales were identified by X-ray diffraction as α-cristobalite on both bars.

The results suggest that Type 2 α-SiC (boron, carbon) made from commercially available powder, has oxidation resistance comparable to Carborundum α-SiC, the current state-of-the-art material.

## 4. Concluding remarks

The studies reported here show that "as-received" commercially available α-SiC powder containing boron and carbon sintering aids can be pressureless sintered to a density of more than 96 per cent of theoretical. Room temperature and high tem-

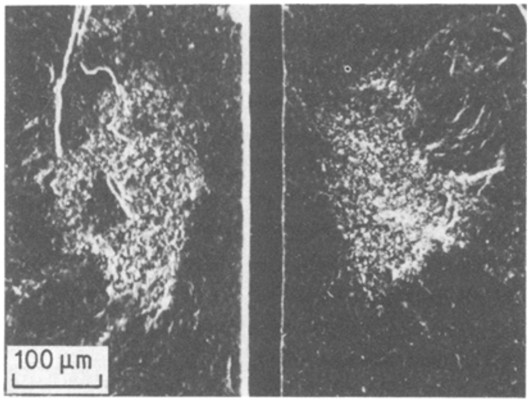


*Figure 8* SEM of room temperature fracture of sintered α-SiC (boron, carbon) showing failure from a low density region. Machined surface 298 MPa (43.2 k.s.i.).

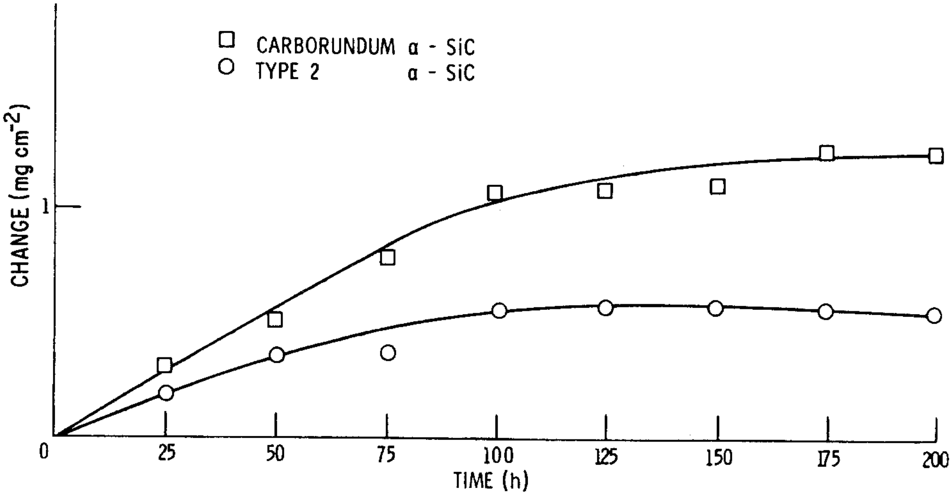


*Figure 9* Weight change in air at 1370° C (2500° F) of sintered α-SiC.

perature (1370° C) flexure strength and oxidation characteristics appear comparable to that of Carborundum sintered α-SiC, the current state-of-the-art material. The results of tests to date are very encouraging; they suggest that using commercially available powder, it is possible to produce high density sintered α-SiC having properties suitable for high temperature applications.

## References

1. F. F. LANGE and J. L. ISKOW, in "Ceramics for High Temperature Applications", edited by J. J. Burke, A. E. Gorum and R. N. Katz (Brook Hill Publishing Co., Chestnut Hill, MA, 1974) pp. 223–238.
2. G. E. GAZZA, *J. Amer. Ceram. Soc.* 56 (1973) 66.
3. E. H. CRAFT and J. A. COPPOLA, in "Ceramics for High Performance Applications", edited by J. J. Burke, E. N. Lenoe and R. N. Katz (Brook Hill Publishing Co., Chestnut Hill, MA, 1978) pp. 1023–1038.
4. S. DUTTA, *J. Amer. Ceramic Soc.* **65** (1982) C-2.
5. S. PROCHAZKA, "Ceramics for High Temperature Applications", edited by J. J. Burke, A. E. Gorum and R. N. Katz (Brook Hill Publishing Co., Chestnut Hill, MA, 1974) p. 239.
6. J. A. COPPOLA, H. A. LAWLER and I. H. McMURTY, US Patent 4123 286, October (1978).
7. C. GRESKOVICH and J. H. ROSOLOWSKI, *J. Amer. Ceram. Soc.* 59 (1976) 336.
8. W. D. CARRUTHERS, D. W. RICHERSON and K. W. BENN, "3500-Hour Durability Testing of Commercial Ceramics Materials", Interim Report, July (1980), AiResearch Manufacturing Company of Arizona, DOE/NASA/0027-80/1.
9. D. C. LARSEN and J. W. ADAMS, "Property Screening and Evaluation of Ceramic Turbine Materials", Semiannual Interim Technical Report No. 11, Contract F33615-79-C5100, IIT Research Institute, November (1981) p. 37.

*Received 9 June*
*and accepted 28 July 1983*