SINTERING, HIPPING AND SINTER-HIPING PROCESSES ON DENSIFICATION, MICROSTRUCTURE, AND STRENGTH OF SILICON CARBIDE

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ABSTRACT

A comparative study of sintering, sinter-HIPing, and HIPing processes on densification, microstructure, and strength of α-SiC was made. The commercial high purity α-SiC powder containing pre-mixed sintering aids (boron and carbon) was cold formed by slurry pressing and hot-formed by sintering, sinter-HIPing, and HIPing. The results indicated that a high final density > 96 percent of theoretical can be achieved at 2150° C by sintering. By contrast, a much lower temperature of 1900° C was required by HIPing to achieve a final density > 97 percent of theoretical. Pore size distribution was significantly improved by the slurry-pressing technique.

A baseline average flexure strength of 348 MPa was achieved in α-SiC by dry-pressing and sintering. When slurry pressing was used to minimize agglomerates from the powder, an improved baseline flexure strength of 428 MPa was achieved. However, the HIPed α-SiC showed a significant improvement as high as 655 MPa. This strength value was ∿60 percent higher than the slurry-pressed/sintered strength and ∿90 percent higher than the dry-pressed/sintered strength. By contrast, sinter-HIPed specimens did not result in any noticeable strength improvement over sintered specimens.

In the HIPed specimens, processing flaws, such as large voids, shrinkage cracks, etc., were not observed as compared with sintered and sinter-HIPed specimens which are discussed.

Introduction

The potential of silicon carbide for heat engine and other high temperature structural applications is well

known for more than two decades. This ceramic offers outstanding high temperature creep resistance and strength along with good oxidation resistance. Numerous work has been reported on processing of this ceramic. These processes include green forming such as die pressing, slurry pressing, slip casting, and injection, molding, etc.; and hot forming such as conventional sintering, hot pressing, hot isostatic pressing, (HIPing) and sinter-HIPing etc. The common goal was to achieve high density, reliable material with improved strength. Earlier work has shown that the massive bridging of agglomerates during dry compaction causes large voids and shrinkage cracks because of differential sintering [1-3] and thereby found to control strength. Later it was demonstrated that slurry-pressing could reduce agglomerate-size resulting in improved strength and critical flaw size [4,5]. However, process-related flaws were still present in slurry-pressed/sintered material. Recently, Dutta demonstrated that hot isostatic pressing (HIPing) essentially eliminate the process-related shrinkage voids/flaws[6] and thereby further improve strength.

It is the purpose of this paper to present and analyze recent data on sintering, HIPing and sinter-HIPing of silicon carbide and to compile and relate this information to our knowledge of this structural ceramic material.

Experimental Procedures

Commercial high-purity α-SiC powder was used in this study. The powder contained premixed sintering aids (boron and carbon) as received from the manufacturer. Chemical analysis of the as-received powder is shown in Table 1. As-received powder was sieved through 100-mesh screen, and 3 g of powder was dry-pressed to bars (3.81 by 0.79 by 0.45 cm) followed by cold isostatically pressing at 413 MPa.

For slurry pressing, 200 g SiC powder was milled with 225-ml solution of water/ammonium hydroxide (pH = 11) in a polyethylene jar with 200 g SiC grinding media. After the slurry had been mixed for 48 hr., it was pressed at 14 MPa. The disk-shaped specimens (4.7 cm in dia. by 0.6 cm thick) were slowly dried and then isostatically pressed at 413 MPa . The details of the slurry-pressing process was described in earlier

work[3,5].

Pressureless sintering was carried out on both dry-pressed and slurry-pressed specimens at 1900 to 2200° C for a period of 10 to 240 minutes under 0.1 MPa flowing argon pressure. Sinter-HIPing was carried out on pre-sintered disks having densities greater than 90 percent theoretical, where almost all open pores were eliminated. The pre-sintered disks were placed in the HIP furnance without any encapsulation and HIPed at 2100° C to 2200° C for 30 to 60 minutes at 138-MPa argon pressure. For hot isostatic pressing (HIPing), the disks were encapsulated with tantalum cans. After outgassing for 6 to 8 hr. at 1100° C, the cans were vacuum sealed. After a through leak check, the cans were HIPed at different temperatures varying from 1850 to 2000° C for 30 to 120 minutes at 138 argon gas pressure.

Sintered, Sinter-HIPed, and HIPed specimens were machined into test bars (2.54 by 0.64 by 0.32 cm), and surfaces were ground with a 400-grit fine diamond wheel to a final surface finish of 8 rms. Flexure strength tests were conducted by fourpoint loading using 0.95 cm loading span and a 1.87 cm support span test fixture. Microstructural characterization was made by optical and electron microscopy. Fracture surfaces were examined by scanning electron microscopy to identify critical flaws.

Results and Discussion

Isothermal densification of both dry-pressed and slurry-pressed specimens are plotted in Figures 1 and 2 as percent relative density against log time. A density greater than 96 percent of theoretical was obtained after sintering for 30 minutes at 2150° C. With longer sintering time of 60 minutes, a final density 97 percent of theoretical was achieved. The results suggest that a temperature of 2150° C for 30 to 60 minutes seem to be adequate to achieve a final density greater than 96 percent of theoretical for both dry-pressed and slurry-pressed α-SiC specimens containing B and C sintering aids. Prochazka[7] reported that densification is promoted because the $\gamma GB/\gamma SV$ of the particle boundary energy γGB and the surface energy γSV is reduced due to boron segregation at the grain boundaries where-

as carbon deoxidizes the SiC particle surfaces and increases the surface energy γ_{SV}.

Thus the ratio of γ_{GB}/γ_{SV} in the equation $\gamma_{GB}=2\gamma_{SV}$ cos $\theta/2$ decreases and promotes densification during sintering.

In sinter-HIPing, further density improvements were observed in sintered α-SiC specimens by sinter-HIPing at 2100 to 2200°C. For example, a final density equal to 97.4 percent of theoretical was achieved by HIPing 95-percent dense pre-sintered specimens at 2150°C for 30 minutes at 138 MPa argon pressure. Similarly, Sinter-HIPing of 96.5-percent dense, pre-sintered specimens at 2150 for 30 minutes produced a final density ∿98.5 percent of theoretical. The results are in good agreement with Watson et.al.[8] who also reported density improvement due to reduction of residual porosity in pre-sintered α-SiC.

The densification behavior of encapsulated α-SiC hot isostatically pressed (HIPed) at 1800 to 2000°C for 30 minutes is shown in Figure 3. A final density >98% of theoretical was achieved at 1900°C compared with 2200°C required for pressureless sintering (to achieve a final density of 97% of theoretical). No further increase in final densities were observed with further increases in temperature up to 2000°C. The result suggests that a temperature of 1900°C is adequate to fabricate near-theoretical-density SiC bodies by the hot isostatic pressing.

Microstructural examinations were made on polished and etched specimens. Figure 4 shows typical microstructure of dry-pressed and slurry-pressed specimens sintered at 2200°C for 30 minutes. Both types of specimens had more or less equivalent grain morphology with an average grain size of 4 to 6 μm. However, earlier work[5,6] showed that pore size distribution was significantly affected by slurry-pressing. Slurry-pressing significantly improved pore clustures and resulted in a uniform distribution of pores[5]. Pore clustures are often surrounded by cracklike voids at the cluster-matrix interface because of differential sintering. These clustures are often the strength-controlling flaws in the dry-pressed specimens . A detail microstructural and grain size analysis was carried out on slurry-pressed specimens sintered at 2100, 2150 and 2200°C for a period of 30, 60, 120 and 240 minutes. These are shown in Figures 5,6 and 7 respectively. Specimens sintered at 2100°C for 30 minutes exhibited grain structures with a large degree

of porosity (Fig.5) which is gradually diminishing with increasing sintering time. Average grain size indicated very little grain growth occurred in specimens sintered for different times at 2100° C. At 2150° C, (Fig.6) average grain size was equivalent for 30 to 60 minutes and for 120 to 240 minutes-sintered specimens. By contrast, predominant grain growth was observed in specimens sintered at 2200° C (Fig.7) for a period of 30 to 240 minutes. The grain morphology in specimens sintered for 240 minutes at 2200° C was found to be predominantly elongated having aspect ratio 1:3 to 1:10 (Fig. 7). The results indicate that an average grain size of 4 to 6 μm is very common at an optimized sintering temperature of 2150° C for a period of 30 to 60 minutes. In sinter-HIPed specimens, a duplex microstructure was observed at 2150° C, while at 2200° C, a large grain growth was observed and the grains were completely elongated with aspect ratio varying between 1:2 and 1:10. This is shown in Figure 8. By contrast, Figure 9 shows typical microstructures of α-SiC HIPed at 1900 and 2000° C for 30, 60, and 120 minutes. The microstructures consist of ultrafine, equiaxed grains varying between 0.3 and 5 μm as determined by electron microscopy. Average grain size was estimated to be 2.8 μm for encapsulated and HIPed α-SiC. Further annealing at 2200° C for 4 h resulted in much less grain growth (Fig.9) as compared to sintered and sinter-HIPed materials (Fig.7 and 8).

The room temperature flexure strength of sintered, sinter-HIPed and HIPed α-SiC are shown in Figure 10. A baseline average flexure strength of 348 MPa was achieved in α-SiC by dry-pressing and sintering. When slurry-pressing was used to minimize agglomerates from the powder, nearly 25 percent improvement in strength was observed over dry-pressed specimens. Earlier work[5,6] reported that higher strength was due to more homogeneous pore distribution in the slurry-pressed specimens resulting from improved dispersion of agglomerates in the powder. Also, it was observed that slurry pressing, in general, reduced the frequency of large (100-150 μm) flaws in the sintered material.

The flexure strength data of sintered α-SiC were compared with the sinter-HIPed strength which is shown in (Fig.10). No significant improvement in flexure strength was observed. For example, at 2150° C/30 minutes, sinter-HIPed-strength (436±75 MPa) was found to be higher than those of dry-pressed/sintered (348±51 MPa) and slurry-pressed/sintered (344 ±79MPa) strengths

(Fig.10). On the other hand, at higher temperature of 2200° C/30 minutes, the strength (336 ±41MPa) of sinter-HIPed specimens was lower than the slurry-pressed/sintered strength (428 MPa). The lower strength of sinter-HIPed specimens at 2200° C was attributed to excessive grain growth (Fig.8) when compared to 2200° C-sintered microstructure (Fig.7). For example, at 2150° C, the grain structure was primarily equiaxed (Fig.8), while at 2200° C, the grain structure was predominantly elongated with aspect ratios ranging from 1:2 to 1:9. The sinter-HIPed strength was found to be dependent on final grain structure which was in good agreement with Watson et. al.(8). The room-temperature flexure strength of hot isostatically pressed α-SiC are compared with sintered and sinter HIPed specimens. The hot isostatically pressed α-SiC exhibited an average flexure strength of 576 MPa. This value was 60% higher than the dry-pressed/sintered strength and 40% higher than the slurry-pressed/sintered strength. The high strength was attributed to finer grain size α-SiC material obtained during hot isostatic pressing. A further improvement in strength to ∿ 655 MPa was achieved by heat-treating the hot isostatically pressed specimens. This strength improvement was attributed to healing of grinding damage during machining of the test bars. When the material was heat-treated in air, surface oxidation tended to "heal" the flaws, which enabled the material to exhibit a higher strength.

CONCLUDING REMARKS

The studies reported here show a significant strength improvement by improved processing. A baseline flexure strength of 348 MPa was achieved in α-SiC by dry-pressing and sintering. By utilizing slurry-pressing to minimize agglomerates from the powder, an improved baseline strength of ∿ 428 MPa was achieved. However, further improvement in strength was not achieved by sinter-HIPing due to excessive grain growth occurred during sinter-HIPing. On the other hand, an additional improvement in strength of ∿655 MPa was achieved by HIPing of encapsulated green compacts. In the HIPed specimens, strength-controlling critical flaws such as large voids, shrinkage cracks, etc., were not observed as compared to sintered specimens. Thus hot isostatic

pressing overcame the formation of critical flaws resulting from residual agglomerates in the powder. Instead , the critical flaws were predominantly surface related. Therefore, surface finish such as lapping, polishing, and/or heat treatment might further improve both strength and Weibull modulus in hot isostatically pressed α-SiC.

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Table I. Analysis of As-Received α-SiC Powder: Impurity Analysis (PPM)

Element	Impurity analysis (PPM) Type 2 α-SiC (B, C)
Al	140
Ca	40
Fe	10
Ti	30
V	20
B	0.60*
Free C	7.31*
Surface area (BET) m^2/g	22

*Wt%.

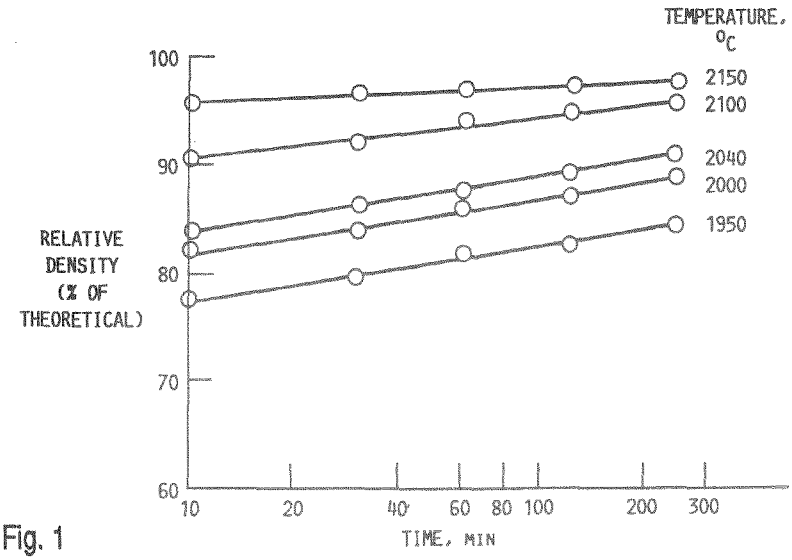


Fig. 1

ISOTHERMAL DENSIFICATION OF DRY-PRESSED α-SiC POWDER

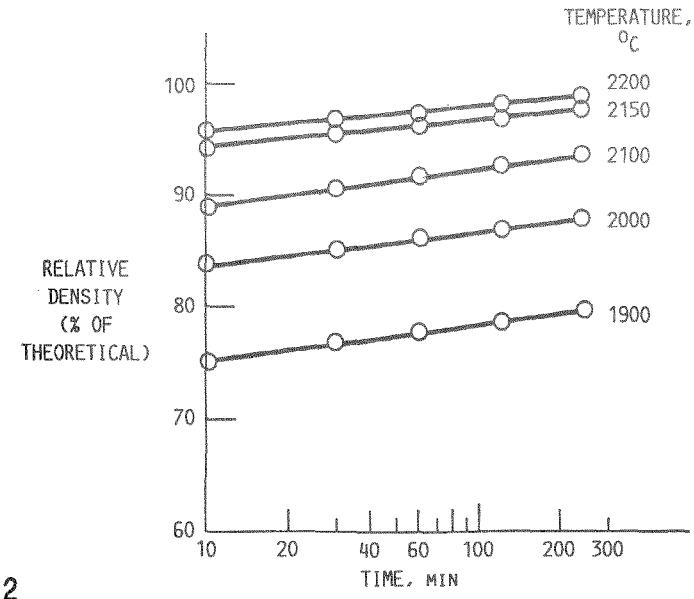


Fig. 2

ISOTHERMAL DENSIFICATION OF SLURRY-PRESSED α-SiC POWDER

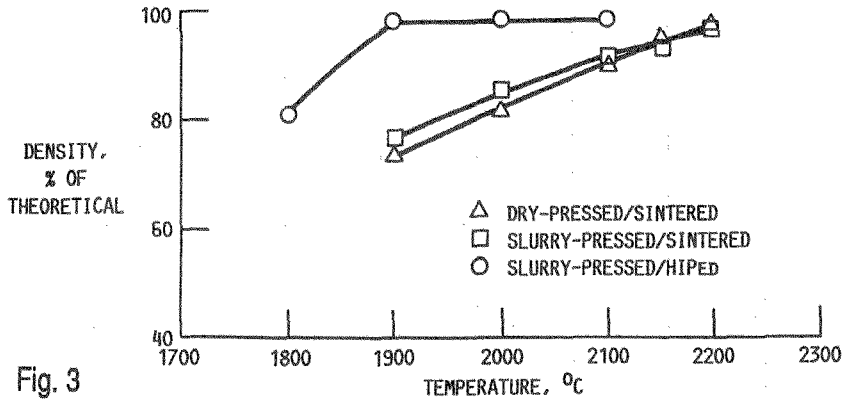


Fig. 3

RELATIVE DENSITY OF α-SiC POWDERS SINTERED AND HIPed FOR 30 min VERSUS SINTERING TEMPERATURE

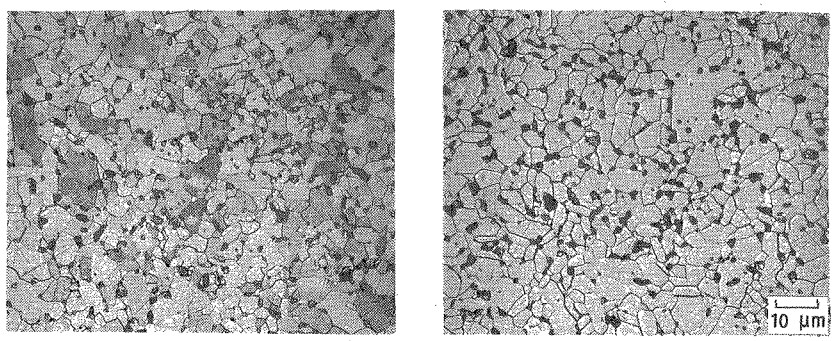


Fig. 4

MICROSTRUCTURE DEVELOPMENT IN DRY-PRESSED VS SLURRY-PRESSED α-SiC

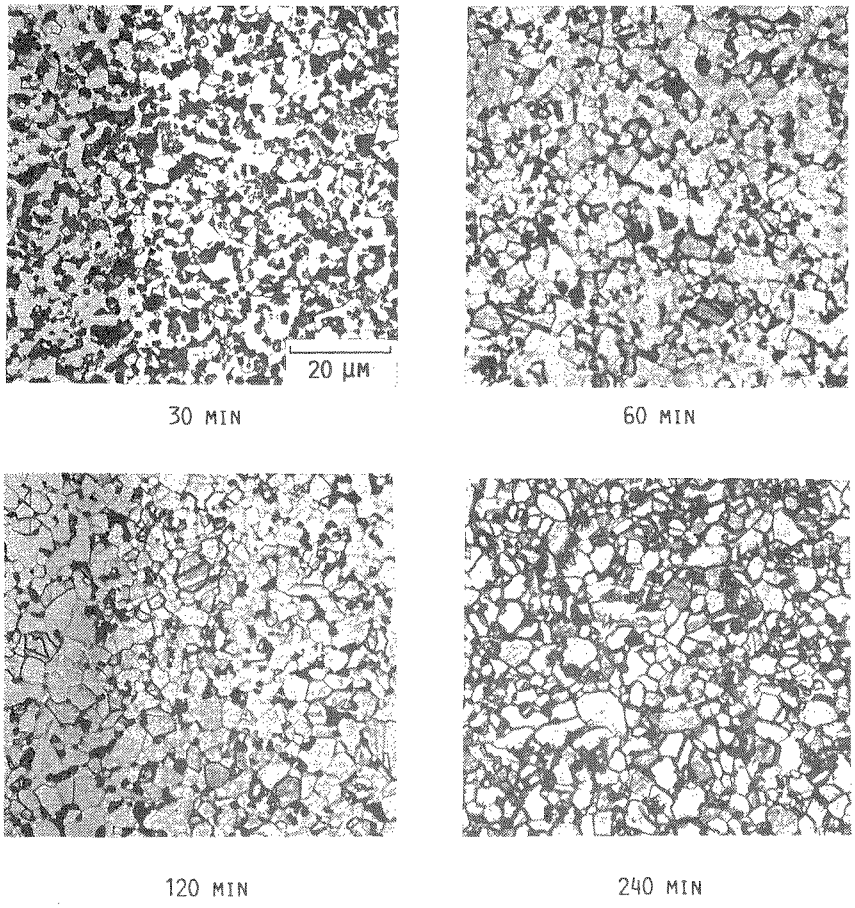


Fig. 5

MICROSTRUCTURE DEVELOPMENT IN SLURRY-PRESSED α-SiC SINTERED AT 2100 °C

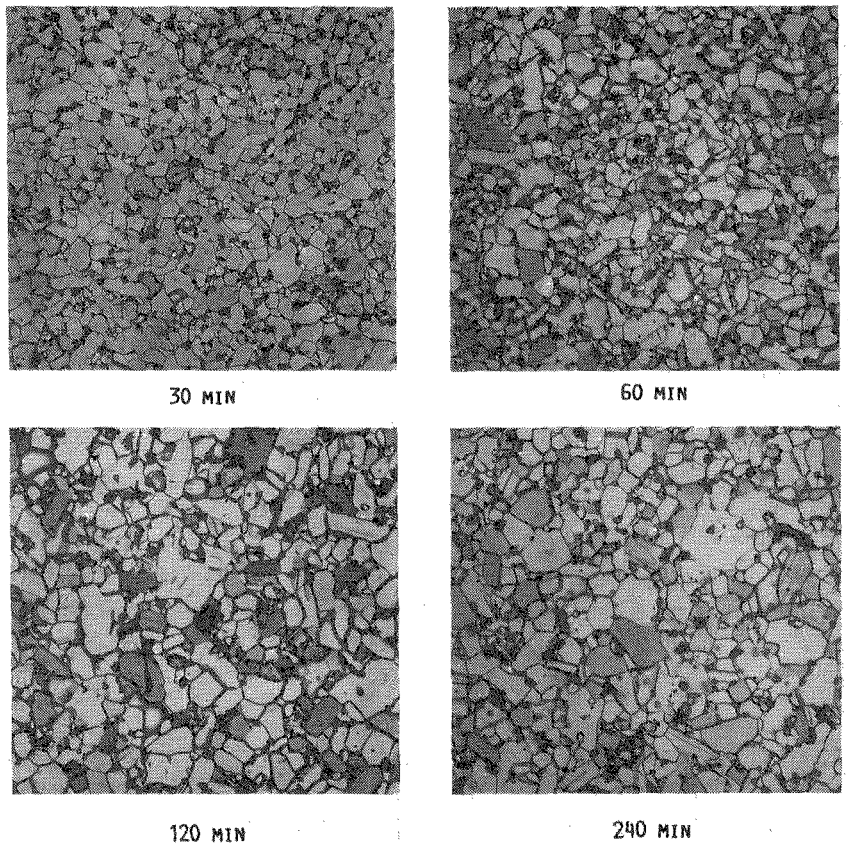


Fig. 6

MICROSTRUCTURE DEVELOPMENT IN SLURRY-PRESSED α-SiC SINTERED AT 2150 °C

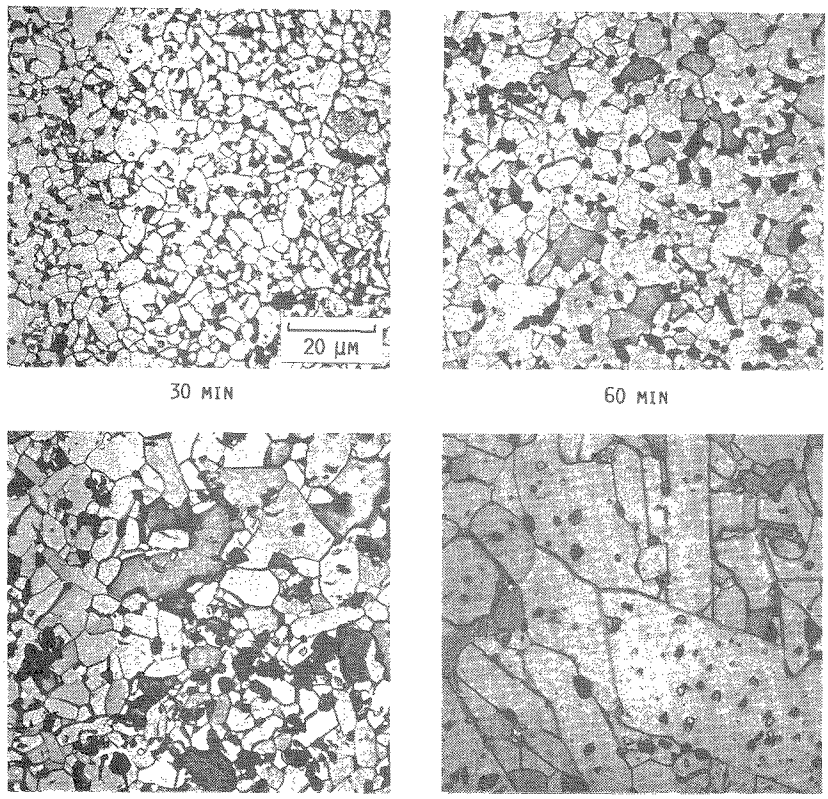
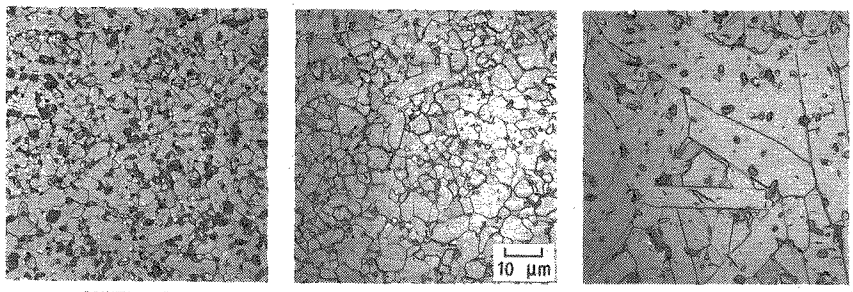


Fig. 7

MICROSTRUCTURE DEVELOPMENT IN SLURRY-PRESSED α-SiC SINTERED AT 2200 °C

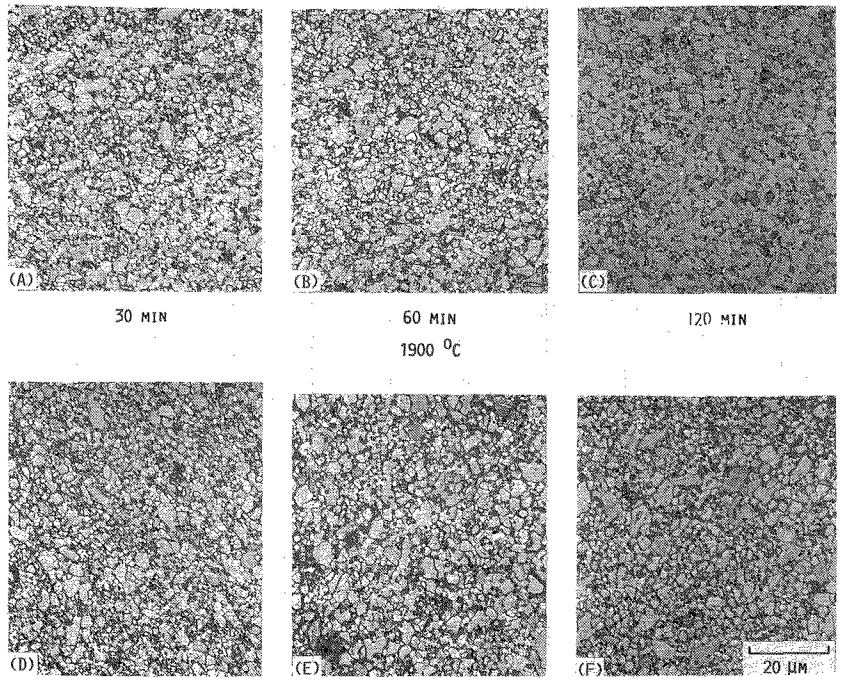


SINTER-HIPED
2100 °C/60 MIN
D = 94%

SINTER-HIPED
2150 °C/30 MIN
D = 97%

SINTER-HIPED
2200 °C/30 MIN
D = 98.5%

Fig. 8 MICROSTRUCTURE DEVELOPMENT IN SINTERED-HIPed α-SiC



30 MIN

60 MIN
1900 °C

120 MIN

30 MIN

60 MIN
2000 °C

120 MIN

Fig. 9 MICROSTRUCTURES OF HOT ISOSTATIC PRESSED α-SiC (II)

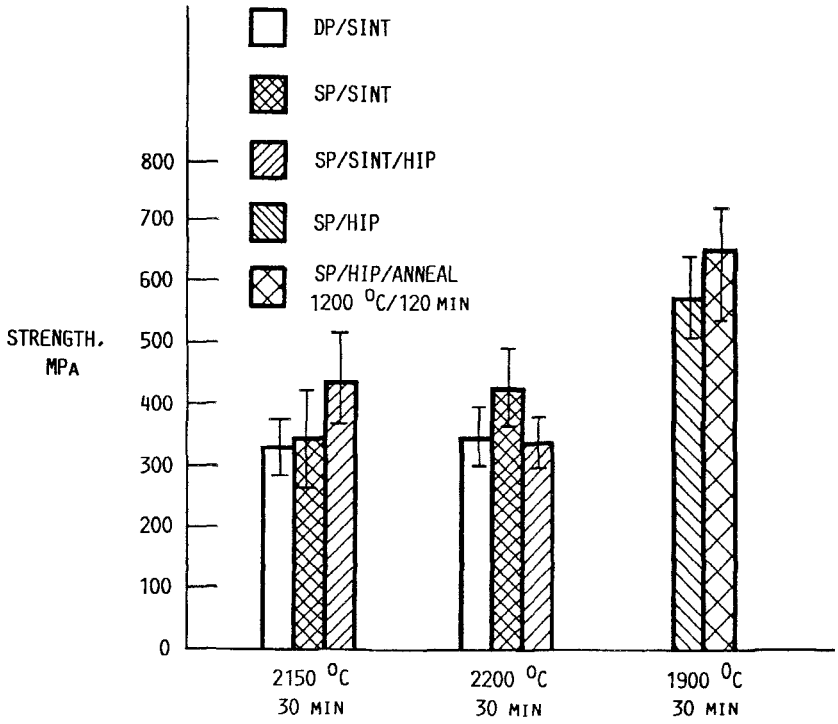


Fig. 10

ROOM TEMPERATURE FLEXURE STRENGTH OF SINTERED, SINTER-HIPed AND HIPed α-SiC ($\pm$1 S.D.)