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CERAMIC SINTERING

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Measurement of the rate of oxidation and creep rate in air of chemically vapor deposited Si_3N_4 at around 1500°C are reported. Attempts to prepare pure, dense Si_3N_4 bodies by hot pressing powder at ultra-high pressures were unsuccessful. Resistance heaters made of dense, sintered SiC were tested and found to have in-use lifetimes very much longer than those of commerically available heaters tested in the same way. Microscopic

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examination of the structures developed during the initial stage sintering of SiC doped with C and B indicates that these dopants inhibit surface diffusion until densification begins at around 1500°C. Bodies of B_4C having about 94% of theoretical density were made by using conventional sintering processes and doping the powder with either SiC or Be_4C.

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FOREWORD

This research was sponsored by the Advanced Research Projects Agency and carried out in the Physical Chemistry Laboratory of the General Electric Corporate Research and Development Center under U.S. Navy Contract N00014-74-C-0331 entitled "Ceramic Sintering".

This work was performed during the period April 01, 1974 to October 31, 1974.

The authors gratefully acknowledge the contributions of Dr. R. C. De Vries and Mr. J. F. Fleischer to the hot pressing studies and the assistance of Dr. C. A. Johnson with the creep studies. Dr. S. Prochazka did the work on B_4C. Also, Dr. R. J. Charles supplied helpful technical guidance. C. Bobik and C. O'Clair performed ceramic processing and heat treatment operations. Dr. R. A. Giddings made some of the surface area measurements.

SUMMARY

The principal objective of this investigation during the first three months of the contract period was to measure the oxidation and high temperature creep properties of pure, dense Si_3N_4 ceramic in the form of a coarsely crystalline deposit formed by chemical vapor deposition. Attempts were also made to produce a pure, fine grained ceramic for these studies by hot pressing a powder of good purity at very high pressures. In addition, the temperature capability and lifetime in use of some experimental, oxidation resistant resistance heaters made of dense SiC were determined and compared to those of porous, commercial heaters.

The attempts to make a relatively pure, dense Si_3N_4 ceramic by hot pressing were not successful. Pressures up to 60 kilobars and temperatures up to 1750°C were tried. High density could only be achieved at high temperature, but this always resulted in reaction of the Si_3N_4 with the various containers tried.

No creep deflection was observed in a sample tested in 3 point bending after 198 hours at 1560°C and with an outer fiber stress of 10,000 psi. An upper limit for the creep rate under these conditions of $1.6\times10^{-7}hr^{-1}$ was deduced from this observation. This value is several orders of magnitude less than that expected for either reaction sintered or hot pressed, MgO doped Si_3N_4 under these conditions based on extrapolations from published data.

The oxidation rate of chemical vapor deposited, dense Si_3N_4 at 1550°C in air was determined to be such as to preduce a weight change of less than about $0.01\ mg/cm^2\text{-}hr^{\frac{1}{2}}$. This upper limit is about equal to the average rate of oxidation over 100 hours at 1100°C of hot pressed Si_3N_4 doped with MgO. It is

probably also very much less than the oxidation rate of porous, reaction sintered Si_3N_4, which has only been observed qualitatively.

In tests where the peak surface temperature of SiC resistance heaters was cycled between room temperature and 1600°C, the experimental samples made of dense SiC survived up to 2544 cycles with no failures or apparent degradation of properties. All equivalent commercial SiC heaters tested failed by a combination of cracking and surface oxidation after less than 200 cycles. These results indicate that resistance heaters made of dense SiC could be operated in air at power loadings, expressed in watts per unit area of radiating surface, considerably higher than those recommended for commercial heaters and would have an indefinately long lifetime in use.

Work in the remaining portion of the reporting period was devoted to initiating an investigation of sintering in covalently bonded solids. Two materials were studied, SiC and B_4C.

The early stage of sintering of β-SiC powders containing carbon only, boron only, and carbon plus boron was studied by surface area and shrinkage measurements as well as by scanning electron microscopy. β-SiC powder containing 0.8 wt% C and 0.6 wt% B began to exhibit surface area reduction and densification at temperatures near 1500°C, whereas β-SiC powder containing only free carbon was characterized by a decrease in surface area at a temperature near 1250°C but no densification for temperatures up to 2000°C. The boron dopant essentially impeded surface diffusion and inhibited grain growth in silicon carbide until the initiation of the densification process. The grains developed during the sintering of boron- and carbon-doped β-SiC remained equiaxed at least up to 1900°C, but the grains formed during the sintering of β-SiC containing only free carbon were clustered into dense regions separated by large pores which developed in the structure.

In the absence of free carbon, sintered compacts of boron-doped β-SiC powder densified only a few percent and then stopped. The grains were essentially equiaxed and small in size but the appearance of well-defined, grain boundary-solid-vapor intersections indicated that this structure was approaching geometrical equilibrium.

This work on elucidating the microstructure development during sintering of doped β-SiC will be continued. Similar work on sintering Si is being initiated.

In the work with B_4C, a material which is now commercially densified by hot pressing, bodies of up to 94% of the theoretical density were produced by the cold-press and sinter method using powders to which either SiC or Be_4C had been added.

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I. Introduction

The principal technical objectives of the work performed during the initial three months of this contract were to make initial determinations of the oxidation and creep resistance of pure, dense, polycrystalline Si_3N_4. The material to be investigated was a coarsely crystalline planar deposit of Si_3N_4 obtained from General Electric's Re-entry and Environmental Systems Division$^{(1)}$. This material was made by a chemical vapor deposition (CVD) process in which $SiCl_4$ was reacted with NH_3 at 1400°C and the resultant Si_3N_4 deposited on a graphite substrate. Concurrently, attempts were to be made to produce a fine grained, dense ceramic by hot pressing a relatively pure Si_3N_4 powder in a high pressure apparatus of the type used in diamond synthesis. If these attempts proved to be successful, the oxidation and creep properties of this material too would be measured.

A secondary technical objective was to compare the performance of dense, sintered rods of SiC used as resistance heaters operating in air, to commercial, porous rods of SiC used in the same manner.

The work is described below, starting with the experiments aimed at hot pressing pure Si_3N_4 powder.

II. Hot Pressing Pure Si_3N_4

The powder used was obtained from the Plessy Co. of Frenchtown, N.J.$^{(2)}$ The vendor's analysis showed it to be 91% alpha Si_3N_4 and the rest beta. The impurity content, as determined spectrometrically was given as

Na, K - not detected

Ca - 1-10 ppm

Al - 100 ppm

Cu - 10-100 ppm

Fe - up to 1000 ppm.

The oxygen content was given as lying between 1.3 and 1.5 weight percent and the average particle size was about 2 microns.

The hot pressing was done in a belt apparatus. In this technique, an essentially hydrostatic pressure is applied to a sample by placing it in the center of a cell filled with a salt which becomes plastic at high temperature and pressure. The high temperature is achieved by passing an electrical current through a hollow graphite cylinder surrounding the salt, and the pressure is generated by movable rams bearing on the ends of the cell. The sample is separated from the salt by a thin liner.

The peak pressures, temperatures, hold times and liner materials used for the runs made are given in Table I. The heat-up time was 20 minutes in every case except for the last run listed, where it was 1 hour.

The results were disappointing because in all cases but one, there was a considerable degree of reaction of the Si_3N_4 with the liner. The exception was the case when the liner was omitted and the Si_3N_4 was in direct contact with the NaCl in the cell. In that case, however, the pressed sample had only achieved 85% of theoretical density after 4 hours of sintering. Appreciable porosity was also evident in most of the other samples.

TABLE I

Parameters of the Hot Pressing Experiments

Pressure Kb	Temperature °C	Hold Time hr	Liner
60	1650	0.5	BN
60	1200	2	Ni
60	1500	2	Mo
60	1200	3.5	Mo
40	1200	2.5	Mo
40	1200	4	NaCl
57.5	1550	1	Al_2O_3
57.5	1300	2.75	Mo
60	1750	0.5	BN
60	1750	0.5	C

The test samples were cylinders about 2 mm in diameter and about 4 mm long. They tended to break up into lamellae on removal from the apparatus. Fig. 1 is a back lighted micrograph through one such lamella, about 1/3 mm thick, from the sample pressed at 60 Kb and 1750°C using a BN liner. This and the other specimen pressed at 60 Kb and 1750°C, but using a carbon liner, were the densest made. The dark area around the periphery is due to reaction with the liner material. The central portion is transparent and of 95+ percent density.

The results obtained in these experiments were not encouraging enough to engender a reasonable hope that the problems associated with making dense, pure samples of a size required for the objectives of the contract could be solved in anything like the time available. Accordingly, work in this area was terminated.

III. Creep of CVD Si_3N_4

The investigation of creep in air of a pure, polycrystalline α-Si_3N_4 was conducted on chemically vapor deposited material made as described in the Introduction. The deposit, after removal from the carbon substrate, was measured with a micrometer and found to have a thickness of 16 mils. It was coarsely crystalline and quite rough, with single grains extending through the whole of the thickness. Its density is 99.5% of theoretical. Figure 2 is a scanning electron micrograph of the exposed surface of the deposit. The side which was against the carbon substrate does not show crystal faces.

No chemical analysis of the material is available, however, the method of its formation insures that it is considerably purer than either reaction

Fig. 1 Transmitted light micrograph of a thin piece of Si_3N_4 formed by pressing a pure powder for one-half hour at 1750°C and 60 Kb. 48X

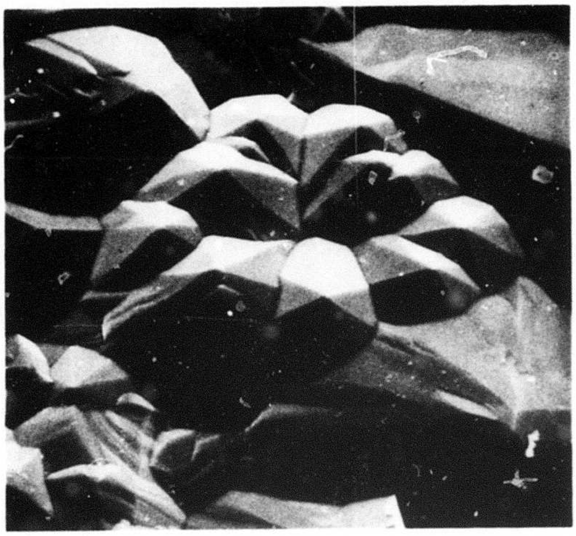

Fig. 2 Scanning electron micrograph of the exposed surface of the CVD Si_3N_4. 500X

sintered or hot pressed Si_3N_4. The optical reflectance spectrum indicates that the oxygen content is probably less than around 30 ppm. It has also been determined that there are residual stresses present in the deposit at room temperature.

Creep was measured in three point bending. The sample was about 1 inch long by 0.2 inch wide and supported at its ends on SiC knife edges. These rested on a SiC plate, having a hole in its center, which lay on a geometrically similar alumina plate placed in the center of a platinum wound, horizontal tube furnace of 1¼ inches i.d. Load was applied to the sample by means of a SiC "picture frame", the top side of which was a knife edge resting across the middle of the sample. This picture frame hung down through the holes in the base plates and its bottom side fit into a slot ground into a SiC rod which passed through the wall of the furnace to the outside. A beaker attached to the end of the rod contained the loading weights. The knife edge on the picture frame and one in the slot cut in the rod formed a universal joint which insured that the load was applied uniformly across the width of the sample (neglecting roughness).

The ends of the furnace were fitted with fused silica windows and the sample was photographed periodically. The amount of creep was determined by measuring the distance between the top of the picture frame and the point where it passes through the SiC support plate. This measurement was made on the photographic negative using an X-ray film reader which has an accuracy of 2 microns. Even without going to the trouble of enlarging the image obtained on the 35 mm film, a sample deflection of 15 microns should be readily resolvable by this technique. This corresponds to an outer fiber strain of about .01%, calculated from the formula obtained assuming that the strain rate is proportional to stress. That formula is

$$y = \frac{\varepsilon \ell^2}{6h} ,$$

where y = deflection at center of span

ε = outer fiber strain

ℓ = distance between beam supports ($\sim$.65 inch)

h = thickness of beam ($\sim$0.013 inch).

The following runs were made:

A. A sample was loaded, cold, so that the outer fiber stress was about 20,000 psi. This was calculated using the formula

$$T = \frac{3}{2} \frac{P\ell}{wh^2} ,$$

where T = stress

P = load

w = width of beam

and the other symbols have the same meanings as before. This sample remained loaded and cold over a weekend. It broke on heat-up when the temperature reached 700°C, which occurred about 20 minutes after start-up.

B. Another sample was loaded to an outer fiber stress of 5000 psi and brought up to 1400°C (2552°F). This temperature was chosen because it is somewhat above the peak temperature expected to be encountered in gas turbines of the type for which parts made of Si_3N_4 are being considered. After 70 hours the film was developed and no creep deflection was observed.

C. With the temperature maintained at 1400°C, the loading on the sample was increased so that the outer fiber stress was 10,000 psi. After 118 hours, no creep deflection was observed.

Early in the course of this run a voltage transient on the line caused the fuse in the furnace power supply to blow during the night. The cold furnace and sample were reheated the following morning and the run was taken to start when the furnace temperature reached 1400°C again.

D. With the load maintained at 10,000 psi, the furnace temperature was raised to 1500°C (2732°F). After 92 hours no creep deflection was observed. The run was continued but the furnace winding burned out during one night. The sample was at room temperature and intact when examined at 8 a.m. the following morning but was found to have broken when examined an hour later. It is not known what caused the sample to break in this way, either during this experiment or during that described in Section A above.

E. The furnace was rewound and another sample was loaded to 10,000 psi and held at 1560°C (2840°F). No creep deflection was observed after 198 hours at temperature. The furnace winding failed during the night and the sample was found to be at room temperature and broken the following morning.

These results only allow an upper limit to be established for the creep rate. Assuming that a 20 micron total sample deflection had occurred, it can be estimated that the creep rate at 1560°C and an outer fiber stress of 10,000 psi is less than about $1.6\times10^{-7}hr^{-1}$ for the silicon nitride investigated. This value is about the same as the lowest steady state creep rate measured on reaction sintered, impure silicon nitride of around 75% of theoretical density in experiments run in the temperature range between 1200°C and 1315°C (the highest temperature investigated) and outer fiber stresses between 10,000 psi and 20,000 psi(3). The creep rates measured on this reaction sintered material are at least an order of magnitude less than those measured on Norton's HS-130 hot pressed silicon nitride for the same conditions(4). Judging from the published data, one can reasonably expect that the upper limit of the creep rate given here for the CVD silicon nitride at 1560°C and 10,000 psi is many orders of magnitude less than that which would be measured for either hot pressed or reaction sintered silicon nitride under the same conditions.

IV. Oxidation of CVD Si_3N_4

Oxidation of the CVD silicon nitride was investigated by maintaining specimens at an elevated temperature in air with periodic removal from the furnace for weighing to determine the amount of SiO_2 formed. During oxidation, the specimens lay on a bed of silicon nitride powder, the same as that described in Section I of this report, which was held in a silicon carbide boat.

The principal difficulty in the experiment arose from the fact that the surface area of the samples could not be determined. In spite of the roughness apparent in Fig. 2, the total surface area was far too small to be determined by the BET method. Accordingly, the surface area of the samples was taken to be that of smooth pieces having the same shape and a thickness of 0.013 inch. The weight increase of each sample due to oxidation was then expressed in milligrams per square centimeter and those data plotted as a function of the square root of time in hours.

Figure 3 is a plot of the data obtained in this way at 1410°C. The abscissa of every point on the true oxidation curve is, of course, obtained by dividing the abscissa of every point on the curve shown by the ratio of the actual sample area to the area assumed. It is estimated that that ratio lies between 2 and 4.

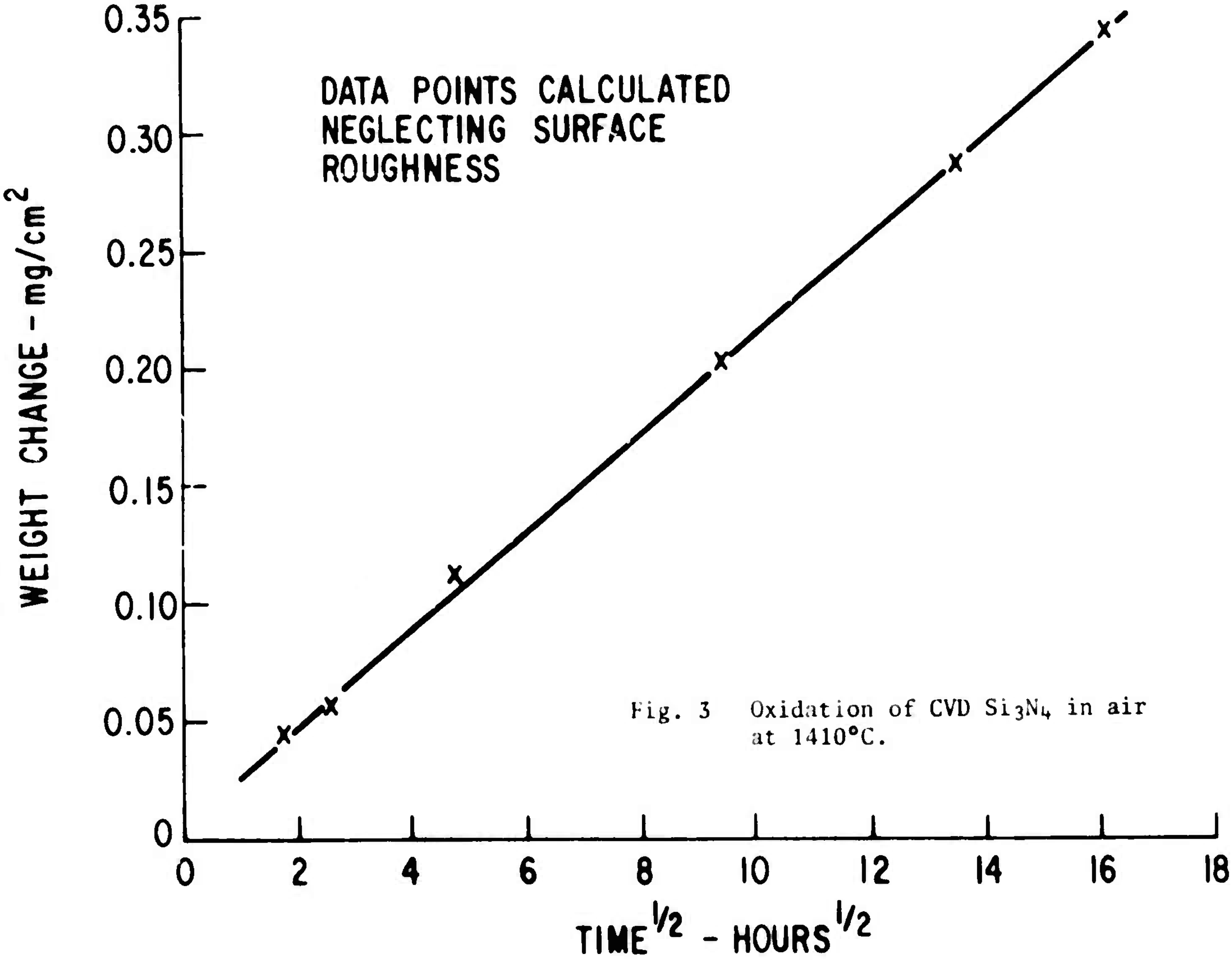

Fig. 3 Oxidation of CVD Si_3N_4 in air at 1410°C.

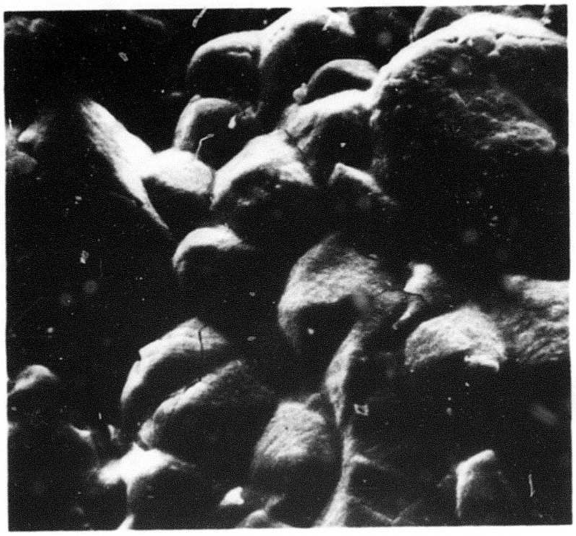

Fig. 4 Scanning electron micrograph of the surface of the CVD Si_3N_4 after oxidation for 259 hours in air at 1410°C. 500X

Figure 4 is a scanning electron micrograph of the oxidized surface of one of the samples at the end of the 1410°C run. The oxide layer, although cracked, is seen to be adherent. The oxide was determined to be α-Cristobalite. This was also the crystalline form of the oxide on the powder on which the samples lay.

Figure 5 shows oxidation data obtained at 1550°C. Comparison with the data in Fig. 4 shows that the oxidation rate at this temperature is apparently less than that at 1410°C. To check this, one of the samples used in the 1410°C run was soaked in HF to remove most of the oxide and placed in the boat with the other samples. Its rate of weight gain was significantly greater than that of the other samples as well as being greater than that which it had experienced at 1410°C. Accordingly it was concluded that the apparent decrease in oxidation rate on going from 1410°C to 1550°C probably results from a difference in the roughness (i.e. specific surface area) of the samples used in the two runs, with the samples run at 1410°C being the rougher. It may be further mentioned that the individual weight gains of the samples in each run were consistent with each other. Also, all of the samples used in a single run came from the same region of the original CVD deposit.

The oxidation rate of the CVD silicon nitride at 1550°C in air, then, can be taken from these data to be such as to produce a weight change of less than 0.01 $mg/cm^2\text{-}hr^{\frac{1}{2}}$. This is considerably lower than the only other values that were found in the literature. The oxidation rate for hot pressed material containing 5 wt% MgO is given as 1 mg/cm^2 for 100 hours at 1100°C$^{(5)}$. Another reference gives 0.11 $mg/cm^2\text{-}hr^{\frac{1}{2}}$ at 1400°C for an unspecified form of silicon nitride$^{(6)}$. Porous, reaction sintered material has also been qualitatively shown to have a high oxidation rate$^{(7)}$.

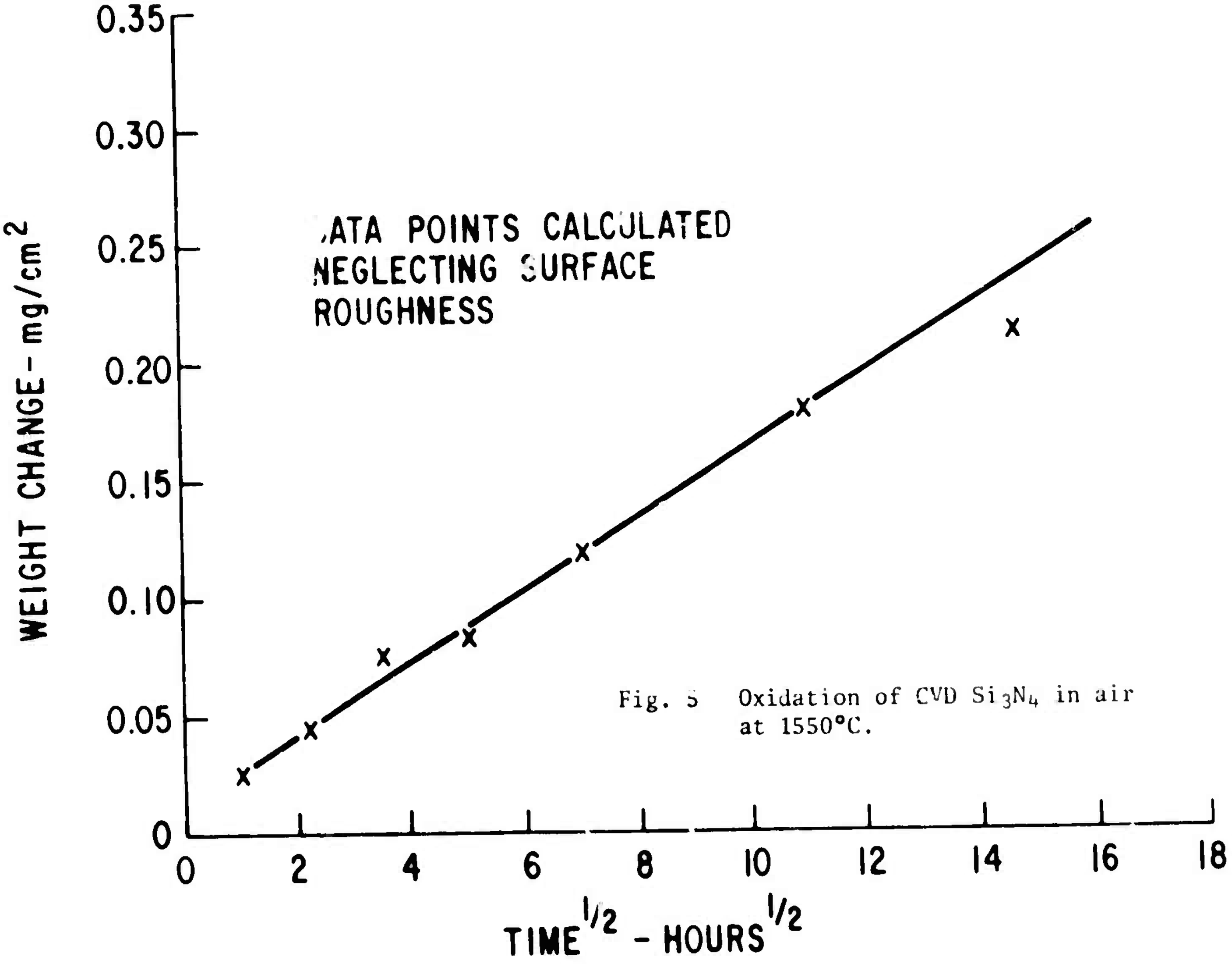

Fig. 5 Oxidation of CVD Si_3N_4 in air at 1550°C.

V. SiC Resistance Heaters

The development of a technique of producing SiC ceramic bodies of 90+ % density and controlled electrical resistivity by cold pressing and sintering(8) opens the possibility of making resistance heaters of this material. Commercial SiC resistance heaters are highly porous, coarsely crystalline bars produced by a reaction sintering technique. They are subject to oxidation when used in air, the SiO_2 thus formed reducing the contact area between grains and so increasing the resistance of the heater. This oxidation process restricts their use in air to temperatures below about 1400°C if reasonable lifetimes are to be achieved. Furthermore, it is recommended that they not be allowed to cool below about 700°C during use since cooling below that temperature leads to cracking of the oxide formed on the SiC grains thus exposing fresh surface to rapid oxidation. It was expected that a resistance heater made of dense SiC would have only a small surface area accessible to oxidation and should therefore last much longer in use than the currently available commercial heater.

Accordingly, rods of dense SiC having a length of 6 inches and ¼ inch in diameter were prepared by firing isostatically pressed silicon carbide powder containing boron and carbon for ½ hour at 2100°C in an argon-nitrogen atmosphere. The resulting rods were 91% dense and had an end to end room temperature resistance of about 2 ohms. The average grain size was about 4 microns. Rods of similar dimensions were prepared from commercial, ½ inch diameter SiC resistance heater rods by cutting and grinding to size.

Parallel flats were milled on the end 3/4 inch of each rod and, after copper plating, indium-gallium liquid was applied. The ends were held between water cooled copper blocks which served as the heat sinks and current leads to the rods. The peak current through the rods was adjusted so that a temperature of 1600°C was achieved at the hottest point on the surface. Each rod was fully exposed to the air and the temperature was measured with an optical pyrometer.

The current through the rod was controlled so that the full current was maintained for 5 minutes. This was followed by two steps of reduction by 1/3 of the peak current. Each of these current levels was maintained for 20 seconds. On the first, the peak rod surface temperature dropped to about 1250°C and the rod surface was only faintly self luminous on the second. This was followed by a final reduction to zero current which was maintained for 30 seconds, after which the current was increased to the peak value again in a manner inverse to that by which it was decreased.

Three of the rods made of commercial material were tested. They survived 129, 147 and 192 heating and cooling cycles, respectively. Failure occurred by a crack across the bar that had an oxidized surface. The face of one such cracked surface is shown in Fig. 6. The lighter material is SiO_2, which was also present in quantity on the outside surface of the rod. Figure 7 is a micrograph of the cross section of a commercial rod sample before use. The large grain size and porosity are apparent.

Observation of these rods during testing revealed that the cracks formed many cycles before the rod finally failed to conduct current. The rigid rod supports apparently kept the pieces in contact and maintained current continuity until the crack surface became badly oxidized.

None of the dense SiC rods failed during testing. One was run for 1587 cycles and another for 2544 cycles. The only change in the latter was a decrease

Fig. 6 Cracked surface of a commercial SiC heater rod which failed during cyclic testing. 15X

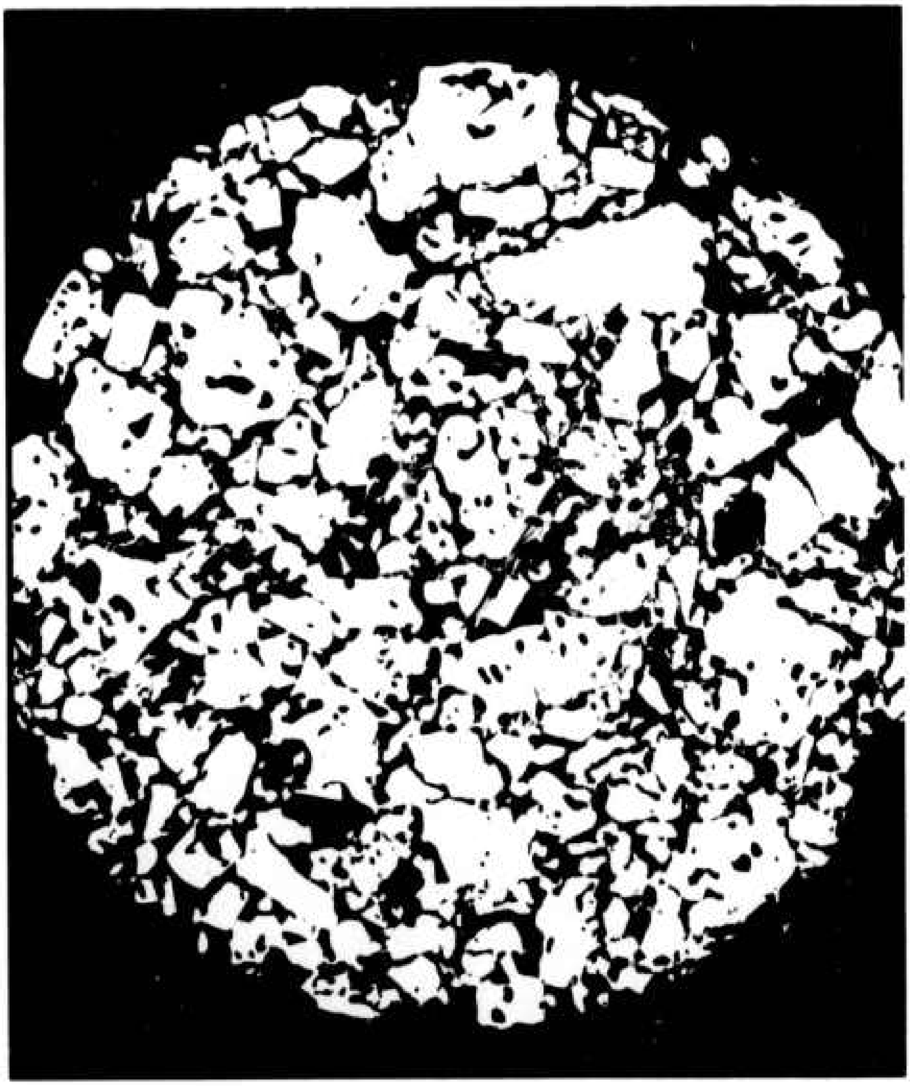

Fig. 7 Cross section of a commercial SiC heater rod before use. 20X

in its room temperature resistance; going from 2.05 ohms when the test started to 1.5 ohms when it was terminated. The peak current in both of these rods was around 30 amperes when the applied voltage was about 41 volts. The outer surface took on a yellowish color after the first few cycles which did not change appreciably thereafter. Figure 8 is a cross section of the rod that had run for 2544 cycles. It looks no different from a pristine rod. In particular, there is no evidence of a thick oxide layer on the outer surface. There was no indication that the dense SiC rods could not have endured the test indefinately.

In the light of these results, it was decided to raise the peak surface temperature to 1700°C. When this was done, it was observed that those portions of the rod surface whose temperature was around 1630°C or higher were oxidizing rapidly. Bubbles of silica could be seen being blown out of the surface. These were initially clear but soon became opaque. In Fig. 9, the lower rod had been run for 1587 cycles at a surface temperature not exceeding 1600°C. The upper rod had been run for 10 cycles with a peak surface temperature of 1700°C. This latter rod was not uniform in resistivity along its length so the hottest region, indicated by the bubbly surface, did not occur in the center of the rod. The bubbling did not extend into the portion of the rod where the temperature was less than 1630°C.

Figure 10 is a micrograph of the bubbly surface and Fig. 11 is a cross section of the bubbly portion of the rod. The latter shows that a structural transformation had occurred. The central portion has the original structure of the rod but the surrounding material is very porous and composed of large crystals (the bright areas). Both the core and its surrounding region are composed of β-SiC. There is little oxide in the porous region; most of it is on the outside surface.

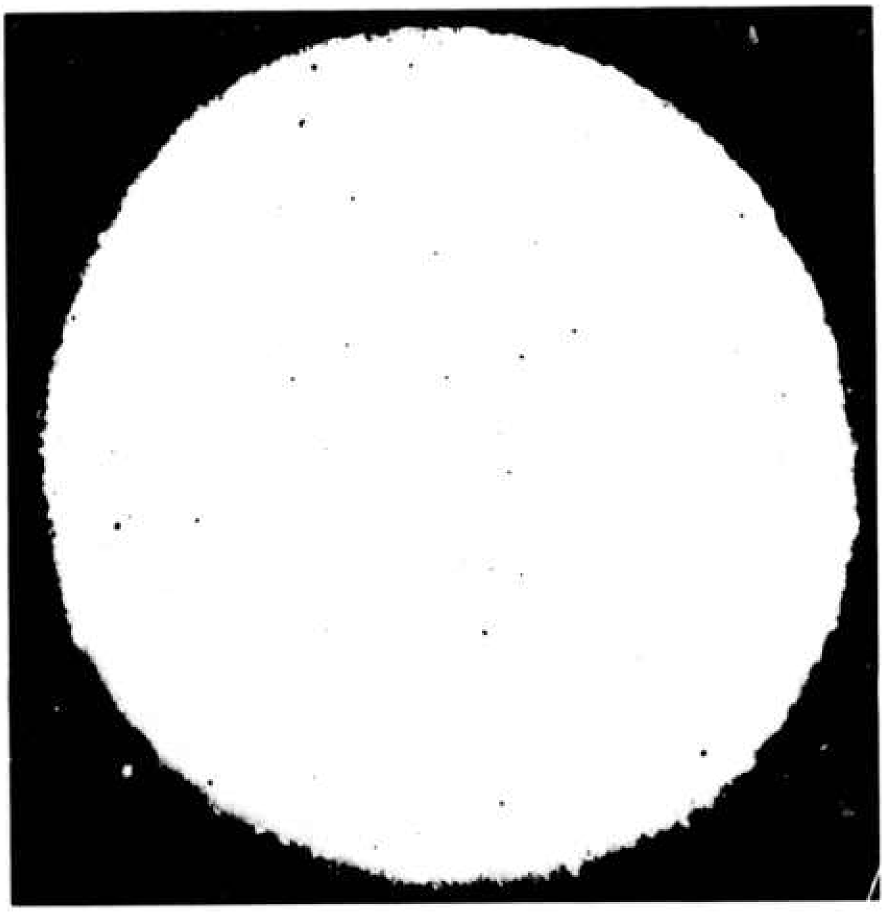

Fig. 8 Cross section of a dense SiC heater rod which had been cycled between room temperature and 1600°C 2544 times. 20X

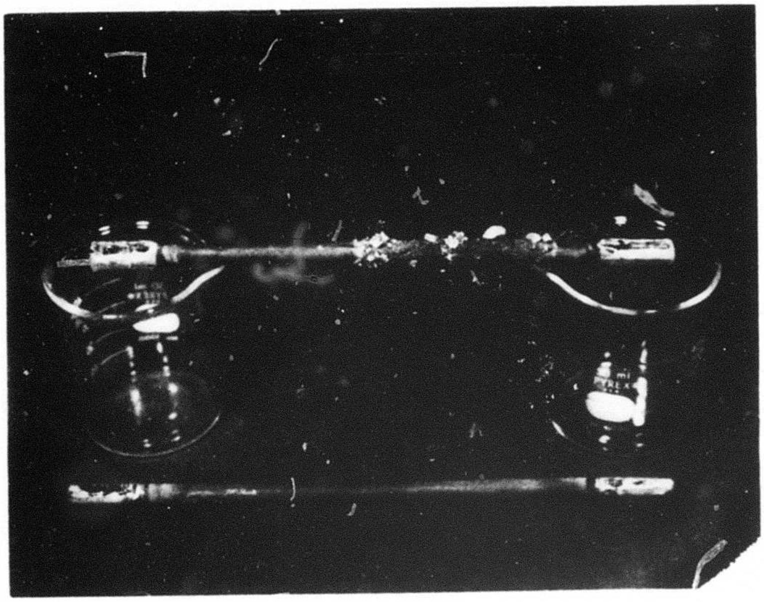

Fig. 9 Lower rod was run for 1587 cycles between room temperature and a peak surface temperature of 1600°C. The upper rod ran 10 cycles to a peak surface temperature of 1700°C.

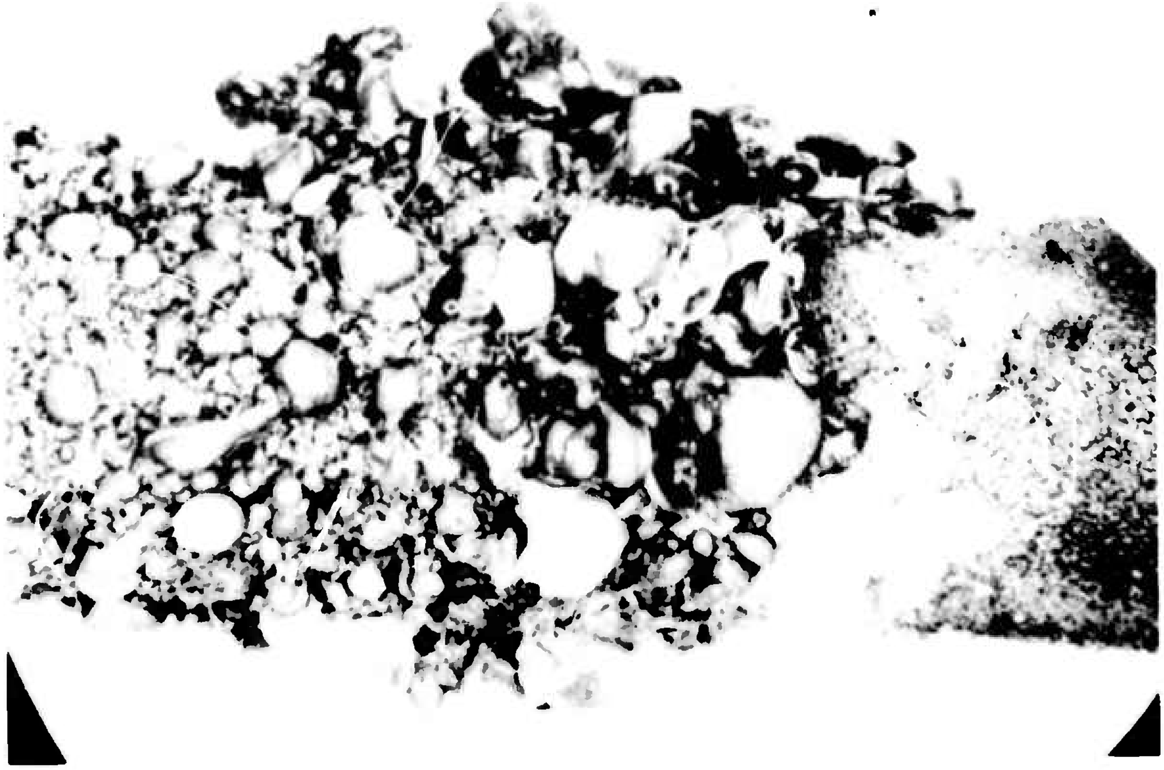

Fig. 10 Silica bubbles on the portion of the rod surface that had been at a temperature greater than 1630°C. 10X

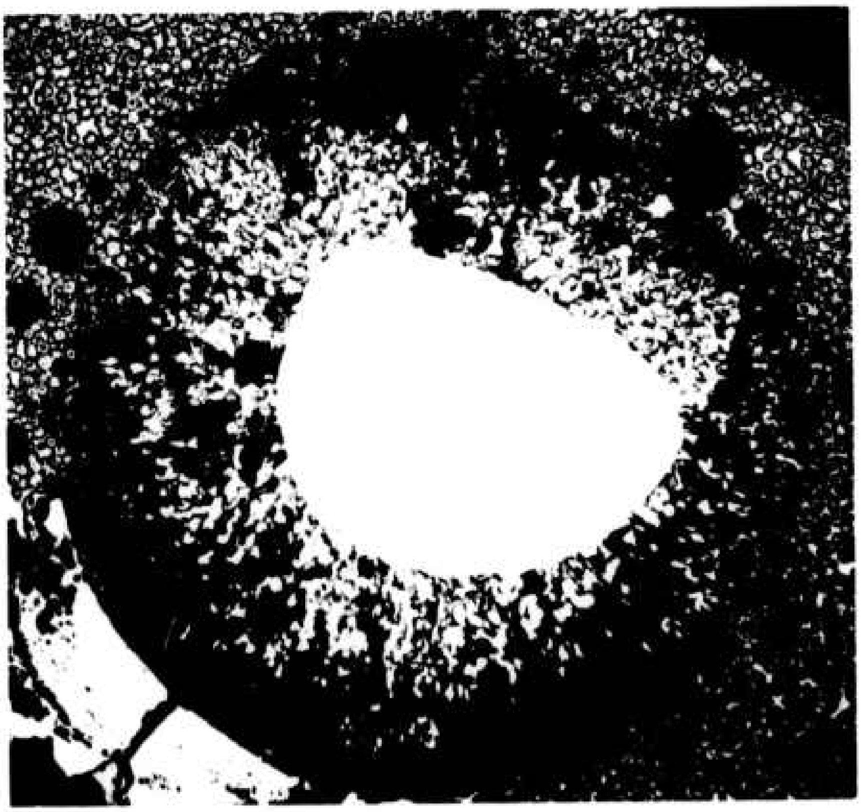

Fig. 11 Cross section of bubbly portion of rod. 20X

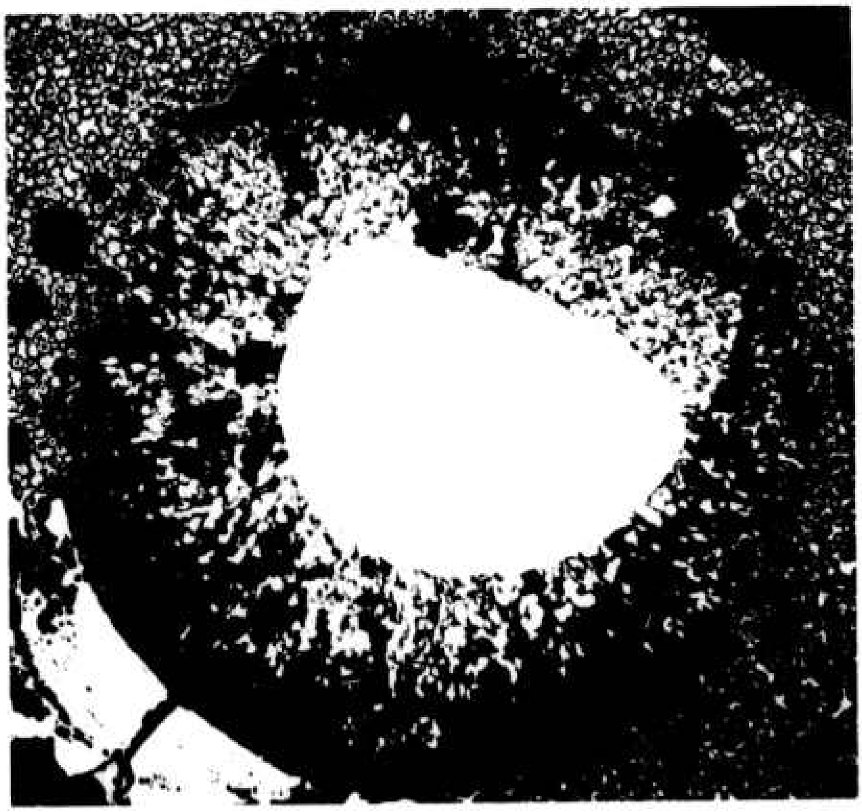

Fig. 11 Cross section of bubbly portion of rod. 20X

These tests indicate that resistance heaters made of dense SiC would be clearly superior to those currently offered commercially since they could be operated at higher power loadings (in watts per unit area of radiating surface) than those recommended for the commercial product and still have a very long service life. In addition, they could be cooled to room temperature after use without being adversely affected.

VI. Sintering of SiC

A. Introduction

At the conclusion of the first three months of the contract period, the focus of the work turned to investigating the sintering behavior of covalently bonded solids. Ceramics made of these are in a special class in that they are difficult to fabricate by conventional sintering processes. Until recently, phase-pure covalent solids such as SiC, Si_3N_4, AlN, and BN could be densified only by the application of high external pressures at high temperatures. The hot pressing of such materials is expensive and limited to fabricating pieces of simple geometry. On the other hand, the densification of powder compacts of several covalent materials (Si_3N_4, AlN) can be achieved by the method of liquid phase sintering in the absence of an externally applied pressure. The presence of a liquid phase on the grain boundaries at high temperature usually has a deleterious effect on high temperature creep and strength and, therefore, limits the usefulness of bodies having this type of structure.

Prochazka(8) recently discovered a method of conventionally sintering SiC in the solid state. He added about 0.5 wt% boron and carbon to submicron β-SiC and demonstrated that sintered densities as high as ∿98% of theoretical could be obtained by pressureless sintering. Single phase microstructures (except for some carbon inclusions located in residual pores) could be developed with an average grain size of 2 to 3 microns. It was hypothesized that the boron segregates in the grain boundaries to reduce grain boundary energy while the carbon deoxidizes the surfaces of the β-SiC grains to increase the solid-vapor surface energy. In this way the ratio of the grain boundary to solid-vapor surface energy (γ_{GB}/γ_{SV}) is decreased in such a direction as to allow the occurrence of densification. Prochazka used a geometrical analysis of the interfacial energies and dihedral angles in a porous structure undergoing sintering and came to the conclusion that the requirement for a pore surrounded by three grains to close or densify is that the equilibrium dihedral angle (Θ) be greater than 60° or that γ_{GB}/γ_{SV} be $<\sqrt{3}$. The equation which connects these two parameters and applies at the grain boundary-solid vapor interface is

$$\gamma_{GB} = 2\ \gamma_{SV} \cos \frac{\Theta}{2} .$$

F. Objectives of the Research

The goal of this research program is to develop a better understanding of the sintering of covalently bonded ceramics with emphasis on advances in sintering theory and the generation of dense structures. Special effort will be devoted to the determination of sintering mechanisms, whereby doping additions and control of sintering atmosphere enable the conventional sintering of silicon carbide. A study of the development of interparticle bonds (necks) as well as changes in the dihedral angle at pore-grain boundary junctions will be undertaken in order to determine the effect of dopants on pore and grain morphology. SiC was chosen for initial study with the hope that understanding the sintering mechanism in this material, for which considerable technology already exists, will allow extension of the science to such covalent elements and compounds such as C, Si, AlN and BN.

C. Early Stage Sintering of Doped-β-SiC

1) Ceramic Powders and Sintering Conditions

The early stage sintering of β-SiC containing carbon only, boron only, and both carbon and boron was investigated by surface area measurements and scanning electron microscopy. In all cases, the amounts of carbon and boron present was 0.8 and about 0.6 wt%, respectively. The β-SiC powders selected for study were characterized by specific surface areas between 8 and 11 m^2/g. All the SiC powders had about the same concentration of all other impurities. Major impurities were (in ppm) oxygen 1700, tungsten 300, iron 200, chloride 200, nitrogen 80, calcium 50, and aluminum < 10.

In some cases the initial sintering of loose powders, as well as that of powder compacts of doped β-SiC, was investigated. Submicron β-SiC powder is generally difficult to die-press without binders, but successful results could be obtained by screening the powder through a -60 mesh nylon screen and die-pressing 3 gram samples in a 5/8" diameter die at 2500 psi. In all cases, the resulting powder compacts were isostatically pressed at 30,000 psi to obtain green densities near 58% of theoretical. (The theoretical density of SiC is about 3.21 g/cc.)

Sintering experiments were performed in flowing Ar (~5 ppm O_2) at one atmosphere in a carbon element resistance furnace at temperatures between 900 and 2000°C. The effective oxygen pressure inside the furnace was not determined. Temperature was measured optically and controlled to ±20°C. Investigation of grain growth during sintering of β-SiC containing excess carbon was carried out at 1300°C for times up to about 85 hours. Graphite crucibles were used as containers in every case.

2) Surface Area Measurements and Results

Surface area measurements were made by the single point B.E.T. method* using a continuous flow of 30% nitrogen in helium. By calibrating the system after each nitrogen desorption run, the uncertainty in the specific surface area based on about 5 measurements was reduced to about ±0.2 m^2/g for samples with specific surface areas between approximately 5 and 10 m^2/g. Figure 12 illustrates the effect of sintering temperature on the specific surface area of loose powder and pressed compacts of β-SiC containing carbon and boron. The sintering time at temperature was 10 minutes. For the case of loose powders there is a decrease in the specific surface area with sintering temperature, the initiation of surface area reduction being noticeable at about 1500°C. Pressed compacts, however, exhibit a higher specific surface area than the loose powder up to about 1800°C at which point there is a reversal. It is suggested that the apparent increased area below 1800°C is caused by N_2 condensation in fine capillaries or pores, perhaps 10 to 100Å in size, that exist in the sintered disks. The difference in specific surface area, of the two types of

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* Surface area analyzer, Quantachrome Corporation, 337 Glen Cove Road, Greenvale, N.Y.

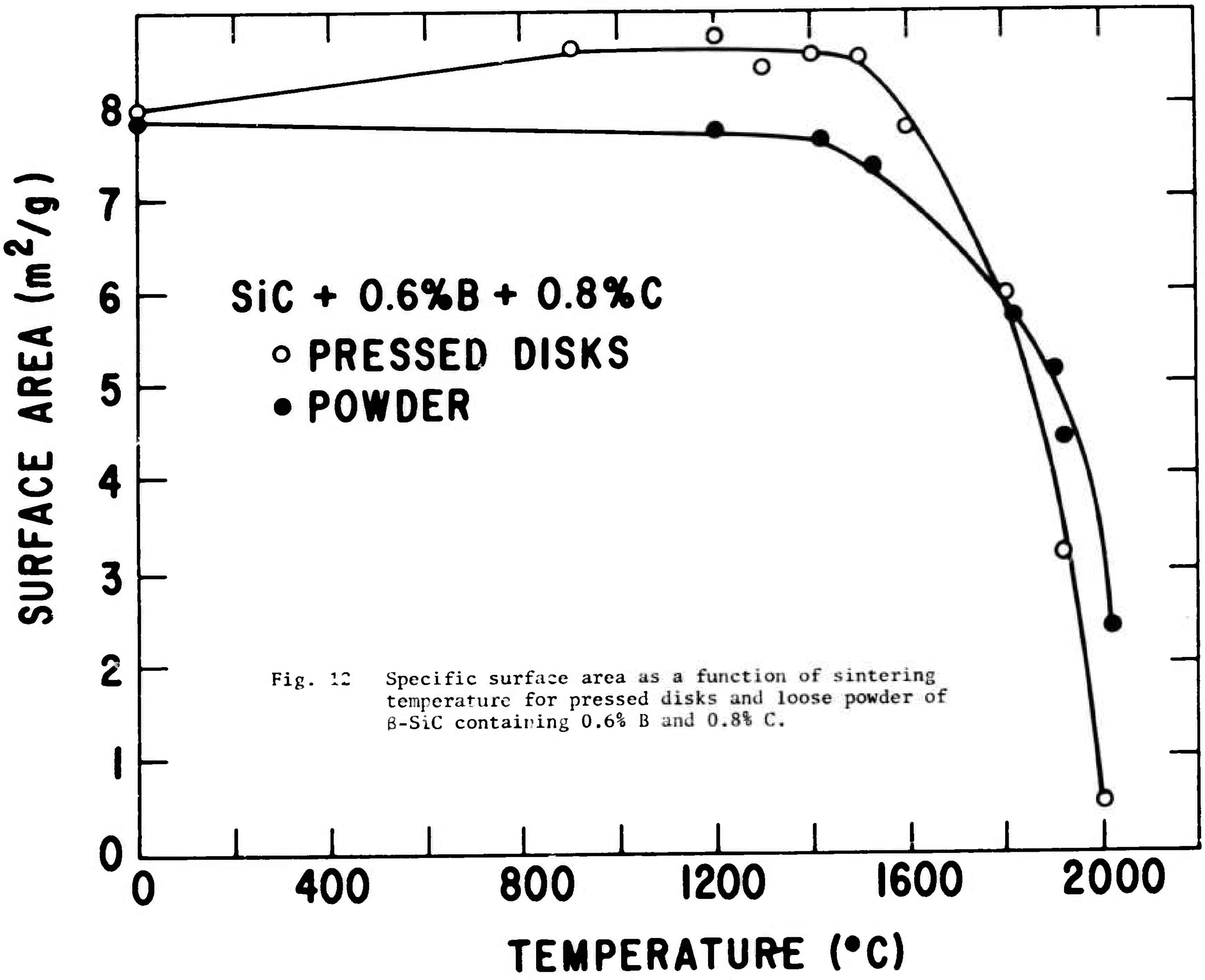


Fig. 12 Specific surface area as a function of sintering temperature for pressed disks and loose powder of β-SiC containing 0.6% B and 0.8% C.

samples sintered above 1800°C is probably caused by the larger number of touching nearest-neighbor grains surrounding a given grain in a pressed compact as compared to that found in a loose powder, thus increasing the number of necks and reducing the solid vapor surface area available for the adsorption or desorption of nitrogen molecules. The specific surface area of sintered, pressed compacts also begins to decrease at about 1500°C with the most rapid reduction occurring between 1800 and 2000°C. It is interesting that shrinkage measurements made on the sintered, pressed compacts (Table II) reveal that the initiation of densification also takes place at about 1500°C.

β-SiC containing 0.7 wt% carbon responds quite differently to temperature than do those compositions containing both boron and carbon. In Fig. 13 and Table II it can be observed that this material exhibits a decrease in specific surface area at much lower temperatures (near 1250°C) but no densification or shrinkage for temperatures up to 2000°C. The greatest change in specific surface area occurs between 1300 and 1500°C.

The kinetics of surface area reduction in highly porous sintered compacts of β-SiC containing 0.7 wt% carbon can be determined by surface area measurements. Ideally, the approximate relationship between the average size (D) of grains (or particles) with spherical or cubic morphology in a lightly sintered powder compact, and the corresponding specific surface area (S) is

$$D = \frac{6}{\rho S} ,$$

where ρ is the density of the solid in g/cm^2 and D is in microns for S

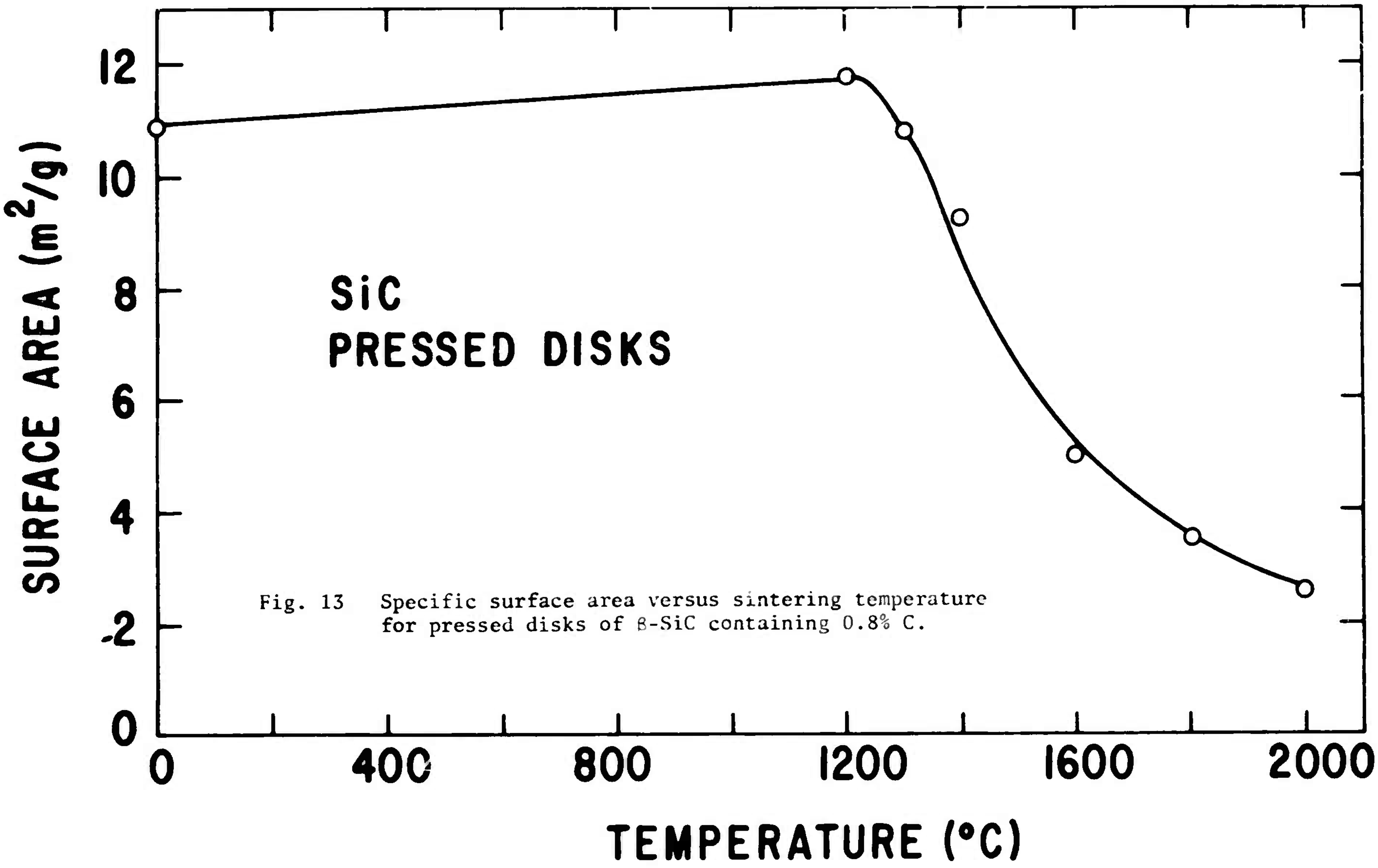


Fig. 13 Specific surface area versus sintering temperature for pressed disks of β-SiC containing 0.8% C.

TABLE II

Sintered Densities of Doped β-SiC Compacts For 1 Hr Hold in Flowing Ar Atmosphere

Composition	D_0/D_t	D_{1500}/D_t	D_{1700}/D_t	D_{1900}/D_t
SiC + 0.7%C	59.2%	59.2%	59.2%	59.2%
SiC + 0.4%B	57.3%	57.3%	58.6%	60.7%
SiC + 0.7%C + 0.4%B	58.6%	59.8%	65.7%	72.3%

D_0 = initial green density

D_t = theoretical density (3.21 g/cc)

D_{1500} = density after sintering at 1500°C measured in m^2/g. A linear fit of the specific surface area data with sintering time at 1300°C (see Fig. 14) was obtained by plotting $(1/S)^4$ versus time at temperature. Since D is proportional to 1/S, this means that the grain, or particle, size increases according to $t^{1/4}$. The significance of this relationship will be discussed later.

3) Observation of Sintered Structures by SEM

Scanning electron micrographs of sintered, loose powders and of fractured surfaces of sintered, pressed compacts show some interesting structural features depending on the dopant(s) added to β-SiC. The general observations described below are independent of temperature between 1500 and 1900°C except that the differences between the various composition are accentuated at higher temperatures. The SEM photomicrographs of aggregates formed during the sintering of loose powders of β-SiC + 0.7% C + 0.4% B shown in Fig. 15 demonstrate that dense, spherically shaped aggregates form in β-SiC containing both carbon and boron, (a material that densifies at 1900°C) but β-SiC having excess carbon (a material which exhibits no densification at 1900°C) consists of an ill-defined aggregated structure which does not "ball-up" upon sintering. Sintered aggregates of β-SiC doped with boron only exhibit a combination of the structural features of the other two powders. Table II shows that this type of powder is characterized by a small amount of linear shrinkage (about 2%) at 1900°C; the same holds true even at higher temperatures.

SEM photomicrographs, shown in Figs. 16 and 17, were taken from fractured surfaces of lightly sintered compacts. These show some striking

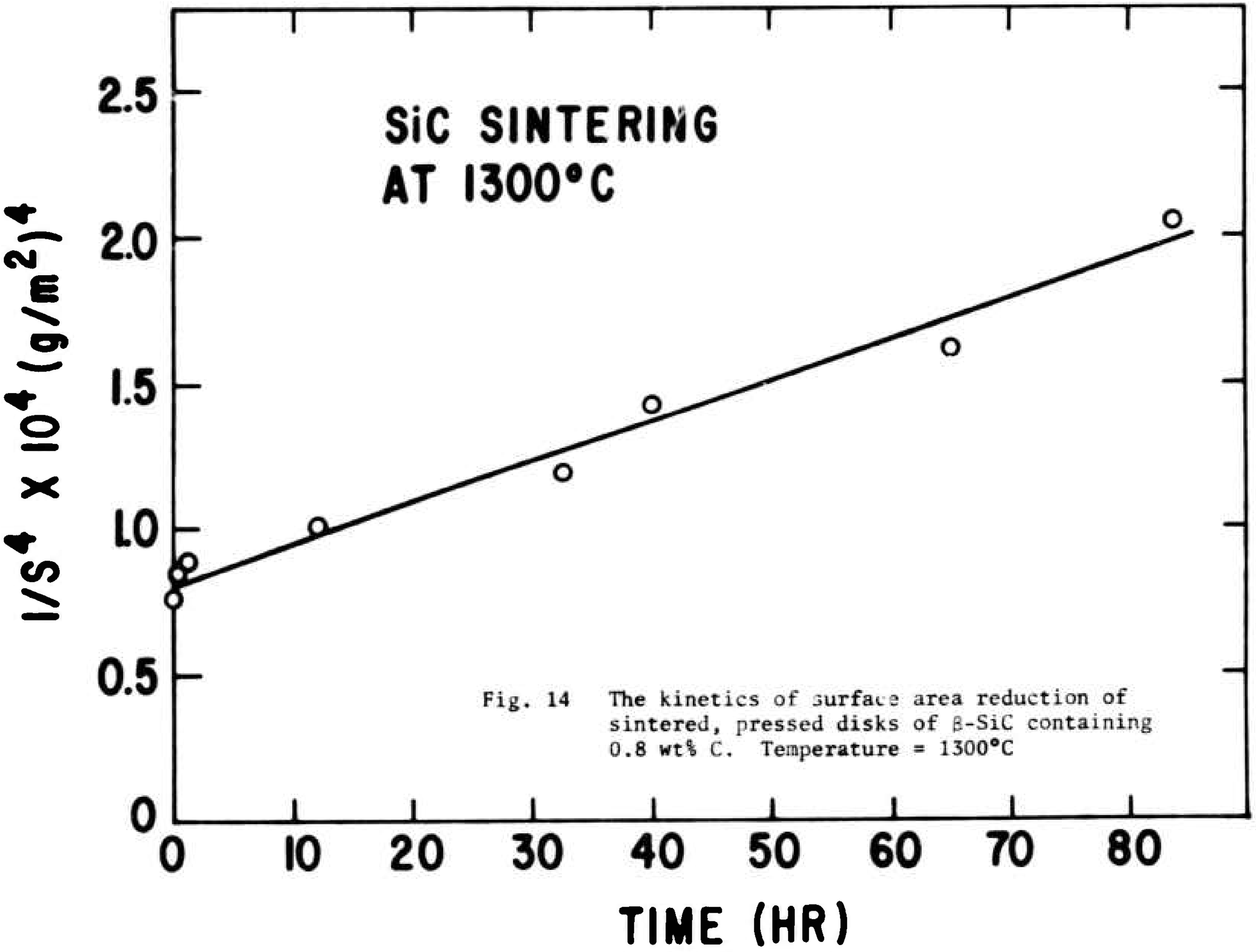
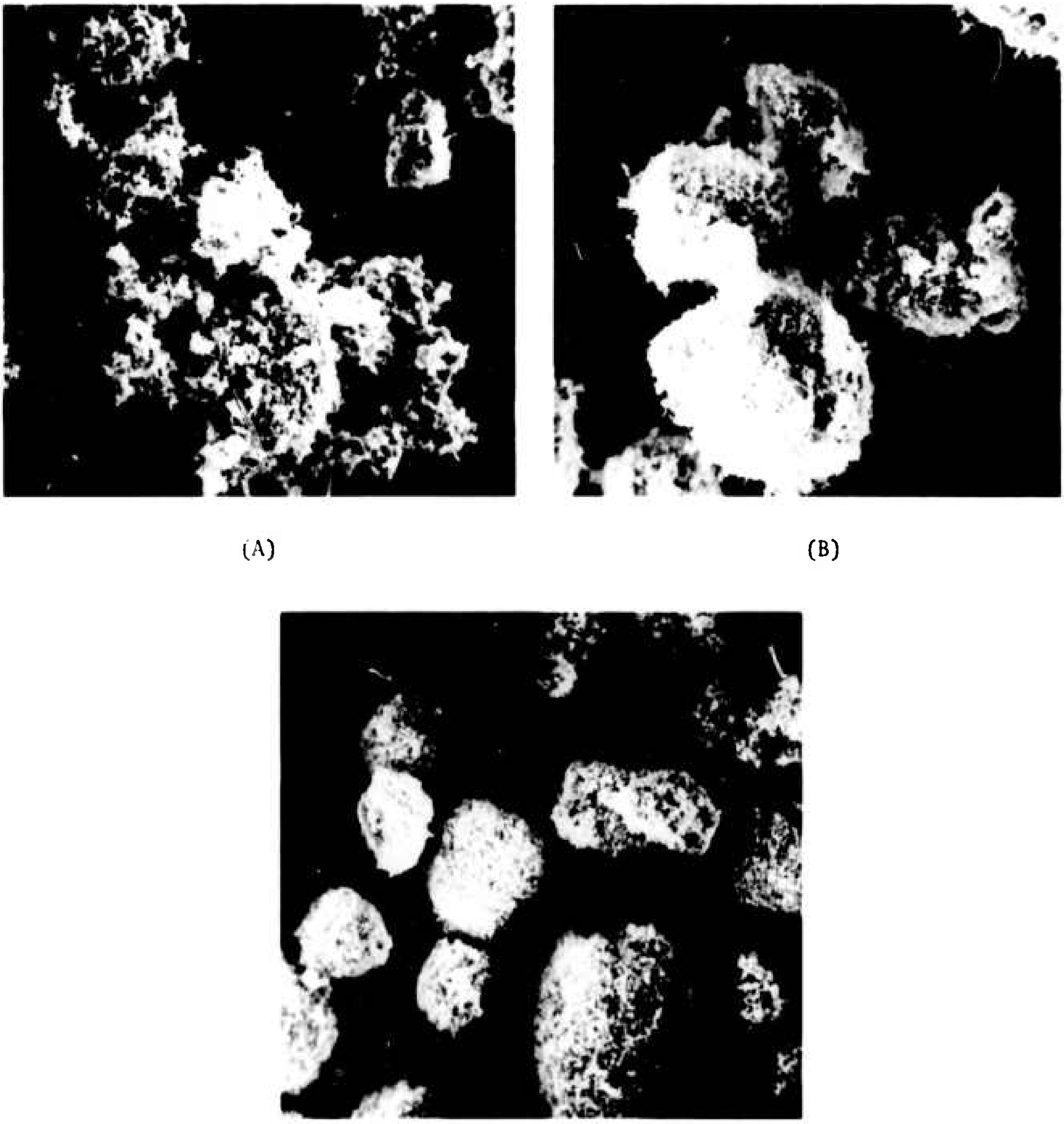


Fig. 14 The kinetics of surface area reduction of sintered, pressed disks of β-SiC containing 0.8 wt% C. Temperature = 1300°C

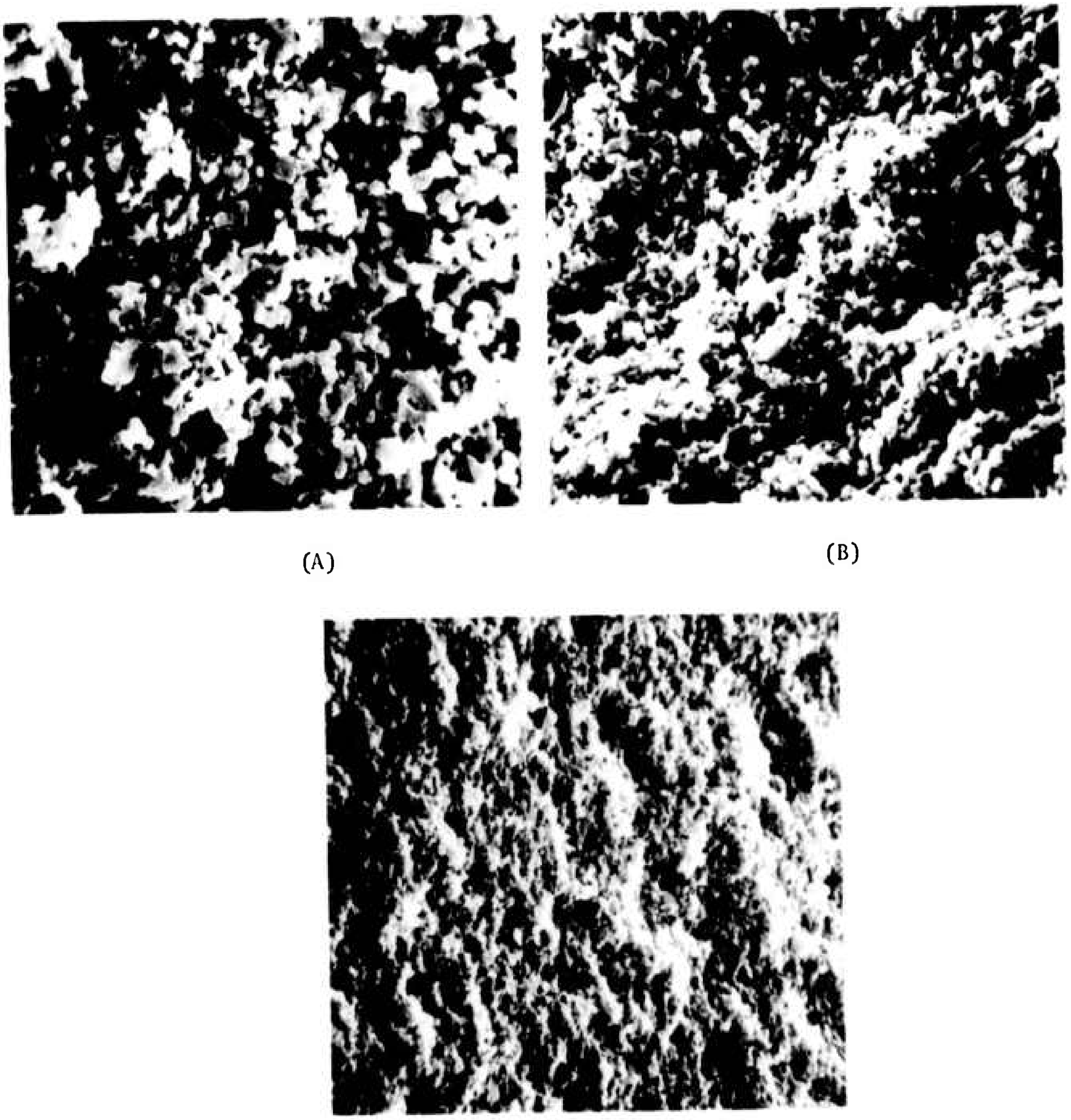


(A)

(B)

(C)

Fig. 15 SEM photomicrographs of aggregates formed during the sintering of loose powders of β-SiC containing (A) 0.8% C, (B) 0.6% B, and (C) 0.8% C and 0.6% B. The samples were sintered at 1900°C for 1 hr. X500

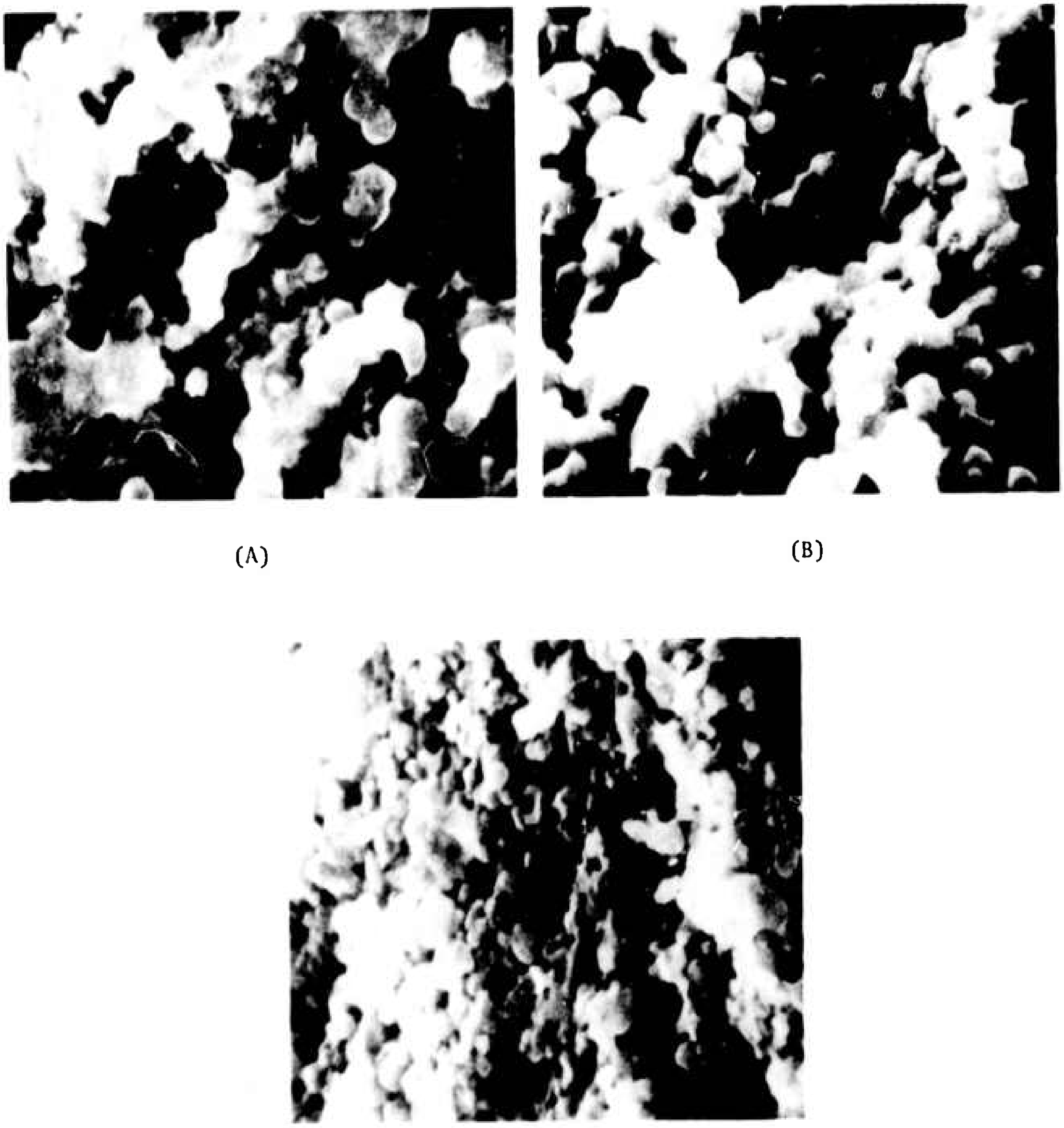


(A)

(B)

(C)

Fig. 16 SEM photomicrographs of fractured surfaces of sintered, pressed disks of β-SiC containing (A) 0.8% C, (B) 0.6% B, and (C) 0.8% C and 0.6% B. The specimens were sintered at 1900°C for 1 hr. X2000



(A)

(B)

(C)

Fig. 17 SEM photomicrographs of fractured surfaces of sintered, pressed disks of β-SiC containing (A) 0.8% C, (B) 0.6% B and (C) 0.8% C and 0.6% B. The specimens were sintered at 1900°C for 1 hr. X10,000 differences in the size, shape and appearance of grains and pores as a function of composition. Sintered β-SiC containing excess carbon is characterized by a highly porous, interconnected structure having randomly distributed solid regions composed of clusters of grains. The average width of pore spaces between the dense clusters of grains is about 0.8μ. This is slightly larger than the average grain size which is about 0.6μ. The dense clusters of grains have an average size of approximately 2.5μ and are, therefore, much larger than the average grain size and pore width.

In contrast, sintered compacts of β-SiC doped with boron and carbon have a fine grain and fine pore structure. The grains appear to be equiaxed and have an average size of about 0.3μ. The average pore size is smaller than the average grain size. Compacts of this composition have densified from about 59 to 72% of theoretical density by firing for 1 hr at 1900°C in flowing Ar.

SEM micrographs of sintered compacts of β-SiC having only boron as the dopant reveal a new structural feature, namely, that the grain boundary solid-vapor junctions appear to be more sharply defined. The grains are equiaxed and have an average size of about 0.4μ. Pore structure can be seen, with the average pore size being about the same as the average grain size.

D. Discussion

Surface area and shrinkage measurements as well as direct observation by scanning electron microscopy can provide considerable information about the development of structure in porous solids undergoing sintering. For example, the early stage sintering behavior of β-SiC doped with carbon and boron shows that specific surface area reduction and the initiation of densification take place almost simultaneously at 1500°C in a submicron powder. This is a very unusual finding in that most submicron powders of ionic (oxide) materials generally coarsen by surface diffusion at temperatures well below the temperature at which densification begins. The fact that β-SiC powder containing carbon exhibits a decrease in surface area at a temperature near 1250°C and no densification up to 2000°C indicates that the addition of boron to β-SiC containing excess carbon impedes surface diffusion and inhibits grain growth at temperatures up to 1500°C, but permits densification at higher temperatures. The presence of boron and carbon in β-SiC enables the generation of anequiaxed fine-grain structure with a uniform dispersion of small pores. The addition of boron to pure β-SiC gives rise to sintered material characterized by a relatively small grain size (ie. grain growth by surface diffusion is still minimized) but only a few percent of linear shrinkage takes place. Furthermore, the grain boundary-solid-vapor junctions are clearly evident which indicates that the material is approaching geometrical equilibrium.

The kinetics of grain growth, as deduced from specific surface area reduction, shown in Fig. 14, strongly indicate that the mechanism is one of surface diffusion. Greskovich and Lay(9) showed that grain growth or particle coarsening in porous compacts may be viewed as the growth of the neck regions between two particles followed by the rapid migration of the grain boundary developed between the particles through the smaller of the two. They used Nichols and Mullins(10) equations for the time required to fill a neck between two spheres of arbitrary size by surface diffusion and arrived at the conclusion that surface diffusion-controlled grain growth in very porous compacts should approximately follow a $t^{1/3}$ dependence. Our experimental data agree well with this prediction.

VII. Sintering of B_4C

A. Introduction

As a preliminary work in this study, various compounds suitable for the investigation of the sintering phenomena in covalent solids were considered. One of the selected materials was boron carbide for the following reasons:

1) The study of bonding and bond lengths in B_4C justifies this material to be classified as a typical covalent solid.

2) In contrast with silicon carbide, which is believed to have an extremely narrow region of nonstoichiometry, B_4C is known to have a wide region of nonstoichiometry covering at least the compositional interval from $B_{13}C_2$ to $B_{12}C_3$. Consequently, it may be a useful model material for the investigation of the effect of structural defects in covalent solids.

3) It is a very stable compound with a low vapor pressure up to the melting point, which makes it particularly attractive for sintering experiments.

4) B_4C ceramic is now being fabricated exclusively by hot-pressing. It has several important applications due to its hardness, low specific

weight, high thermal conductivity and neutron absorption properties. Thus, new information on its sintering may be of technological interest.

The objective of the following paragraphs is to describe introductory sintering experiments performed with B_4C in order to determine whether or not it can be successfully sintered at all without using pressure, and hence used as a model material in the planned sintering studies. We refrain at this time from reviewing the complex crystal chemistry of B_4C and the yet not fully understood phase relations in the boron-carbon system.

B. Powder Specifications

B_4C from two different sources was procured and characterized by spectrographic analyses. Oxygen and nitrogen were determined by vacuum fusion and surface area by low temperature nitrogen adsorption.

Specimen No. 1: B_4C - Poly Research Corporation, New York
Cat. No. B-315, specified as 99.9% pure, -325 mesh.
Specimen No. 2: B_4C - Grade HP - Boride Products, Inc., Michigan
Specified as 99.0 pure with Fe, Mg and O as main impurities,submicron particle size.

The first powder was gray, highly crystalline and too coarse for sintering experiments. Therefore, a -5μm particle size fraction was separated by sedimentation from an aqueous dispersion. The chemical composition given in Table III refers, however to the original specimen.

TABLE III

B_4C Powder Characteristics

Sample	B_4C-1	B_4C-2	B_4C-2 calcined at 1450°C
Composition %:			
C	21.9	21.1	22.9
N	n.d.	0.3	0.3
O	0.21	4.4	0.55
Fe	0.09	1.0	1.0
Mg	<0.01	2.0	2.1
Ti	n.d.	0.002	n.d.
Al	n.d.	0.02	n.d.
Si	0.11	n.d.	<0.05
B/C Molar Ratio	3.94	-	3.57
Specific Surface Area m^2/g	1.6	17.2	16.1
Density	2.48	n.d.	n.d.

The response of this powder to sintering was, in general, not favorable as shown in Table IV.

The powder from the second source had a specific surface area corresponding to 0.08μm average particle size. The morphology of its particles is shown in Fig. 18, which also demonstrates the very wide crystallite size distribution. The striations seen in some of the particles are probably stacking faults. The aggregates of very fine particles could be free carbon which also has been detected by electron diffraction. As shown in Table III, the purity of this powder is much less than specified by the supplier. The high oxygen content, however, can be reduced to an acceptable level of 0.5% by calcination of the powder at 1450° in 100 Torr argon for one hour.

The high magnesium content is obviously the result of the preparation technique which uses reduction of B_2O_3 by Mg metal in the presence of carbon.

Mg has been recently claimed to be an effective sintering aid in densification of B_4C (U.S. Pat. No. 3.749571 of July 1973) see also T. Vasilos and S. K. Dutta, Bull. Amer. Cer. Soc., Vol. <u>53</u>, 453 (1974)). This impurity has not been considered deleterious.

C. Processing and Sintering

For preparation of the sintering specimens, the powders were dispersed in a ½% benzene solution of an organic pressing aid and in some experiments, 50g batches were milled 5 hrs by 3/16" cemented carbide balls in

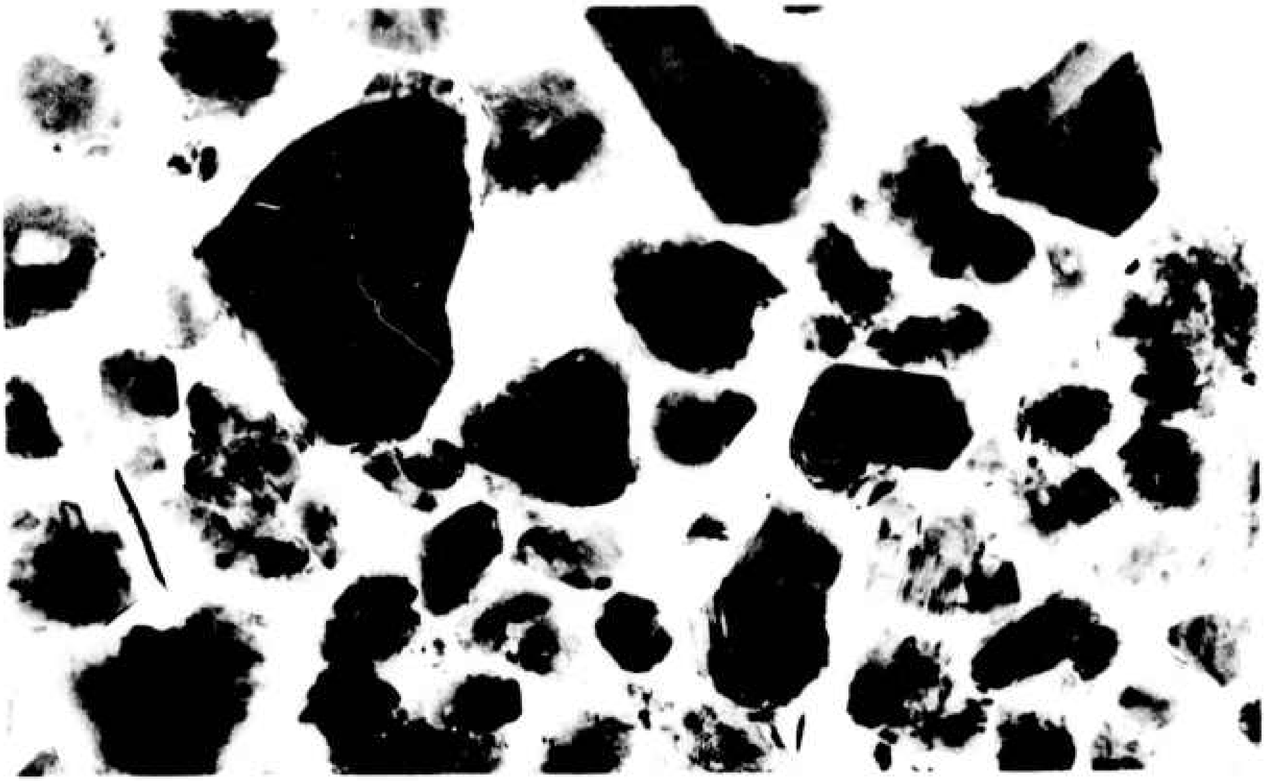


Fig. 18 Boron carbide, grade HP from Boride Products, Inc. TEM, 40,000X.

TABLE IV

Summary of Sintering Experiments with B_4C

Exp. No.	Powder No.	Addition % by wt.	Sint. Temp. °C	Final Density g/cc	Final Density %	Shrinkage %	Comment
1	1	none	2100	1.55	61.8	nil	
2	1	none	2300	1.60	63.5	1.5	
3	1	none	2350+	-	-	-	melting
4	2	none	2120	1.65	65.5	4.2	
5	2	none	2260	1.81	71.9	6.6	
6	2	0.5 Be_4C	2130	2.05	81.6	9.4	
7	2	1.0 Be_4C	2130	2.01	80.1	8.9	
8	2	same	2230	2.14	85.5	11.0	
9	2	same	2280	2.38	94.0	16.5	
10	2	same	2300+	-	-	-	partial melting
11	2	1% SiC	2150	1.96	77.8	n.d.	
12	2	10% SiC	2150	2.07	80.6	n.d.	
13	2	1% SiC	2300+	2.37	93.6	n.d.	melting in contact with setter

plastic containers. The dispersion was then dried and the powder screened through a 60-mesh sieve. Die pressing of 2g pellets at 6000 psi yielded a green density of about 60% of the theoretical -2.54 g/cc.

In the course of this investigation, additions were made to B_4C in hope of aiding its sintering. For this purpose, two compounds were selected: SiC and Be_2C. The first was chosen as a species which was expected to bring about liquid formation at high temperature and hence aid densification via liquid assisted sintering. This choice was essentially an extension of observation of sintering in the system SiC-B_4C (see S.R. Billington, J. Chown, A.E.S. White in "Special Ceramics", P. Popper, ed., Vol. 2, 1962).

Be_2C on the other hand, was chosen as a species which was not expected to bring about liquid formation when added to B_4C in small amounts. The choice of the additions was made without knowledge of the high impurity content of B_4C which may have changed the phase relations considerably.

A further addition was elemental boron to all compositions made from powder 2, calculated so as to compensate for the hyperstoichiometric carbon determined by analysis (Table III). For this purpose Elemental Amorphous boron, obtained from Callery Chemical Co., Pa. (Tech. Bulletin, No. C-1400) was used.

The compacts were sintered in a high-temperature carbon element resistance furnace at temperatures between 2100° and 2300°C in flowing argon or argon-nitrogen atmospheres. Commercial high purity gases were used with oxygen content less than 10 ppm as determined by the supplier. The furnace and its performance has been described previously (P. D. St. Pierre, M. J. Curran, G.E. TIS Rept. 72CRD012, Dec. 1972).

Temperature measurement was done with an L&N pyrometer by directly viewing the sintering object. The pyrometer was calibrated at the melting point of a saphire single crystal, i.e., at 2050°C. No other corrections, such as for emissivity or reflectance of the viewing part were considered. The reading is believed to be accurate to within ±25°C; the main source of uncertainty arising from occasional slight fogging of the window.

The density of the sintered specimen was determined by liquid displacement and metallography was done after sectioning, polishing and electrolytic etching in 10% KOH.

The results in terms of density and fractional density based on theoretical specific weight 2.54 g/cc are summarized in Table IV.

D. Results

In the series of experiments 1 to 3 done with powder No. 1, there was little sintering, even at temperatures close to where melting occurred. Melting was probably due to the contact with carbon, which resulted in the formation of a eutectic between B_4C and C. (The eutectic temperature is somewhat uncertain and has been placed by various authors anywhere between 2200 and 2400°C. More recent investigations agree on the high region of this interval (see for instance R. Kieffer, et al., Ber. Dt. Ker. Ges. 48, 385 (1971)). However, shrinkage and some indication of densification has been detected in this relatively pure and coarse B_4C powder.

The finer powder, No. 2 (which also contains appreciable amounts of Mg and Fe) responds to the same sintering conditions by more densification. A density 72% could be obtained at 2260°C. It is, of course, not possible at this point to determine whether the enhanced densification was due to the fine particle size or the impurities in this powder.

An addition of Be_2C to powder No. 2 further provides densification; there was essentially no difference in the effect of 0.5 and 1% addition. At 2260°C, in 30 minutes a density of 2.38 g/cc (corresponding to 94% of the theoretical) was obtained in two experiments. This was the highest degree of sintering achieved in this investigation. At still higher temperature, melting occurred at the contact of the pellet with the carbon boat.

Figure 19 shows the as-polished section of specimen No. 8 sintered to 85% of theoretical density at 2230°C. Figures 20 and 21 give the as-polished and etched appearance of specimen No. 9 which yielded the highest density. The microstructure shows large, equiaxed grains, approximately 300μm in diameter, and large rounded-off closed pores mainly at the grain

Fig. 19 B_4C sintered with 1% Be_2C at 2230°C in argon to 85% density. As polished section, 500X.

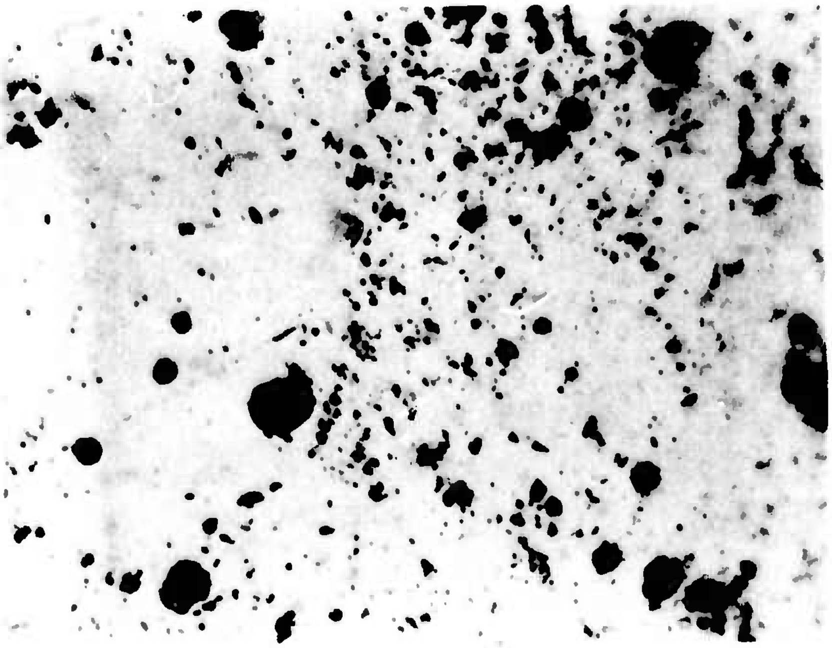


Fig. 20 B_4C sintered with 1% Be_2C at 2280°C in argon-nitrogen atmosphere to 94% theoretical density. As polished specimen. 500X

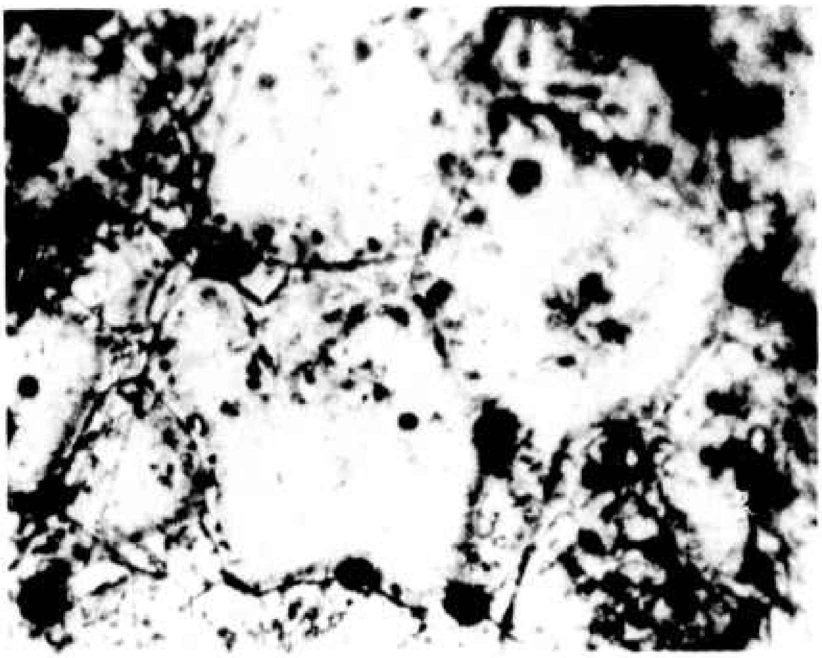


Fig. 21 Same specimen as Fig. 20, electrolytically etched in KOH.

boundaries. Some small spherical pores have been obviously trapped in the growing grains. There are also small grains of a second phase distributed near grain boundaries.

A 1% SiC addition to B_4C also brought about enhancement of densification at 2150°C. The degree of densification was somewhat increased where the addition was increased to 10%, however, the difference is only marginal. At 2300°C a density of 2.37 g/cc was obtained corresponding to 93.6% of the theoretical (Fig. 22). At this temperature, however, partial melting occurred due to interaction with the carbon setter.

E. Conclusion

It has been shown that submicron B_4C is amenable to sintering to relatively high densities in the presence of Be_2C or SiC. Whether or not the impurities contained in the powder, i.e., Fe and Mg also assisted the sintering process has not been established. Sintering was observed to occur above 2100° and the highest density was obtained only close to the temperature where melting occurred in contact with carbon. The highest density achieved was 94% of the theoretical.

Thus, it appears that B_4C is indeed a promising material for the planned investigation of sintering in covalent solids. It also appears that further study of sintering in B_4C may result in a practical process amenable to B_4C ceramic part fabrication.

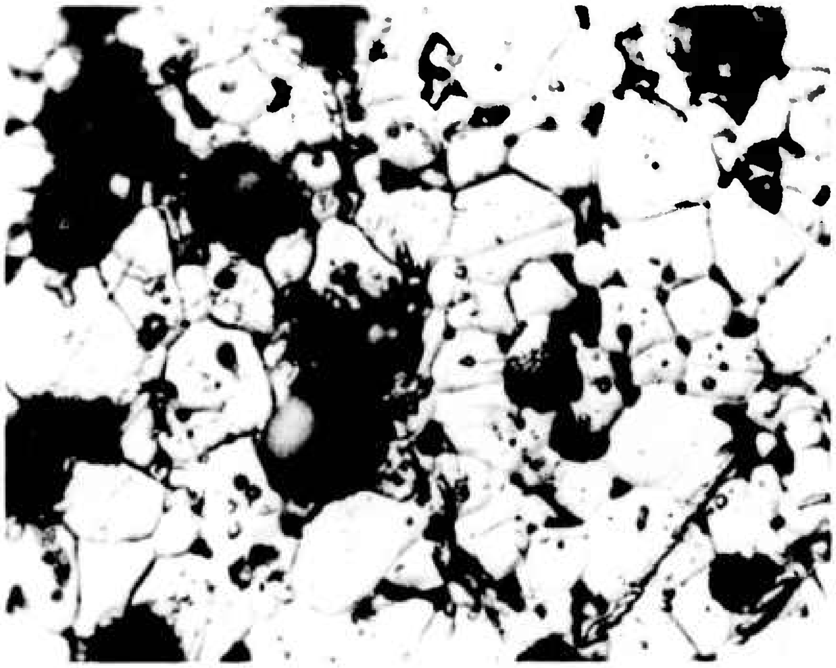


Fig. 22 B_4C sintered with 1% SiC at 2300°C in argon to 93.6%. 500X

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