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Effect of Milling and Leaching on the Structure of Sintered Silicon

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EFFECT OF MILLING AND LEACHING ON THE STRUCTURE OF SINTERED SILICON

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ABSTRACT

The effects of attrition milling and acid leaching on the sintering behavior and the resultant structures of two commercial silicon powders were investigated. Sintering was performed in He for 16 hours at 1200°, 1250°, and 1300° C. Compacts of as-received Si did not densify during sintering. Milling reduced the average particle size to below 0.5 μm and enhanced densification (1.75 g/cc). Leaching milled Si further enhanced densification (1.90 g/cc max.) and decreased structural coarsening. After sintering, the structure of the milled and leached powder compacts appears favorable for the production of reaction bonded silicon nitride.

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INTRODUCTION

Sometimes in the production of reaction bonded silicon nitride (RBSN) the compacted silicon (Si) powder is sintered before it is nitrided. It is technically desirable to perform these steps independently, because some shrinkage does occur in the sintering step. Resultant distortions can be eliminated inexpensively by machining the sintered Si with conventional tooling, while after nitridation diamond grinding must be employed. Fortunately almost no dimensional change occurs during the nitriding step.

It is reasonable to expect that the structure and the properties of RBSN are dependent on the structure and density of its precursor. While there have been numerous publications on the subject of RBSN,[1] few have discussed the control of structure of the sintered Si compacts relative to the properties of the final RBSN. A recent paper by H. R. Baumgartner[2] discusses some aspects of the relations between the structure of Si compacts and the final RBSN. Two earlier papers investigated the effect of nitrogen permeability through silicon compacts on the degree of nitridation, but the conclusions were contradictory.[3,4]

The objective of this study was to determine the effect of variations in powder processing on the sintering behavior of Si powder compacts. Comminution, in the form of wet attrition milling, and acid leaching were used to vary the nature of the Si powders used. Test bars prepared from two commercial Si powders in the as-received, milled, and milled and leached condition were sintered in a helium atmosphere. Evaluation of the powders and the sintered specimens included chemical analysis, density, surface area, mercury porosimetry, metallography, and room temperature bend strength.

EXPERIMENTAL PROCEDURES

Two commercial Si powders*, designated KBI and UC respectively, were used in this study. Each of the two as-received powders was wet attrition milled for 4 hours in a stirred ball mill using hardened steel balls as media and heptance as a milling fluid. The milled powders were designated KBIM and UCM. Attrition milling of Si was described in detail in an earlier paper.[5] The milled powders were further modified by acid washing (leach-

*Supplied by Kawecki-Berylco Industries, P.O. Box 1462, Reading, PA 19603 and Union Carbide, Marietta, OH 45750.

ing) to produce two additional powders designated KBIML and UCML. The effect of leaching as-received powder was not determined. Leaching was done using an 1:1 volume ratio of concentrated HCl and distilled water. 70 grams of milled powder were stirred into 770 ml of the acid solution. After 24 hours of leaching with intermittent stirring, the powder was recovered by filtering (S a S No. 565 analytical filter paper). The residue was rinsed with distilled water until no acid was detected by pH paper. After air drying, the powder was sieved through a 70 mesh sieve.

Iron (Fe), carbon (C) and oxygen (O) contents of each as-received, as-milled, and as-milled and leached powder were determined by chemical analysis. Powder surface areas were determined by the three point BET (Brunauer, Emmett, and Teller) technique.

The as-received KBI and UC powders could not be compacted by uniaxial pressing. However, cylindrical bars about 1.3 cm diameter could be made by hydrostatic pressing in a rubber sleeve at 350 MPa. For convenience of evaluation and testing, these cylindrical bars were cut into rectangular bars approximately 0.3 by 1 by 5 cm using a diamond saw prior to sintering.

The attrition-milled and the milled and leached powders were easily die pressed into bars of approximately 0.3 by 0.9 by 7.5 cm at 60 MPa. These bars were subsequently repressed hydrostatically at 350 MPa to increase their strength.

In order to minimize the weight loss the bars during sintering, samples were buried in loose KBI Si powders in a high purity Al_2O_3 boat and then were loaded in an Al_2O_3 tube furnace with provisions for a flowing helium atmosphere. Two bars of each powder were put in the same boat and sintered at the same time. A more detailed description of the sintering furnace and procedures can be found in an earlier publication.[6]

Bars were sintered for 16 hours at 1200°, 1250° and 1300° C. Temperature was increased from ambient to the sintering temperature at a linear rate over a period of 4 hours.

Weights and dimensions of the bars were measured before and after each sintering run. Density was calculated from these measurements. Two bend test specimens were cut from each sintered bar. Room temperature four-point bend strength was determined for all with their surfaces in the as-sintered condition samples. Light microscopy, mercury intrusion porosimetry analysis, and chemical analyses were performed on most samples before and after sintering. Samples for light microscopy were infiltrated with epoxy resin prior to polishing.

Reported densities and BET surface areas are an average of two determinations, strengths are an average of four. One specimen was used for each mercury intrustion porosimetry and chemical analysis.

RESULTS AND DISCUSSION

To show the effects of milling and milling and leaching, Table I lists the Fe, C, O contents and Table II lists the BET specific areas of the Si powders under investigation. For convenience of comparison, also listed in Table II are the particle sizes calculated from the corresponding measured BET surface areas assuming uniform spherical particle shape. It is apparent that milling drastically increased the impurity contents and the specific surface areas of the as-received powders; and leaching of the milled powders significantly reduced iron content, but only slightly altered the surface area. The variations in impurity contents and surface areas (or equivalent particle sizes) will be correlated with the sintering behaviors of the powders and the structures of the sintered materials to be presented in the following discussion.

The densities of silicon specimens, green and after sintering in helium for 16 hours at 1200°, 1250°, and 1300° C, are shown in a block diagram in Fig. 1. In the diagram the specimens are grouped into two families in accordance with the starting powder type. In each family, M stands for specimens made from milled powders, and ML stands for specimens made from milled and leached powders. Each row corresponds to a given sintering temperature marked on the left face of the block and the as compacted state (unsintered) labeled "Green." The densities shown in Fig. 1 range from a minimum of 1.35 to a maximum of 1.90 g/cc, corresponding to from 58 to 82 percent theoretical density of silicon (2.33 g/cc). The 1.90 g/cc specimen has the potential of forming a 3.15 g/cc Si_3N_4 body corresponding to 99 percent of the theoretical density of β-Si_3N_4 (3.18 g/cc); this is based on the theoretical weight gain value, 66 percent, for a complete conversion of Si to Si_3N_4. A more generally observed weight gain is 60 percent; a corresponding final density would be 3.04 g/cc or 95.6 percent of theoretical. The ability of such dense sintered silicon samples to be fully nitrided is currently under investigation.

As-received KBI and UC powders did not exhibit appreciable densification. This is in agreement with the predicted behavior of Si powder with a particle size larger than about 0.5 micron.[7] The milled and the milled and leached KBI and UC powders (designated KBIM, KBIML, UCM and UCML), all have a particle size in the submicron range (Table II). These all showed a continued increase in density with sintering temperature as might be expected for Si powders less than 0.5 μm diameter. More interesting to note is the higher degree of densification with increasing temperature of KBIML and UCML specimens than of their KBIM and UCM counterparts.

One of the reasons for the common practice of sintering Si powder compacts prior to nitriding is to increase their strength for ease of handling during machining into a desired shape. The average bend strengths of the sintered bars are plotted in a block diagram, Fig. 2. The measured strengths of the sintered bars reflect the bond (or neck) formation between particles. The formation of necks between adjacent particles during sintering of covalently bonded materials could be caused by mass transport through evaporation-condensation and surface diffusion mechanisms, which do not result in densification, as well as by volume and grain boundary diffusion mechanisms, which do lead to densification.[7] The phenomenon of forming necks without densification is clearly reflected by the steady increase in strength with temperature in both the KBI and UC samples, Fig. 2, which did not show appreciable densification, Fig. 1. In contrast milled and milled and leached specimens showed increases in both strength and density, Figs. 1 and 2. Leaching appeared to enhance both densification and strength development.

The changes in sintered bar strength and density were reflected also in the porosimetry measurements. For the purpose of comparison the characteristic pore size, defined as that pore size corresponding to 50 volume percent mercury penetration, was used. This characteristic pore size is plotted as a function of sintering temperature in Fig. 3. Note that the pore sizes of the four milled and the four milled and leached powder compacts were almost identical at room temperature (the green state). The pore sizes of these four samples increased, with some spread, from about 0.12 to about 0.22 μm after sintering at 1200° C. The pore size continued to increase with sintering temperature at different rates, UCM having the highest and KBIML having the lowest. We believe it is significant that the two

leached powder compacts (KBIML and UCML) exhibited less pore growth than the unleached counterparts (KBIM and UCM). This lower pore growth exhibited by the leached powder, relative to the unleached counterpart, is consistent with the higher degree of densification of the leached powder results presented earlier in Fig. 1. Another interesting observation on the four finer powders (KBIM, KBIML, UCM and UCML) is that the degree of pore growth of the samples increased with the Fe content (Table I). The significance of this parallel trend between Fe content and degree of pore growth requires more detailed experimental investigation before a definite correlation can be made.

Pore size was also measured on two KBI powder compacts and all the UC powder compacts. The trend of an increase in pore size with sintering temperature is also evident in Fig. 3.

The effects of milling and of milling and leaching on the microstructures of the sintered samples are shown in Fig. 4, which compares the microstructures of UC, UCM, and UCML after sintering at 1300° C for 16 hours. Similar microstructural behavior was also observed among KBI, KBIM and KBIML samples. The variation in observed pore structures was in agreement with the porosimetry results presented in Fig. 3. The retention of fine pore and particle size in the leached powders, even after sintering for 16 hours at 1300° C, was consistent with the increased degree of shrinkage observed for leached powders.

CONCLUSION

Attrition milling, as a powder preparation procedure, enhanced the densification during sintering of two commercial silicon powders. Acid leaching further enhanced the densification of the milled powders. Increasing sintering temperature increased the density of milled and milled and leached

powder compacts but compacts made from as-received powders coarsened without densification. After sintering the milled and leached silicon material exhibited a uniformly fine structure with densities up to 1.90 g/cc, which may be beneficial in subsequent nitridation.

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TABLE I. - Fe, O AND C CONTENTS IN Si POWDERS,

WEIGHT PERCENT

	KBI*	KBIM	KBIML	UC	UCM	UCML
Fe	0.36	3.53	1.28	0.56	4.93	1.75
O	.13	2.96	3.30	.7	4.11	4.36
C	.085	.77	.57	.3	.7	.42

*KBI = as-received Kawecki-Berylco Si powder.
KBIM = milled KBI.
KBIML = milled and leached KBI.
UC = as-received Union Carbide Si powder.
UCM = milled UC.
UCML = milled and leached UC.

TABLE II. - SPECIFIC SURFACE AREA AND PARTICLE SIZE

OF Si POWDER

	KBI*	KBIM	KBIML	UC	UCM	UCML
BET surface area, M^2/g	0.5	11.42	13.04	2.99	12.33	8.28
Particle size, μm**	5.20	.22	.20	.90	.21	.30

*KBI = as-received Kawecki-Beryleo Si powder.
KBIM = milled KBI.
KBIML = milled and leached KBI.
UC = as-received Union Carbide Si powder.
UCM = milled UC.
UCML = milled and leached UC.
**Equivalent spherical particle size calculated from BET surface area.

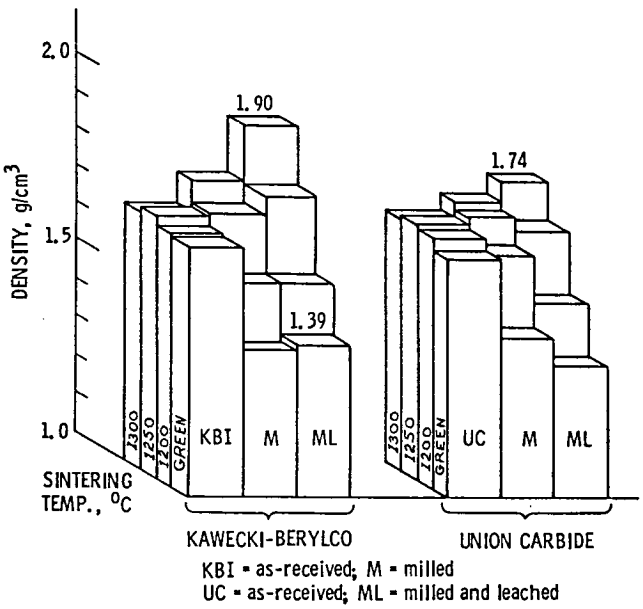


Figure 1. - Density of Si powder compacts, green and after sintering for 16 hours.

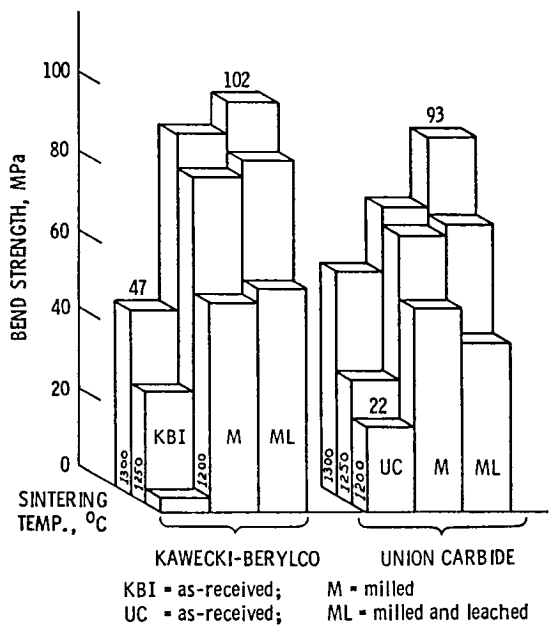


Figure 2. - Bend strengths of silicon samples sintered for 16 hours at 1200, 1250, or 1300° C.

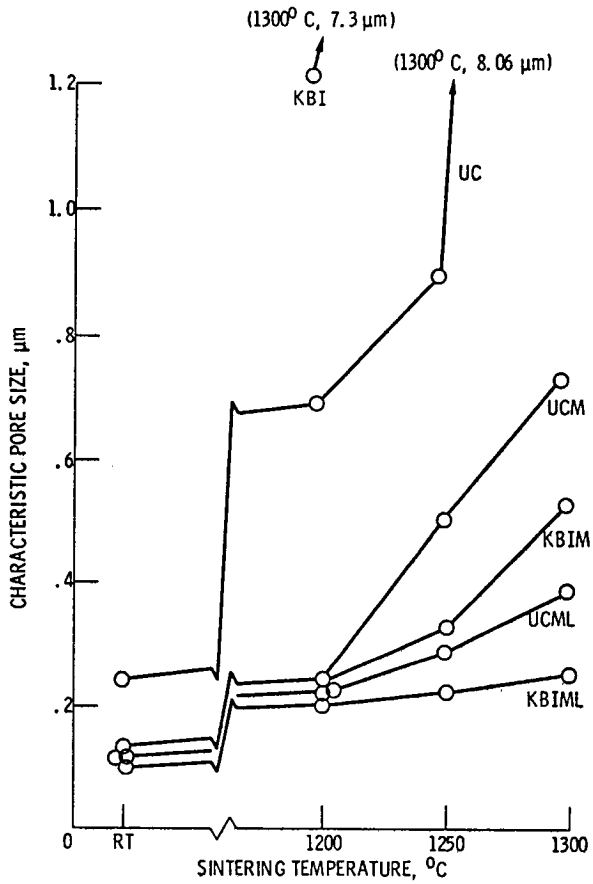
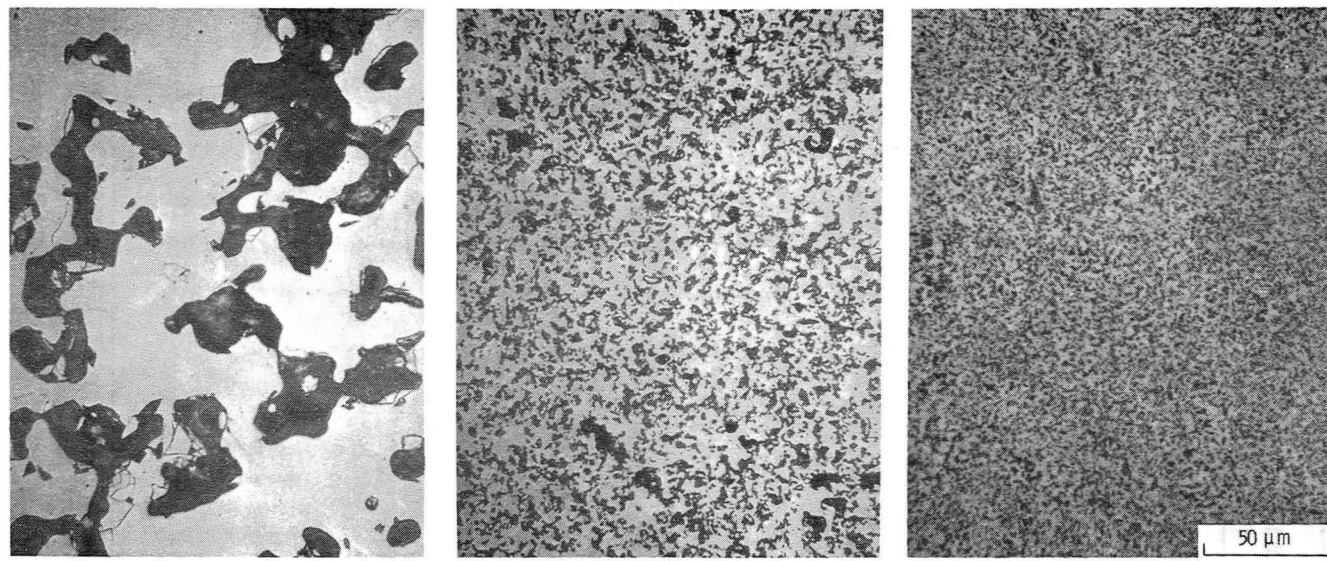


Figure 3. - Characteristic pore size versus sintering temperature (16 hr.) UC = as-received union carbide Si powder; UCM = milled UC; UCML = milled and leached UC; KBI = as-received Kawecki-Berylco Si powder; KBIM = milled KBI; KBIML = milled and leached KBI.



(a) AS-RECEIVED UC SILICON p = 1.67 g/cm^3.

(b) ATTRITION MILLED UC SILICON (UCM) p = 1.71 g/cm^3.

(c) ATTRITION MILLED AND LEACHED UC SILICON (UCM) p = 1.74 g/cm^3.

Figure 4. - Effect of milling and milling and leaching on UC (union carbide) Si Powder compacts sintered for 16 hours at 1300^{0}C (M= milled; ML= milled and leached).

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