Optical Engineering

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Abstract. Densification behavior of alpha silicon carbide (SiC) during vacuum hot pressing was studied up to 1900°C with sintering additives based on AlN and Y_2O_3 in different proportions. Near theoretical density was obtained with a total sintering additive content of < 4 vol.%. The microstructure of SiC sintered with $AlN + Y_2O_3$ revealed fine equiaxed grains against the additional elongated grains exhibited by SiC sintered with AlN alone. The SiC having high density exhibited very good strength, elastic modulus, high thermal conductivity, low coefficient of thermal expansion and excellent polishability for telescope mirror applications. [DOI: 10.1117/1.3610987]

Subject terms: silicon carbide; hot pressing; densification; thermal conductivity; mirror.

Paper 110487LR received May 5, 2011; revised manuscript received Jun. 2, 2011; accepted for publication Jun. 24, 2011; published online Jul. 27, 2011.

1 Introduction

Silicon carbide (SiC) is a key material for important technological applications including mirrors in space-based optics. Mirror blanks of SiC are produced either by a CVD process or by sintering the powder material. With CVD being a very slow and highly cumbersome process, powder processed blanks are more popular. The difficulty in sintering SiC to high density, due to its high covalency and low self-diffusion coefficient, is overcome by adding sintering additives. These additives can promote densification either in solid state or by the formation of a liquid phase. The solid state sintering process invented by Prochazka and Scanlan[1] uses B and C as sintering additives, requiring a high processing temperature in the range of 2100 to 2200°C, which often results in excessive grain growth and poor fracture toughness. AlN, which forms a solid solution with SiC, is used as a sintering aid but a processing temperature of over 2050°C is required for full densification.[2] Various researchers have successfully demonstrated the feasibility of processing SiC to near theoretical density through liquid phase sintering at temperatures below 2000°C using Al_2O_3 (Ref. 3), $Al_2O_3 + Y_2O_3$ (Ref. 4), and $AlN + Y_2O_3$ or rare earth oxides.[5,6] However, most of them used sintering additives of 10 vol.% or more to achieve good densification. The use of a large quantity of sintering additives often compromises the fundamental properties of SiC, such as its thermal conductivity and creep resistance. For applications like space borne optical systems, where SiC is replacing beryllium and zerodur materials, processing conditions that result in a homogeneous microstructure with very high density are essential, while at the same time not significantly affecting the fundamental properties of the material. Densification of SiC with minimal addition of sintering aids can be considered an important objective in this direction. Perusing the literature, we found that the densification behavior of SiC at low sintering additive contents, while limiting the sintering temperature to 1900°C, is not investigated adequately. We have studied the densification behavior of alpha SiC powders through hot pressing using AlN and $AlN + Y_2O_3$ additives, whose total content was kept below 4 vol.%. Important properties of the processed SiC blanks for mirror application were evaluated and polishability to the required optical finish was demonstrated.

2 Experimental

2.1 *Material Preparation*

Powder compacts were prepared from the commercially available alpha 6H-SiC powder (Saint Gobain, Sika FCP 13C, d_{50}-0.7μm) using AlN (H. C.Starck, Grade B, d_{50}-4μm) and Y_2O_3 (H. C. Starck, Grade B, d_{50}-2μm) as sintering additives in varying combinations as given in Table 1. The powder mixtures were wet milled using agate jars and balls in isopropanol in a planetary ball mill. The slurry was dried and processed into blanks by vacuum hot pressing in a graphite die assembly at 1900°C under 28 MPa pressure.

2.2 *Characterization*

These hot pressed materials were characterized for their density by the Archimedes method with water as the immersion medium and the phases by x-ray diffraction (XRD). Microstructural features were observed in a scanning electron microscope (SEM) by viewing the samples that were polished and etched using a boiling solution of $K_3Fe(CN)_6 + KOH + H_2O$. SiC sintered to the highest density was tested for hardness and flexural strength in three point bending. Additionally, thermal conductivity, coefficient of thermal expansion, and elastic modulus were measured for this blank by the laser flash method, using a dilatometer and by pulse echo method, respectively.

3 Results and Discussion

The relative density of SiC obtained for each of the sintering additive systems is presented in Table 1. Among the three additive combinations studied, SiC sintered with AlN ("E1" in Table 1) showed the lowest relative density of 88%. The AlN and Y_2O_3 combination resulted in high relative densities of 98.2% and 99.6%, respectively, for the total additive content of 2.65 and 3.95 vol.% ("E3" and "E2," respectively, in Table 1).

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Table 1 Silicon carbide compositions processed and the results.

Id. no.	Sintering Temperature °C	Composition of powder mix (vol.%)			Relative density of powder mix (g/cc)	Density of hot pressed blanks (%)
		SiC	AlN	Y_2O_3		
E1	1900	97	3	–	3.22	88
E2	1900	96.05	2	1.95	3.25	99.6
E3	1900	97	2	0.65	3.23	98.2

The densification of SiC with AlN occurs through the solid state sintering process. The silica layer present on the SiC particles affects the solid state sinterability of SiC. The reaction between SiC and SiO_2 (Ref. 7), which is prevalent in the temperature regime of 1500 to 1650°C is utilized to overcome the effect of the oxide layer as per the following chemical reaction.

$$SiC(s) + SiO_2(s) \rightarrow SiO(g) + CO(g). \quad (1)$$

In the presence of vacuum the gaseous phases are removed effectively. Once the effect of the oxide layer is overcome, SiC and AlN come into direct contact, forming a solid solution at high temperatures. AlN activates SiC grain surfaces and increases the grain boundary diffusional kinetics thereby promoting densification.[2]

In the case of the system containing AlN + Y_2O_3, sintering is achieved by the formation of a transient liquid phase between AlN and Y_2O_3 followed by a solution reprecipitation mechanism.[5,6] The densification was significant (99.6%) for the additive system with a total sintering additive content of 3.95 vol.%. We believe it is the first time that such a high density is achieved with the AlN-Y_2O_3 sintering additive system at lower levels of total additive content (< 4 vol.%) while processing under vacuum at 1900°C. Other researchers have reported this level of densification either through higher sintering additive content or sintering temperature as compared to what is reported here.[1–6] The XRD results for the SiC compacts indicate the presence of the $Y_{10}Al_2Si_3O_{18}N_4$ phase in SiC sintered with AlN + Y_2O_3 in addition to 6H SiC phase. This phase is the product of the reaction between the sintering additives and remnant SiO_2 on the SiC particles, which get into the melt during the solution reprecipitation of SiC from the melt. On the other hand, SiC sintered with AlN exhibited 6H SiC phase along with weak peaks of 4H polymorph of SiC, which forms as a result of a SiC-AlN solid solution.The microstructural features of SiC processed with various sintering additives are shown in Fig. 1. While SiC sintered with AlN exhibits elongated grains in addition to equiaxed grains, SiC sintered with AlN + Y_2O_3 additive exhibits uniform equiaxed microstructure.

From the mechanical and thermal properties summarized in Table 2, it can be observed that the material possesses the required properties for the mirror applications. The present

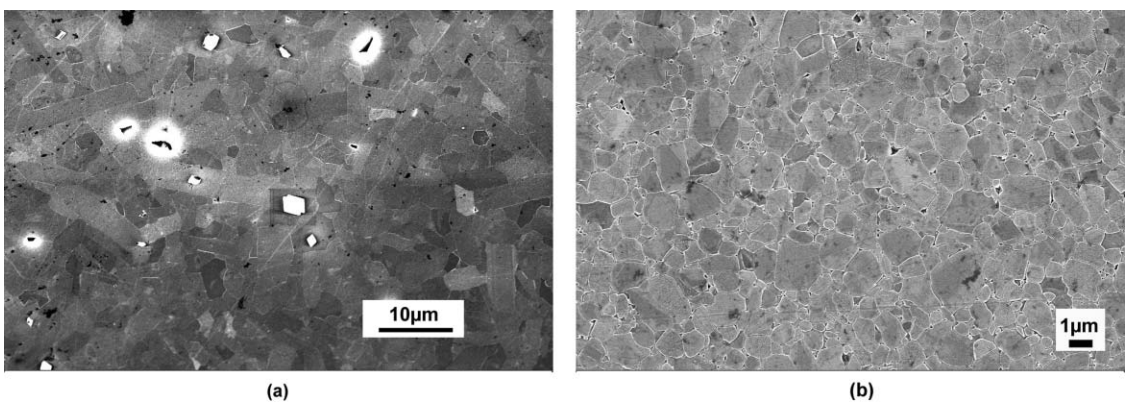

Fig. 1 Microstructure of SiC processed with different sintering aid systems: (a) 3 vol.% AlN and (b) 2 vol.% AlN + 1.95 vol.% Y_2O_3.

Table 2 Mechanical and thermal properties of the blank with the highest density.

Hardness (GPa)	Flexural strength, (MPa)	Thermal conductivity (W/mK)	Linear coefficient of thermal expansion between −70°C to 300°C (ppm/°C)	Elastic modulus (GPa)
24.56 ± 0.62	600 ± 18	145 ± 11	2.2 ± 0.14	405 ± 10

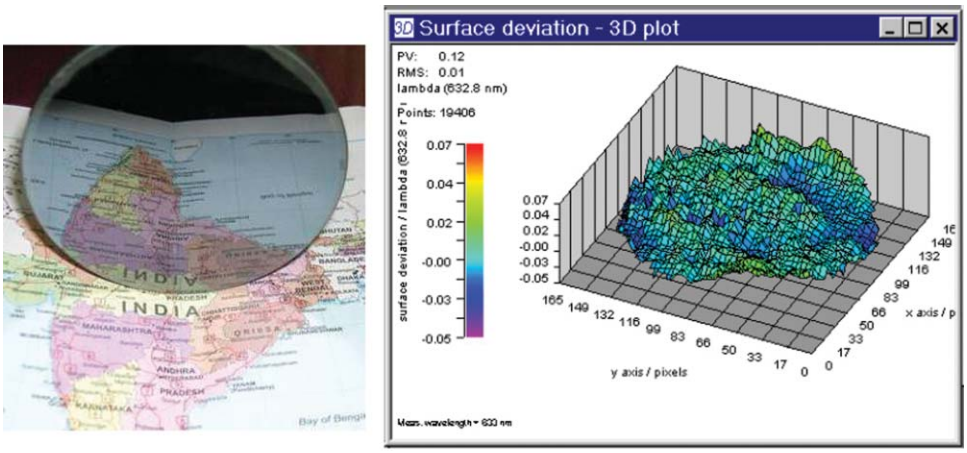

Fig. 2 Surface profile of polished mirror blank: (a) polished mirror and (b) surface figure.

material showed higher thermal conductivity than the one exhibited by SiC sintered with an additive based on B and C (Ref. 8) or alumina and yttria.[9] The conduction of heat through ceramic materials occurs by transfer of energy between vibrating atoms. At low temperatures, energy travels in the material predominantly via phonons. Phonons travel through the material until they are scattered, either through phonon-phonon interactions or at lattice imperfections. The high thermal conductivity indicates the large number of SiC grain boundaries free of sintering additive film. The low volume of sintering additives used, and the typical hot pressing cycle practiced in processing the material, are the reasons for this. The additives have not affected the coefficient of thermal expansion and elastic modulus of the bulk material which are comparable to those reported for SiC (Ref. 8).

The mirror blank exhibiting the highest relative density (sample no. E2) was mirror finished using conventional grinding and lapping methods. Grinding was carried out with progressively finer diamond wheels from 60 to 400 μm grit. The surface was further polished using diamond slurry of 5 to 0.25 μm. The surface figure was measured using a Zygo He–Ne laser interferometer and is shown in Fig. 2. The flatness was measured to be of 0.12λ (peak to valley [PV]) and 0.01λ (rms), where $\lambda = 632.8$ nm. The roughness (Ra) of the polished surface was measured to be 4.6 nm. From the surface finish data of the SiC processed through different methods summarized in Table 3, it can be observed that the present material is suitable for the telescope mirror applications in the visible and infrared range.

Table 3 Summary of surface finish obtained on polished blanks.

	Flatness		Surface roughness, Ra, nm	Reference
	PV	RMS		
HP SiC	0.12 λ	0.01 λ	4.6	Present work
CVD SiC	0.05 λ	–	2	Ref. 10
Sintered SiC	0.1 λ	–	2.1 (CVD coating and polishing)	Ref. 11
RB-SiC	0.26 λ	0.04 λ	4.05	Ref. 12

4 Conclusions

Sinterability of silicon carbide to a density better than 99% has been demonstrated through vacuum hot pressing at a processing temperature of 1900°C and by limiting total sintering additive content to less than 4 vol.%. The material exhibited very good properties and polishability to the requirements of mirror applications.

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