CONF-950401--32

GELCASTING OF SILICON COMPOSITIONS FOR SRBSN

S. D. Nunn, J. O. Kiggans, Jr., R. E. Simpson II, and J. P. Maria
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6087

ABSTRACT

Compositions of high purity silicon metal containing various oxides as sintering aids were gelcast to prepare green bodies for subsequent nitridation and sintering to form sintered reaction bonded silicon nitride (SRBSN). An acidic aqueous- and an alcohol-based gelcasting system were used. The solids content in the slurry affected the green density of the cast samples, however, there was no apparent correlation between the green density and the percent nitridation. Samples were nitrided under flowing, high-purity nitrogen in either a tungsten element furnace, a graphite element furnace, or in a microwave furnace. The samples nitrided in the graphite and microwave furnaces showed 9-16% higher levels of nitridation than in the tungsten furnace. A N_2-4% H_2 gas mixture was compared to pure nitrogen in the tungsten furnace. The addition of the hydrogen increased nitridation levels by 14-19%. The nitrided and sintered SRBSN ceramics had densities of 95-98% of theoretical, with no direct relationship being observed between the level of nitridation and the fired density. The average 4-point flexure strength of the samples ranged from 428 to 741 MPa.

INTRODUCTION

Sintered reaction bonded silicon nitride (SRBSN) which is formed by reacting silicon powder with nitrogen gas to form silicon nitride has been studied for many years.[1,2] The properties of SRBSN are usually inferior to those of silicon nitride materials formed from high quality silicon nitride powders, especially at elevated temperatures. This is because metal impurities (typically Fe) are usually added to the SRBSN composition to enhance the nitridation reaction. Reduced high temperature capability has limited the potential applications of SRBSN; however, on a cost basis, SRBSN is an attractive alternative to silicon nitride materials formed from silicon nitride powder.[3] The cost of high purity silicon powder is only about 20% of the cost of silicon nitride powder. In addition to lower raw material costs, the reaction of silicon with nitrogen to form silicon nitride results in a volume increase of about 21.6% over the original silicon powder volume. This normally occurs by the growth of the silicon nitride crystals into the pore structure of the powder compact and results in an increase in density without an accompanying reduction in the size of the part.[4] This can reduce the amount of shrinkage observed during the sintering of the component to form a densified material, and make net-shape forming and dimensional control more manageable. Recently, it was demonstrated that SRBSN could be fabricated from high purity silicon powders without metal additions by using microwave heating and that the resulting material had improved properties compared to conventional SRBSN.[3] Further studies of the fabrication of SRBSN compositions using high purity silicon powder are described in the present work.

Both conventional and microwave heating methods for firing SRBSN were examined in this study. The conventional process typically involves two distinct steps: the nitriding reaction and the sintering run.[4] This is primarily because typical sintering processes for silicon nitride containing low amounts of refractory sintering aids involve packing the parts in a bed of powder (usually silicon nitride) to minimize weight loss at high temperatures. If a silicon part is packed in a powder bed prior to nitridation, the powder can act as an insulating blanket holding in the heat generated by the exothermic reaction of the silicon metal converting to silicon nitride. Under these conditions, it is difficult to control the exothermic heating of the part which can result in melting of the silicon metal before complete nitridation can occur. In microwave heating, it has been demonstrated that due to the volumetric heating effect, silicon compacts can be nitrided and sintered in a single processing step.[3,5,6]

To take full advantage of the desirable characteristics which are offered by SRBSN materials, a viable and economical forming method for producing complex shapes needs to be developed. One such forming process which was utilized in this study is gelcasting. Gelcasting is a powder forming process which offers distinct advantages as an alternative to the more conventional ceramic forming methods such as dry pressing, slip casting, and injection molding.[7-10] Principal advantages include near-net-shape forming, high green density, and low organic levels in the dried green ceramics. A wide variety of ceramic materials have been prepared using the gelcasting process. These include silicon nitride, silicon carbide, alumina, and zirconia, among others.

Initial efforts to gelcast silicon metal compositions using the currently available process were unsuccessful. Two principal difficulties were observed, both of which could be traced to the fact that the typical gelcasting slurry is aqueous and basic (having a pH of about 8.4). The first was the poor dispersion characteristics of the silicon powder in the slurries. The second was the generation of gas bubbles in the slurry caused by reaction of the silicon metal with water. Attempts at surface modification of the powder to improve dispersion and reduce reactivity were unsuccessful, primarily because the slurries needed to be milled to obtain uniform mixing of the constituent powders and to achieve high solids loading. The milling action generated clean particle surfaces which negated any positive effects of the prior surface treatment.

Experimental investigations showed that these processing difficulties could be overcome in two ways: by reducing the pH of the aqueous slurry or by using isopropyl alcohol as the solvent system in place of water. However, the available gelcasting systems could not be used under these conditions. An effort was undertaken to identify chemicals which might be utilized to form gelcast bodies under the required processing conditions. Both an acidic aqueous system and an alcohol-based system were developed and successfully adapted for SRBSN gelcasting. The solids loading was limited to 35-40 vol % in the acidic aqueous system while slurries containing 50 vol % solids were prepared in the alcohol-based system. These new gelcasting systems are at present proprietary and will not be discussed in detail here. This paper describes the characteristics of the gelcast silicon green bodies, the nitriding and sintering behavior of a number of gelcast SRBSN compositions, and the preliminary evaluation of the mechanical properties of the sintered materials.

EXPERIMENTAL PROCEDURES

Batches were prepared by milling the constituents in an attritor mill (Union Process, Model 01) using a Teflon-lined jar, a high density polyethylene rotor, and high-density zirconia milling media. There was no measurable change in the weight of the media after the milling operation, indicating negligible wear and contamination of the slurries. The compositions which were prepared are listed in Table I, where both the as-prepared composition and the theoretical composition after nitriding are shown. High-purity silicon powder (Elkem, grade HQ, 99.95% purity) was used. The oxide sintering aids are typical of those being used in the preparation of high quality silicon nitride materials. The batches labeled Nd and Y were prepared in the acidic aqueous-based gelcasting system, and the slurries contained 35-40 vol % powder. Batches PM1, PM2, and PM3 were prepared in the alcohol-based gelcasting system and contained 48 vol % solids.

Table I. Compositions for Gelcasting of Sintered Reaction Bonded Silicon Nitride

	Composition, wt %					
Batch	Si	Si_3N_4	Al_2O_3	Y_2O_3	Nd_2O_3	SiO_2
As-prepared						
Nd	64.17	13.58	4.08		18.17	
Y	74.65	15.80	5.24	6.94		
PM1	84.39		6.71	8.90		
PM2	70.61	14.70	6.32	8.38		
PM3	68.68	14.57	6.26	8.30		2.19
After nitriding (theoretical)						
Nd		84.41	2.86		12.74	
Y		92.00	3.44	4.56		
PM1		90.00	4.30	5.70		
PM2		90.00	4.30	5.70		
PM3		88.50	4.30	5.70		1.50

Si: Elkem Metals Co., Buffalo, NY: Grade Si-HQ, 99.95%; 4.2 µm
Si_3N_4: Ube Industries, Japan; Grade E-10
Al_2O_3: Reynolds, Malakoff, TX; Grade RC-HP DBM
Y_2O_3: Molycorp, White Plains, NY; Grade 5600, 99.99%
Nd_2O_3: Molycorp, White Plains, NY; Grade 5410, 99.9%
SiO_2: U. S. Silica, Berkeley Springs, WV; Micronized silica, 5 µm

After milling, the slurries were vacuum deaired and cast in 101.6 x 254 x 9.53 mm (4 x10 x 0.375 in.) plate molds made of aluminum. The castings were then gelled by placing them in an oven at 65°C for 1h. The molds were cooled to room temperature and the gelled plates were removed. The plates were placed in a closed container to prevent rapid drying of the surface during the initial drying stage when the part shrinks until particle-particle contacts are formed. The initial drying stage typically lasted for about 12 h, after which no additional shrinkage was observed. The drying was then completed by allowing the remaining liquid to evaporate under ambient conditions.

The organic binders were removed from the dried parts by slowly heating the samples in air. Most of the organic was burned off at less than 400°C, but the parts were heated to 600°C to insure complete combustion of any residue. The green density of the samples was estimated by weighing the parts and measuring their dimensions. Most of the samples prepared using the aqueous gelcasting system were isopressed at 69-379 MPa (10-55 ksi) to increase the green density.

Nitriding of the gelcast samples was done in three different furnaces: a graphite element furnace, a tungsten element furnace, and a microwave furnace. The nitriding was done using a flowing atmosphere of high-purity nitrogen. One run in the tungsten furnace used a N_2-4% H_2 atmosphere. These nitriding conditions are summarized in Table II. The temperature profiles used for the nitriding runs are shown in Fig. 1. The profiles for the aqueous and the alcohol gelcastings varied slightly, with the aqueous system samples having an initial 1-h hold at 1250°C, while the initial hold for the alcohol system samples was at 1200°C. The extent to which the silicon was converted to silicon nitride during the nitridation cycle was calculated based on a theoretical weight gain for the silicon of 66.5% for 100% conversion. The presence of oxygen on the surface of the silicon particles was not taken into consideration. Knowing the amount of silicon in each sample before the nitriding run and the weight gain of the sample during the run, the percent nitridation was calculated. The samples which were nitrided in the microwave furnace were taken directly from the 1450°C hold temperature to the sintering temperature of 1800°C while maintaining the flowing nitrogen atmosphere. The estimate of the percent nitridation for these samples was affected by any weight loss which may have occurred during the sintering part of the run.

Table II. Nitriding of Gelcast Sintered Reaction Bonded Silicon Nitride

Sample	Green Density (kg/m^3)	Nitriding Furnace	Nitriding Atmosphere	Percent Nitridation*
		Acidic aqueous gelcasting		
Nd 1	1220 (43%)	Graphite	N_2	96.8
Nd 2	1540 (54%)†	Graphite	N_2	96.3
Nd 3	1670 (59%)†	Graphite	N_2	96.5
Nd 4		Graphite	N_2	87.8
Y 1	1610 (64%)†	Graphite	N_2	92.0
Y 2	1610 (64%)†	Graphite	N_2	91.5
Y 3	1610 (64%)†	Graphite	N_2	83.8
Y 4	1590 (63%)†	Graphite	N_2	83.8
Y 5	1600 (64%)†	Graphite	N_2	89.9
		Alcohol-based gelcasting		
PM1 1-2	1380 (55%)	Tungsten	N_2	78.9
PM2 1-2	1340 (51%)	Tungsten	N_2	82.2
PM3 1-2	1400 (53%)	Tungsten	N_2	79.6
PM1 3-2	1380 (55%)	Tungsten	N_2-4% H_2	89.7
PM2 3-2	1340 (51%)	Tungsten	N_2-4% H_2	96.0
PM3 3-2	1400 (53%)	Tungsten	N_2-4% H_2	95.0
PM1 4-2	1380 (55%)	Graphite	N_2	91.8
PM2 4-2	1340 (51%)	Graphite	N_2	91.2
PM3 4-2	1400 (53%)	Graphite	N_2	88.4
PM1 9-1	1380 (55%)	Microwave	N_2	90.3**
PM2 9-1	1340 (51%)	Microwave	N_2	92.0**
PM3 9-1	1400 (53%)	Microwave	N_2	87.2**

*Based on starting silicon content in the sample and the measured weight gain after nitriding.
†After isopressing.
**Microwave processing was done in one step which included both nitriding and sintering. The calculation to estimate the percent nitridation was affected by weight loss during the sintering portion of the firing cycle.

The samples which were nitrided in the tungsten and graphite furnaces were packed in coarse silicon nitride powder inside a graphite crucible and placed in a graphite resistance furnace for sintering. The samples were heated at 10°C/min to 1800°C and held at that temperature for 2h. The sintering took place under a static nitrogen pressure of 172 kPa (25 psia).

The sintered materials were machined to form B-size (MIL-STD-1942A) 4-point bend test bars. Densities of the machined bars were measured by Archimedes method using high purity ethyl alcohol. The test bar dimensions were 3 x 4 x 50 mm, with the edges of the bars chamfered at a 45° angle. The fixture used in testing the bars had an outer span of 40 mm and an inner span of 20 mm. The bars were loaded to failure in a screw-driven universal testing machine (Instron Model 4465). The fracture strength, σ_f, was calculated using the following equation:[11]

$$\sigma_f = \frac{3P(l_1 - l_2)}{2bd^2} \qquad (1)$$

where P is the applied load at fracture, l_1 is the outer span of the test fixture, l_2 is the inner span, b is the width (or breadth) of the test bar, and d is the thickness (or depth) of the bar. The Weibull modulus, m, was estimated using the following equation:[12]

$$m = 1.21\left(\frac{\overline{\sigma}_f}{s}\right) - 0.47 \tag{2}$$

where σ_f is the average fracture strength of a group of test specimens and s is the standard deviation of the fracture strength.

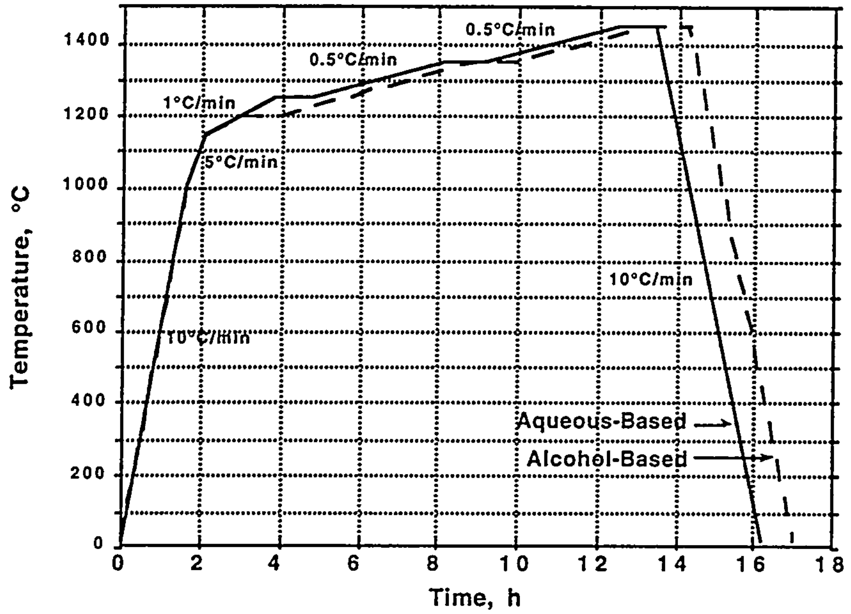

Fig. 1. Firing schedules used for nitriding of the SRBSN compositions.

RESULTS AND DISCUSSION

The green density of the as-cast samples showed a distinct difference between the aqueous- and the alcohol-based gelcastings. The lower solids content in the aqueous slurries resulted in green densities of about 43%; the alcohol-based samples had green densities of 51-55%. Most of the aqueous-based samples were isopressed prior to nitriding. Sample Nd 1 remained as-cast, Nd 2 was isopressed at 69 MPa (10 ksi), sample Nd 3 at 345 MPa (50 ksi), sample Nd 4 and all of the Y samples were isopressed at 379 MPa (55 ksi). The resulting green densities are shown in Table II.

A high green density can be detrimental in conventional nitriding processes due to the tendency of the nitriding reaction to start at the surface of the sample and progress inward. The volume expansion can close off the pore structure and prevent the nitrogen gas from reaching the unreacted silicon in the interior of the sample, especially in thick samples. However, as shown by the results in Table II, the percent nitridation of the gelcast samples showed no consistent dependency on the green density. There were, however, significant effects due to the gas composition and the type of furnace. The addition of 4% H_2 to the nitriding gas increased the nitridation by 14-19% in the tungsten furnace. This result was not surprising, since the hydrogen acts to decompose the oxide layer on the surface of the silicon particles making them more reactive. Both the graphite and the microwave furnaces showed improved nitridation over the tungsten furnace when using a pure nitrogen atmosphere. Samples in the graphite furnace showed 11-16% higher nitridation levels, while those in the microwave were 10-14% higher, even though the percent nitridation of the microwave samples was probably underestimated due to weight losses which typically occur during the sintering part of the cycle.

The density of the fired samples is summarized in Table III. Examination shows a slightly higher density for the samples fired in the one-step process in the microwave furnace. Selected data are plotted in Figs. 2a and 2b to aid in determining relationships between the process variables and the measured properties. There is no apparent correlation between the percent nitridation and the final density. Only the Nd samples show a direct relation between green density and fired density. For the PM samples, the density appears to depend more upon the starting composition than on any other factor.

Table III. Density and Strength Measurements of Gelcast SRBSN

Sample	Fired Density (kg/m^3)	Fired Density (%)	Flexure Strength (MPa)	Number Tested	Weibull Modulus*
Acidic aqueous gelcasting					
Nd 1	2830	81.8			
Nd 2	3150	91.0			
Nd 3	3220	93.1			
Nd 4	3380	97.7	369 ± 43	13	9.9
Y1	3150	96.5	497 ± 71	8	8.0
Y2	3170	97.1	560 ± 88	8	7.3
Y3	3170	97.2	489 ± 58	15	9.8
Y4	3190	97.8	595 ± 74	17	9.3
Y5	3210	98.3	430 ± 54	17	9.2
Alcohol-based gelcasting					
PM1 1-2	3200	97.7	609 ± 39	10	18.6
PM2 1-2	3160	96.4	587 ± 46	8	15.2
PM3 1-2	3110	95.1	428 ± 111	10	4.2
PM1 3-2	3190	97.3	668 ± 59	6	13.2
PM2 3-2	3190	97.2	574 ± 184	5	3.3
PM3 3-2	3150	96.0	574 ± 133	6	4.8
PM1 4-2	3190	97.5	509 ± 54	6	10.9
PM2 4-2	3160	96.4	741 ± 75	3	11.5
PM3 4-2	3140	95.8	529 ± 34	5	18.2
PM1 9-1	3220	98.3	601 ± 94	10	7.3
PM2 9-1	3210	98.1	599 ± 128	10	5.2
PM3 9-1	3200	97.6	531 ±107	10	5.5

*Estimated using the equation: $m = (1.21 \times (\text{Average Strength}/\text{Standard Deviation})) - 0.47$.

The strength and Weibull modulus are shown in Table III and the strength is plotted in Figs. 2a and 2b. Again, the values show no correlation with the percent nitridation. For each of the alcohol-based gelcast batches, the strength shows a weak relationship with the fired density, except for the PM*n* 4-2 samples which show no correlation. The strength and Weibull modulus values obtained in the present study compare favorably with the results reported in earlier work.[3]

CONCLUSIONS

Compositions of high purity silicon metal containing various oxides as sintering aids were gelcast to prepare green bodies for subsequent nitridation and sintering to form sintered reaction bonded silicon nitride (SRBSN). An acidic aqueous- and an alcohol-based gelcasting system were used. In the aqueous system the solids loading was 35-40 vol %, while the alcohol-based slurries contained 48 vol % solids. The solids content in the slurry affected the green density of the cast samples, however, there was no apparent correlation between the green density and the percent nitridation. Samples were nitrided under flowing, high-purity nitrogen in either a tungsten element furnace, a graphite element furnace, or in a microwave furnace. The samples nitrided in the graphite and microwave furnaces showed 9-16% higher levels of nitridation. In the tungsten furnace, a N_2-4% H_2 gas mixture was also examined in the nitriding runs. The addition of the hydrogen increased nitridation levels by 14-19%. The sintered ceramics had densities of 95-98% of theoretical, with no direct relationship being observed between the level of nitridation and the fired density. The average 4-point flexure strength of the samples ranged from 428 to 741 Mpa.

ACKNOWLEDGMENTS

Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the Ceramic Technology Project of the Propulsion System Materials Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES

1. A. J. Moulson, "Reaction-Bonded Silicon Nitride: Its Formation and Properties," *J. Mater. Sci.*, 14 1017-1051 (1979).

2. F. L. Riley, "Nitridation and Reaction Bonding," pp. 265-288 in Nitrogen Ceramics, ed. F. L. Riley, Noordhoff, The Netherlands (1977).

3. T. N. Tiegs, J. O. Kiggans, Jr., and K. L. Ploetz, "Sintered Reaction-Bonded Silicon Nitride by Microwave Heating," *Mat. Res. Soc. Symp. Proc.*, 287 283-288 (1993).

4. J. A. Mangels and G. J. Tennenhouse, "Densification of Reaction-Bonded Silicon Nitride," *Am. Ceram. Soc. Bull.*, 59 [12] 1216-1222 (1980).

5. J. O. Kiggans, Jr. and T. N. Tiegs, "Characterization of Sintered Reaction Bonded Silicon Nitride Processed by Microwave Heating," *Mat. Res. Soc. Symp. Proc.*, 269 285-290 (1992).

6. J. O. Kiggans, Jr., C. R. Hubbard, R. R. Steele, H. D. Kimrey, C. E. Holcombe, and T. N. Tiegs, "Characterization of Silicon Nitride Synthesized by Microwave Heating," in Ceramic Transactions, Microwaves: Theory and Applications in Materials Processing, Am. Cer. Soc., Westerville, OH 267-272 (1991).

7. M. A. Janney and O. O. Omatete, "Method for Molding Ceramic Powders Using a Water-Based Gelcasting," U. S. Pat. No. 5 028 362, July 2, 1991.

8. A. C. Young, O. O. Omatete, M. A. Janney, and P. A. Menchhofer, "Gelcasting of Alumina," *J. Am. Ceram. Soc.*, 74 [3] 612-618 (1991).

9. O. O. Omatete, M. A. Janney, and R. A. Strehlow, "Gelcasting—A New Ceramic Forming Process," *Am. Ceram. Soc. Bull.*, 70 [10] 1641-1649 (1991).

10. M. A. Janney and O. O. Omatete, "Method for Molding Ceramic Powders Using a Water-Based Gelcasting Process," U. S. Pat. No. 5 145 908, Sep. 8, 1992.

11. Y. Murakami, Editor-in-Chief, Stress Intensity Factors Handbook, Pergamon Press, 1987.

12. Jeffrey Neil, GTE Laboratories Incorporated, unpublished work.