Studies On The Scale-Up Of The Microwave-Assisted Nitridation And Sintering Of Reaction-Bonded Silicon Nitride

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Abstract

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Studies using laboratory test samples have shown that microwave heating produces sintered reaction-bonded silicon nitride materials with improved properties [1,2]. The final challenge for processing this material by microwave heating is the development of a technology for processing larger batch-size quantities of these materials. Initial microwave scale-up experiments were performed using powder compacts of a bucket tappet geometry. In experiments using microwave-transparent boron nitride sample crucibles, temperature gradients within some crucibles led to larger variations in the sample densities than were obtained with the conventionally processed samples. The use of a microwave-susceptor type crucible made of silicon carbide and boron nitride resulted in an improved temperature uniformity and in density variations comparable to those obtained for the control groups.

Introduction

Silicon nitride-based materials are the leading candidates for use as high-temperature structural ceramics due to their excellent overall combination of mechanical and physical properties [3,4]. Significant progress has been made in recent years in producing materials with superior strength, fracture toughness, wear, and creep resistance. However, these materials tended to be prohibitively expensive due to the high cost of the silicon nitride powders used to produce them. Reduction of cost has been recognized as a major factor for the introduction of silicon nitride ceramics into the marketplace [5].

Sintered reaction-bonded silicon nitride (SRBSN) is an attractive alternative to the use of expensive high purity powders for a number of reasons. Most importantly, silicon is economical compared to high purity silicon nitride powders. Another advantage of SRBSN is that during sintering there is less shrinkage than for compacts starting with silicon nitride powders. During the nitridation reaction, growth of silicon nitride occurs in the pore space between the initial silicon particles, consequently, densities for SRBSN materials prior to sintering are relatively high; typically about 65 to 75% theoretical density [6,7].

Traditionally, the production of SRBSN has been accomplished using resistance-heated furnaces in a two-step process. In recent years, microwave heating has been introduced as an alternative and an advantageous process for producing SRBSN materials [1,2,8]. The present study is meant to build on previous studies in which small lab-scale SRBSN shapes were processed by microwave heating to include the ability to uniformly process multiple industrial-type parts [9].

EXPERIMENTAL PROCEDURES

Injection-molded powder compacts^a of a bucket tappet geometry were purchased for the microwave scale-up studies. The green bucket tappet samples consisted of a cup-like structure with the dimensions of 4.08 cm outside diameter, 3.38 cm height, and with a 0.381 cm wall thickness. The buckets were bisque fired in nitrogen by the supplier to provide green strength for shipment. The samples had a nominal composition of silicon containing 30 wt.% Si₃N₄ and

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5 wt.% each of Al_2O_3 and Y_2O_3 sintering aids. The green density of the buckets was 1.72 g/cm³.

Nitridation and sintering of the bucket tappets was conducted in a 500-liter cylindrical multimode cavity equipped with a 6-kW, 2.45-GHz power supply. Samples were placed into crucibles composed of boron nitride^b (BN), BN and silicon carbide^c (SiC), and reaction-bonded silicon nitride (RBSN), which were then insulated by a 5-cm layer of powder consisting of 83 wt.% Si_3N_4 ^d, 15 wt.% boron nitride (BN), and 2 wt.% Y_2O_3 ^e. The crucibles and powder were held in 2.5 cm wall thickness alumina fiberboard^f box (Figure 1a).

Two sets of microwave experiments were performed in this study. The first set involved three nitridation and sintering runs, in which parts were placed in one of three different (BN) cylindrical crucibles either in a single layer of four samples, two layers of four samples each, or three layers of seven samples each (Figure 1b). In the second series of microwave heating experiments, samples were processed in one of three crucibles, each designed to accommodate a single layer of nine samples, as shown in Figure 2. The three crucibles were made of three different material combinations. Crucible 1 was made of all BN. Crucible 2 had a BN top and bottom, and SiC sides. Crucible 3 consisted of a RBSN box with a removable RBSN lid, and contained a bottom BN setter plate within the crucible.

Figure 1. Drawing showing the insulation package used for the first series of microwave processing experiments including a) a cross section view of the entire package and b) a top view of the two possible sample arrangements used.

Figure 2. Drawing of insulation package used in the second series of microwave processing experiments including a) a cross section view and b) a top view.

^bAdvanced Ceramics Co., Cleveland, Ohio; Grade HCP BN

^cNorton Co., Worcester, MA

^dStarck, Berlin, Germany; Grade S1 Si_3N_4

^eMolycorp, White Plains, NY; Grade 5600

^fFoseco, Inc., Cleveland, Ohio; Grade Procal HT-310C

After assembly of an appropriate sample package, the microwave furnace was evacuated and back-filled with nitrogen. Experiments were performed with flowing nitrogen. Both nitridation and sintering were performed in a single heating cycle of 20 hours. The final sintering condition was 1800°C for two hours. In the first set of microwave experiments, a single molybdenum-sheathed type "C" thermocouple located in the center of each BN crucible was used to measure the temperature of the samples. In the second set of experiments, three type "C" thermocouples were used to measure temperature in the microwave test crucibles. The thermocouples were located at 3 cm intervals starting at the center of the crucible. The third thermocouple was at the inner edge of the crucible.

Comparative nitridation and sintering studies were conducted using a graphite resistance-heated furnace. Samples were loaded into BN and RBSN crucibles and then nitrided to a final temperature of 1450°C for 2 hours in flowing nitrogen. After cooling to room temperature, the samples were covered with a 0.6 cm layer of Si₃N₄ powder containing 4 wt.% Y₂O₃ and sintered at 1800°C for two hours in a graphite furnace.

Samples from both the microwave and control groups were weighed before and after experiments. Sample locations and orientations within the crucibles were recorded. Density determinations were made on sintered samples by the Archimedes method. Some sintered buckets from control and microwave tests were sliced into four sections of approximately equal thickness. The slices were made parallel to the base of the bucket tappet. The densities of each section were measured by the Archimedes method.

RESULTS

Table 1 shows a summary of the results from the first series of microwave processing runs along with the results of the two controls obtained from the conventionally processed samples. The four samples processed in run #1 had an average density of 3.26 g/cm³ with a standard deviation of 0.004 g/cm³. Run #2 in the microwave was a scale up from four to eight samples. The samples were stacked in two layers of four samples each, as shown in Figure 1. The average density was 3.27 g/cm³, with a standard deviation of 0.005 g/cm³. The standard deviations of both microwave runs slightly exceeded that of the RBSN control but were lower than the BN control. The success of the eight sample experiment run #2 led to a scale-up to a three layer, twenty-one sample experiment run #3. The average density for this run #3 was 3.25 g/cm³ which was lower than the previous two experiments. More important, the standard deviation increased to 0.022 g/cm³, which exceeded both control values. The densities of the twenty-one samples ranged from a high of 3.27 g/cm³ to a low of 3.17 g/cm³. Analysis of the densities of the samples relative to their positions in the three layer package showed that these differences in densities appeared to be due to temperature differences between the center and the edge of the crucible since the samples in the center of each of the three layers, sintered to higher densities than the samples on the peripheries.

Table I. Densities obtained for SRBSN samples processed by microwave or conventional heating in experiment series 1.

Run #	Processing Method	Crucible	# Layers	# Samples	Avg Dens (g/cm ³)	St Dev Dens (g/cm ³)
1	Microwave	BN	1	4	3.26	0.004
2	Microwave	BN	2	8	3.27	0.005
3	Microwave	BN	3	21	3.23	0.022
4	Graphite Furnace	BN	2	6	3.25	0.014
5	Graphite Furnace	RBSN	1	9	3.26	0.003

In order to further investigate the suspected temperature problem associated with the microwave scale-up runs in the first set of experiments, and to see if susceptor crucibles might offer a solution, a second set of experiments was conducted. Table 2 shows the average densities and standard deviations obtained for the samples processed by microwave heating in the three

types of crucibles tested, and also for samples heated in a graphite furnace in a RBSN crucible. The average density for the samples processed by microwave heating using a BN crucible was 3.27 g/cm^3 . The standard deviation of 0.006 g/cm^3 was double the value of the RBSN control group. The temperature measurements made in this run indicated that the center of the crucible (TC 1) was 12 to 14°C higher than the inner left edge of the crucible (TC 3). This temperature difference resulted in the variations in the densities of the samples as shown in Figure 3a.

Table II. Densities obtained for SRBSN samples processed by microwave and conventional heating in experiment series 2

<u>Processing Method</u>	<u>Crucible Type</u>	<u>Avg Dens</u> <u>g/cm³</u>	<u>St Dev Dens</u> <u>g/cm³</u>
Microwave	BN	3.27	0.006
Microwave	BN-SiC	3.28	0.003
Microwave	RBSN	3.27	0.005
Graphite Furnace	RBSN	3.26	0.003

Figure 3. Block scatterplot showing the densities (g/cm^3) of nine samples versus their positions in a three by three array, for samples processed by a) microwave heating in a BN crucible, b) microwave heating in a BN-SiC crucible, c) microwave heating in a RBSN crucible, and d) conventional heating in a RBSN crucible.

The next crucible tested for microwave processing of the bucket tappets had a BN bottom and top and SiC walls. The average density obtained was 3.28 g/cm^3 with a standard deviation of 0.003 g/cm^3 . This standard deviation is one-half the value obtained with the BN crucible and is equal to the value obtained for the samples processed in the RBSN crucible in the graphite furnace. The block scatterplot shows that the data were actually very uniform (Figure 3b) with

the exception of one sample. This sample was sawed into pieces which revealed an internal crack inside the base of the sample. The low density value of the cracked sample was discarded when calculating the average and standard deviation in density for this group of samples. Temperature measurements indicated that a difference of 8°C existed between the center and inner edge of the BN-SiC crucible. The final crucible tested for use in microwave processing of the bucket tappets was a RBSN crucible. The average density achieved with this crucible was 3.27 g/cm³, with a standard deviation of 0.005 g/cm³. These values were approximately the same as the values obtained for microwave processing in the BN crucible. The thermal analysis showed a maximum of 9°C difference between the center and inside edge of the package. The block scatterplot (Figure 3c) shows a density pattern comparable to that obtained for microwave processing in the BN crucible (Figure 3a). The reason for the poor performance of the RBSN crucible was not expected and is not understood.

After completion of the experimental studies, a one dimensional analysis of heat transfer through a microwave insulation package was done using the "T K Solver" software package^g. The analysis estimated that a 10°C temperature difference would exist between the center and inside edge of a spherical BN crucible. This approximated closely our experimental result of 14°C.

Comparisons were also made to determine the uniformity of individual samples processed by microwave and conventional heating in the previously described experiments. Table III shows that the uniformity of the densities obtained for slices from individual samples was comparable for samples processed by conventional and microwave heating. Thus, although it has been shown that temperature gradients exist in the sample crucibles used in microwave processing runs, density variations did not appear to be a problem in individual samples.

Table III. Densities of slices from SRBSN bucket tappet samples processed by microwave and conventional heating in different crucibles.

Processing Method	Crucible Type	Sample Position	Density (g/cm ³)			
			Slice #1***	Slice #2	Slice #3	Slice #4
Microwave	BN	Center*	3.28	3.28	3.28	3.28
Microwave	BN	Edge**	3.28	3.28	3.28	3.28
Microwave	BN-SiC	Center	3.28	3.28	3.28	3.28
Microwave	BN-SiC	Edge	3.27	3.28	3.27	3.27
Microwave	RBSN	Center	3.28	3.28	3.28	3.28
Graphite Furnace	BN	Edge	3.28	3.28	3.27	3.27
Graphite Furnace	RBSN	Edge	3.27	3.28	3.28	3.28

*Sample was located in the center of the crucible

**Sample was located on the inside edge of the crucible

***Slice one was the top of the bucket tappet

Conclusion

Initial scale-up experiments were performed in which microwave heating was used to nitride and sinter bucket tappet green bodies in both microwave transparent and microwave susceping crucibles. Both techniques were successful in processing multiple parts, however in some tests, the standard deviations in the densities obtained for samples processed in BN crucible and the RBSN crucible were higher than the controls processed by conventional heating. A crucible with silicon carbide walls and a BN top and bottom produced the most uniform group of samples, however further experiments with larger numbers of samples must be done to prove the merits of

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this type of crucible. Also, samples processed by both microwave and conventional heating were shown to have good density uniformity throughout the parts. Although experiments discussed here have been limited to a maximum twenty-one samples, other runs have been made in which to forty samples and two kilograms of materials were processed. Our initial results are promising and new ideas are emerging on how to use computer modeling to help design the proper materials to further scale-up microwave processing of ceramic materials.

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References

1. J. O. Kiggans, 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, edited by D. E. Clark, F. D. Gac, and W. H. Sutton (Am. Cer. Soc., Westerville, Ohio) 267-272 (1991).
2. J. O. Kiggans and T. N. Tiegs, "Characterization of Sintered Reaction Bonded Silicon Nitride Processed By Microwave Heating," in Microwave Processing of Materials III, edited by R. L. Beatty, W. H. Sutton, and M. F. Iskander (Mat. Res. Soc., Pittsburgh, Penn.) 285-290 (1992).
3. R. N. Katz, Nitrogen Ceramics 1976-1981, pp. 3-20 in Progress in Nitrogen Ceramics, ed. F. L. Riley, Martinus Nijhoff Pub., The Hague, Netherlands (1983).
4. D. W. Richerson, Modern Ceramic Engineering, Marcel Dekker, New York (1982).
5. L. M. Sheppard, "Cost-Effective Manufacturing of Advanced Ceramics," Am. Ceram. Soc. Bull., 70[4]692-707(1991).
6. J. A. Mangels and G. J. Tennenhouse, "Densification of Reaction-Bonded Silicon Nitride," Am. Ceram. Soc. Bull., 59 [12] 1216-1222 (1980).
7. A. Ezis, "The Fabrication and Properties of Slip-Cast Silicon Nitride," in Ceramics for High Performance Applications, edited by J. J. Burke, A. E. Gorum, and R. N. Katz (Brook Hill Publishing Co.) 207-222 (1974).
8. T. N. Tiegs, J. O. Kiggans, and H. D. Kimrey, "Microwave Processing of Silicon Nitride," pp. 267-272 in Microwave Processing of Materials-II, Vol. 189, ed. by W.B. Snyder, W.H. Sutton, D.L. Johnson, and M.F. Iskander, Materials Research Soc., Pittsburgh, PA 1991.
9. J. O. Kiggans, T. N. Tiegs, H. D. Kimrey, and C. E. Holcombe, "Processing Of Complex Sintered Reaction-Bonded Silicon Nitride Parts By Microwave Heating," in Ceramic Transactions, Microwaves: Theory And Applications In Materials Processing II, edited by D. E. Clark, W. R. Tinga, and J. R. Laia, Jr. (Am. Cer. Soc., Westerville, Ohio) 269-276 (1993).

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