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COMPARISON OF PROPERTIES OF SINTERED AND SINTERED REACTION-BONDED SILICON NITRIDE FABRICATED BY MICROWAVE AND CONVENTIONAL HEATING

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December 8, 1994

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ORNL 90-0036

COMPARISON OF PROPERTIES OF SINTERED AND SINTERED REACTION-BONDED SILICON NITRIDE FABRICATED BY MICROWAVE AND CONVENTIONAL HEATING

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ABSTRACT

A comparison of microwave and conventional processing of silicon nitride-based ceramics was performed to identify any differences between the two, such as improved fabrication parameters or increased mechanical properties. Two areas of thermal processing were examined: (1) sintered silicon nitride (SSN) and (2) sintered reaction-bonded silicon nitride (SRBSN). The SSN powder compacts showed improved densification and enhanced grain growth. SRBSN materials were fabricated in the microwave with a one-step process using cost-effective raw materials. The SRBSN materials had properties appropriate for structural applications. Observed increases in fracture toughness for the microwave processed SRBSN materials were attributable to enhanced elongated grain growth.

INTRODUCTION

Silicon nitride-based materials are currently the focus of considerable research for potential high-temperature structural ceramics because of their overall combination of mechanical and physical properties.[1] These materials are of interest in numerous applications for such diverse items as cutting tools, rotors and stator vanes for advanced gas turbines, valves and cam roller followers for gasoline and diesel engines, and radomes on missiles to name a few. Because of the broad interest, a considerable database has been generated over the years in processing and fabrication of silicon nitride ceramics.

In particular, microwave processing of silicon nitride has been the topic of several previous studies.[2-13] In these studies, improved densification during sintering, accelerated nitridation of silicon, improved high-temperature mechanical properties with thermal annealing of dense materials, and one-step processing of SRBSN have been reported. In the present paper, microwave thermal processing was compared to conventional heating for fabrication of silicon nitride parts. The advantages and/or disadvantages of the processes were assessed in terms of improved mechanical properties or improvements in fabrication parameters. Two main areas of silicon nitride processing were examined: (1) sintering of powder compacts; and (2) fabrication of sintered reaction-bonded silicon nitride (SRBSN).

EXPERIMENTAL PROCEDURES

Three types of samples were examined in the present study: (1) sintered silicon nitride powder compacts fabricated by St. Gobain/Norton Industrial Ceramics (SG/NIC), (2) sintered reaction-bonded silicon nitride (SRBSN) powder compacts fabricated by SG/NIC, and (3) SRBSN powder compacts fabricated by Oak Ridge National Laboratory (ORNL). The SSN (and SRBSN) powder compacts fabricated by SG/NIC consisted of silicon nitride (or silicon) powders and proprietary sintering aids at either high or low additive contents. The starting materials for the SRBSN fabricated by ORNL consisted of appropriate amounts of silicon, α-Si_3N_4, Al_2O_3, and Y_2O_3 with the final composition after nitriding and sintering estimated to be Si_3N_4 - 9 wt. % Y_2O_3 - 3 wt. % Al_2O_3. Details of the powder processing of these types of materials have been reported previously.[3-6,11-13] The SRBSN samples from ORNL were pre-sintered in argon at 1200°C for 1 hour. The samples were about 13 mm thick at this point with densities of 58-62% of theoretical density (T. D.).

All microwave processing of the samples was conducted in a 500 L cylindrical microwave cavity operating at 2.45 GHz. The samples were packed in Si_3N_4 powder containing 4% Y_2O_3 and 4% SiC, inside of a 15 cm x 15 cm x 12.5 cm alumina fiberboard box. A molybdenum sheathed thermocouple with a boron nitride sleeve was inserted between two samples to measure the temperature. BN heat distributors were used to minimize local hot spots in the samples. Nitridation was performed with N_2-4 % H_2-5 % He at ~0.1 MPa (16 psi) with additional N_2 added as the reaction proceeded. After nitridation, the materials were heated to the sintering temperature and maintained for the appropriate time. An entire heating cycle to 1800-1825°C required approximately 27 h. The SSN tiles were fired in a similar manner in the microwave, but bypassed the nitridation step and were heated directly to the sintering temperature in nitrogen. Further details on the processing can be found in earlier references.[11-13]

The conventional processing for the SRBSN samples fabricated by ORNL was carried out in conventional resistance heated furnaces in a two-step process consisting of nitridation in one furnace followed by a high temperature sintering step in a different furnace The SSN tiles were fired in a similar manner in the graphite furnace, but bypassed the nitridation step and were heated directly to the sintering temperature in nitrogen. The conventionally heated samples fabricated by SG/NIC were processed in a similar fashion.

Densities were determined by the Archimedes method. Samples were machined into bend bar specimens with nominal dimensions of 3 mm x 4 mm x 50 mm. Flexural strength testing was done in four point bending with inner and outer spans of 20 mm and 40 mm, respectively. Fracture toughness and hardness were determined by an indentation/fracture method using a 10 kg load. For the SRBSN samples fabricated by ORNL, flexural creep tests at 1200°C were performed on bend bar specimens in a fixture with same dimensions as the flexural strength testing.

RESULTS

The results on the densification, flexural strength and fracture toughness are summarized in Table 1. Several differences between the microwave and conventional processed materials were observed.

The densities of the microwave processed materials were higher than the conventional samples for the silicon nitrides with high additive contents. However, the opposite was true for the samples containing low additive contents. This difference is attributable to the coupling effect inherent in the silicon nitrides. Pure Si_3N_4 is relatively transparent to microwaves and has low absorption. Silicon nitride-based materials heat in a microwave field by coupling of the energy to the sintering additives or grain boundary phases that are normally present.[14,15] When the secondary phases are minor components, the silicon nitrides will generally have low dielectric loss properties and are difficult to heat. This difficulty translates into lower densities for the samples having low additive contents.

The mechanical properties, also given in Table 1, show that the microwave processed materials exhibit significantly improved fracture toughnesses compared to the conventionally heated samples. The improvement in fracture toughness values for the microwave materials is a result of the increased elongated grain growth observed in these samples as shown in Fig. 1. The samples containing the high additive levels showed generally higher fracture toughnesses and larger differences between the microwave and conventional samples. This is because of the larger amounts of liquid phase present in the samples with high additive contents, which facilitates the elongated grain growth associated with silicon nitride. It is also related to microwave coupling effect where the higher additive contents lead to increased heating efficiency of the samples.

Comparison of the mechanical properties also shows that, with the exception of the SSN samples with low additive content, the microwave processed materials also exhibited higher flexural strengths. In general, strength is related to the density of the material. Thus, the low strength for the SSN samples with low additive content is due to the lower densification. In situations where the densities are the same, increases in the fracture toughness reduce the sensitivity to flaws and higher strengths are typically observed. Thus, for the microwave samples, where the densities are comparable to the conventional samples, the higher strengths are attributable to the improvement in fracture toughness.

The flexural creep results at 1200°C for the SRBSN samples fabricated by ORNL indicate that the microwave-processed material exhibits better creep resistance than the conventional heated materials. The threshold stress above which the microwave material exhibits a high creep rate (and short creep life) is ~ 175 MPa, whereas the threshold stress for conventional materials is ~ 100 MPa. At stress levels between 100 and 175 MPa, the microwave samples exhibit creep rates that are approximately two-order of magnitude lower than the conventional samples. The difference in the creep resistance under the test conditions employed between microwave and conventional SRBSN materials may arise from the differences in elongated grain microstructure. The microwave material has a microstructure that exhibits a larger number density of highly developed elongated grains than that developed in the conventional material (Fig. 2). This is again associated by its higher toughness and strength as compared with conventional SRBSN.

CONCLUSIONS

For SSN and SRBSN materials, densification was dependent on the additive content. At high additive levels, the microwave coupling efficiency is increased resulting in higher densities compared to conventional heating. Thus, microwave sintering appears to be more appropriate for silicon nitride compositions at high additive levels.

The mechanical properties were generally higher for the microwave processed silicon nitrides. In particular, the fracture toughness was significantly improved over the conventional heated materials. This was attributed to enhanced elongated grain growth in the microwave processed samples.

Table 1. Summary of results on microwave and conventional sintering of silicon nitride.

Sample Number / Type	Sintering Aid Content	Processing Type	Sintered Density (g/cm^3)	Flexural Strength (MPa)	Fracture Toughness (K_{Ic}, $MPa\sqrt{m}$)
9054 / SSN[a]	Low	Microwave	3.02	599±18	5.3±0.2
9054 / SSN[a]	Low	Conventional	3.22	638±23	5.0
9059 / SSN[a]	High	Microwave	3.33	925±51	8.8±0.4
9059 / SSN[a]	High	Conventional	3.32	834±85	7.7±0.4
9032 / SRBSN[a]	Low	Microwave	3.22	808±130	7.4±0.1
9032 / SRBSN[a]	Low	Conventional	3.26	804±51	7.0±0.1
9033 / SRBSN[a]	High	Microwave	3.31	876±33	7.3±0.1
9033 / SRBSN[a]	High	Conventional	3.26	694±44	6.5±0.1
TM145X/SRBSN[b]	9Y3A*	Microwave	3.30	744	7.1±0.2
TM145Z/SRBSN[b]	9Y3A*	Conventional	3.25	601	5.0±0.3

[a]Fabricated by SG/NIC. [b]Fabricated by ORNL. * 9 wt. % Y_2O_3 - 3 wt. % Al_2O_3

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Fig. 1. Polished and etched microstructures of SRBSN materials processed by (a) microwave (TM145X) and (b) conventional heating (TM145Z).

Fig. 2. Flexural creep results at 1200°C of SRBSN materials processed by microwave (TM145X) and conventional heating (TM145Z).