MICROWAVE PROCESSING OF SILICON NITRIDE FOR ADVANCED GAS TURBINE APPLICATIONS

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ABSTRACT
The results from previous studies on microwave processing of silicon nitride-based ceramics are reviewed to ascertain the application of this technology to advanced gas turbine (AGT) materials. Areas of microwave processing that have been examined in the past are (1) sintering of powder compacts; (2) heat-treatment of dense materials; and (3) nitridation of Si for reaction-bonded silicon nitride. The sintering of Si₃N₄ powder compacts showed improved densification and enhanced grain growth. However, the high additive levels required to produce crack-free parts generally limit these materials to low temperature applications. Improved high-temperature creep resistance has been observed for microwave heat-treated materials and therefore has application to materials used in highly demanding service conditions. In contrast to Si₃N₄, Si couples well in the microwave and sintered reaction-bonded silicon nitride materials have been fabricated in a one-step process with cost-effective raw materials. However, these materials are also limited to lower temperature applications, under about 1000°C.

INTRODUCTION
Numerous applications exist for silicon nitride-based ceramics in advanced gas turbine (AGT) engines for such items as turbine rotors, vanes, shrouds, stators, bearings, and manifolds. Conventional processing of silicon nitride-based materials is done using a variety of thermal heating techniques and procedures, such as sintering, reaction-bonding, and annealing. For sintering, typical silicon nitride processing starts with high α-phase Si₃N₄ powders mixed with sintering aids, such as Y₂O₃ and Al₂O₃. After consolidation of the mixtures into a shape, they are then heated to temperatures of 1700-1900°C in nitrogen at one atmosphere (0.1 MPa) or greater for densification. The sintering temperature is dependent on the type and quantity of sintering additives utilized. At temperatures above ~1825°C, Si₃N₄ decomposition requires the use of a nitrogen gas overpressure for sintering. Densification of silicon nitride compacts occurs through a number of distinct steps. Initially, liquid phase formation occurs by the reaction between the sintering additives and the silica on the surface of the silicon nitride particulates. This normally takes place in the temperature range from 1200-1400°C depending on the additive chemistry. Initial densification begins via particle rearrangement aided by the liquid phase and capillary action. Further densification takes place by a solution-diffusion-reprecipitation process whereby α-Si₃N₄ is transformed into β-Si₃N₄. An alternative to the above method starts with silicon powder, mixed with the sintering
additives, which is initially nitrided (at temperatures of 1200-1400°C). The materials are then heated to elevated temperatures to densify in a manner similar to that described for the starting α-Si₃N₄ powders. This is done conventionally in a two-step process and the materials produced are referred to as sintered reaction-bonded silicon nitride (SRBSN).

SRBSN has been identified as a cost-effective alternative to silicon nitride made from high cost raw materials. Considerable progress has been made in recent years in producing materials with excellent properties. However, these materials tend to be very expensive and are not competitive with metal parts on a replacement basis in most applications. Reduction of cost has been recognized as a major issue for the introduction of advanced silicon nitride ceramics into the marketplace. SRBSN is an attractive alternative to the materials using expensive high-purity powders for a number of reasons. First, silicon is economical compared to high purity silicon nitride powders. A comparison shows high purity silicon nitride powders typically cost >$55/kg ($25/lb), whereas silicon powders are <$11/kg ($5/lb). The overall raw material cost per pound of the final product is further decreased because the silicon gains about 60 wt.% during nitridation. A second reason SRBSN materials are attractive is that they show improved control over the dimensional tolerances of the parts produced.

Microwave heating has the capability for volumetric thermal heating of ceramic materials. Differences between microwave and conventional heating techniques have been reviewed by Sutton and Binner. Because pure Si₃N₄ has low microwave absorption, silicon nitride-based materials heat in a microwave field by coupling to the sintering additives or grain boundary phases. Microwave processing of silicon nitride has been the focus of much previous research. In these studies, improved densification during sintering, accelerated nitridation of silicon, and improved high-temperature mechanical properties with thermal annealing of dense materials have been reported. In the present paper, the results of these studies on microwave processed silicon nitride ceramics are reviewed and summarized. Areas with potential interest for applications to gas turbine engine materials are identified.

REVIEW OF PREVIOUS RESULTS AND DISCUSSION

Sintering of Powder Compacts - In all reported results, higher densities have been achieved with microwave sintering as compared to firing in a conventional furnace. Conventionally, silicon nitride is densified by liquid phase sintering, and this is also true for the microwave heated materials. While the microwave sintered materials showed improved densification, they also showed a greater susceptibility to cracking, especially at the lower sintering additive contents.

Uniform heating in the microwave is dependent on the uniformity of the microwave field and the uniformity of the dielectric properties of the material being heated. Microwave heating of silicon nitride-based materials occurs predominantly via power absorption by the sintering additives and/or the intergranular phases. In the case of dense materials, the heat is readily transferred to the surrounding matrix because of the high thermal conductivity. With powder compacts, however, the heat transfer is dominated by convection and radiant transfer mechanisms within the compact and consequently is very slow. Problems with non-uniform heating prior to any significant densification can occur due to imperfect sintering aid distribution, inhomogeneities in the powder compact (such as density or agglomerates) and variations in the microwave power field. At low additive contents in powder compacts, these effects are the most critical. They can lead to a sequence of localized thermal runaways or "hot-spots" which cause differential sintering and shrinkage, and finally sample cracking.

To minimize or prevent this series of events, a number of techniques have been developed; these are (1) increasing the sintering additive content, (2) addition of secondary particulates that are good microwave absorbers, (3) use of an insulation package that absorbs microwaves and heats up, or (4) increasing the microwave frequency. Each of these techniques has limitations associated with it. Increasing the additive content increases the volume of grain boundary phases and generally this degrades the
high temperature mechanical properties such as creep. Particulates that have improved heating of powder compacts include Si, SiC, TiC, TiN, and SiAlON particulates. The silicon additions were nitrided to silicon nitride prior to sintering. These materials also have the problem of heat transfer through a powder compact. So while they improve the situation they do not eliminate it. Using an absorbing insulation package lowers the electric field that is "seen" by the parts and makes the system more like a conventional heating source. Thus, much of the advantage of using microwave heating, such as improved densification, is lost. Increasing the microwave frequency increases the capital cost of the furnace >10X for an increase from 2.45 GHz (most common frequency) to 28 GHz.

In addition, the densification aids used for microwave sintering must yield a composition that sinters at temperatures ≤1825 °C and at one atmosphere of nitrogen. At higher temperatures, Si3N4 decomposition is a problem. Current microwave technology is limited in the ability to apply gas overpressures to ≤200 psi. Consequently, the materials are limited to those with less refractory grain boundary phases. Microwave sintering of silicon nitride-based ceramics has also been observed to result in higher weight losses compared to conventional heating.

Measurements of the mechanical properties showed the microwave sintered materials exhibited slightly higher fracture toughness values. The moderately larger grain sizes observed in the microwave sintered samples would account for this difference.

**Annealing of Dense Silicon Nitride**

Microwave annealing of dense silicon nitride was done to determine any differences in microstructure development and intergranular phase crystallization compared to conventional processing. Microstructural changes occurring during the annealing were found to be significant depending on the intergranular phase composition and the annealing conditions.

Enhanced grain growth was observed during microwave heat treatment of specimens with 6% Y2O3-2% Al2O3 as sintering aids at temperatures of 1400°C for 10 h. Accompanying the grain growth was further α-to-β Si3N4 phase transformation. The intergranular phases for conventional annealing at 1400°C consisted of large grain boundary pockets of crystallized Y2Si2O7 with the aluminum existing predominantly in small amorphous pockets, which is also typical for this material composition. When the material was microwave annealed at the same temperature, there was a significant improvement in crystallization and, in fact, no amorphous phases were found in the sample. In the conventionally heated sample, when there was some residual amorphous phases present, they were due to the aluminum segregating into discrete areas as the Y2Si2O7 or other Y-Si-O-N phases crystallized. In the microwave annealed sample, however, the aluminum was found in solid solution within the crystalline grain boundary pockets in a high Y-containing silicate (but not Y2Si2O7).

The mechanical properties of the microwave treated specimens showed only a slight improvement in fracture toughness. However, in the case of the material containing 6% Y2O3-2% Al2O3 as sintering aids, significant decreases in the creep deformation rates at 1260°C were observed.

**Sintered Reaction Bonded Silicon Nitride**

In recent years, microwave heating has been introduced as an alternative process for producing SRBSN materials. In the microwave it has been observed that nitridation occurs at faster rates and initiates at slightly lower temperatures (~50°C) as compared to conventional heating. Normally with conventional heating, SRBSN is produced in a two-step process. However, because of the insulation configuration used during microwave heating, both the nitridation and sintering can be done in a single continuous step. Consequently, microwave heating offers a way to reduce total fabrication times of components and reduce the number of handling operations necessary to produce a part. Thus, the microwave heated materials potentially have an economic advantage over conventionally processed SRBSN materials. Comparison of the raw material costs revealed that SRBSN compositions are less than about 1/4 the cost of those for materials made with high cost silicon nitride powders.

It has been shown that a reverse thermal gradient exists in microwave heated parts. In the SRBSN materials, this will result in nitridation of
internal material first with the reaction moving to the external surfaces. Thus, pore closure by the silicon nitride reaction product growing into the pore space is minimized. This situation is in contrast to conventional heating where the reaction starts at the external surfaces resulting in pore closure and poor penetration of nitrogen into the interior portions of a part. This can become a severe problem, especially for very thick parts.

Densification behavior of the SRBSN shows that microwave sintering is more effective than conventional sintering for similar conditions. This type of behavior has been observed in previous comparisons of microwave and conventional sintering of Si$_3$N$_4$ powder compacts and SRBSN.$^{13,14,19}$

Mechanical testing showed that the most important factor affecting the strength was the type of rare earth additive. Higher strengths were observed by substituting Y$_2$O$_3$ for La$_2$O$_3$. Ambient temperature flexural strengths as high as 785 MPa have been observed. This strength is higher than for similar SRBSN materials processed under similar conditions by conventional heating.$^7$ Flexural testing at elevated temperatures showed samples containing Y$_2$O$_3$ and Al$_2$O$_3$ exhibited good strength retention up to 1000°C. While significant strengths have been achieved, the fracture toughness ($K_{IC}$) values ranged from 4.5 to 5.1 MPa$m$ for the SRBSN materials tested to date. This is lower than the values obtained for the samples starting with the high purity Si$_3$N$_4$ powders which are in the range of 6.8-7.0 MPa$m$.

**CONCLUSIONS AND POTENTIAL APPLICATION TO AGT MATERIALS**

Microwave processing of silicon nitride is an area high in potential for improved material properties, but it also creates other processing problems. Microwave heating of silicon nitride-based materials occurs predominantly via power absorption by the sintering additives and/or the intergranular phases. In the case of SRBSN, the microwave power is substantially absorbed by the silicon.

During sintering of powder compacts with high levels of additives, densification occurs predominantly by particle rearrangement and hence sintered densities are similar, but not equal for both conventional and microwave heating. A modest contribution during the $\alpha$-to-$\beta$ Si$_3$N$_4$ transformation in the microwave sintering improves densities slightly. Thus, to enhance any microwave effect, one would choose to use lower additive contents where solution-diffusion-reprecipitation is a more dominant densification process. However, at low additive contents, problems arise because heating and densification inhomogeneities lead to specimen cracking. Thus, microwave sintering of powder compacts at the present state of technology is limited to materials with relatively high additive contents that must densify at temperatures $\leq$1825°C. AGT materials that would fit this requirement are in some of the less demanding areas in terms of temperature and stress. Unfortunately, the most demanding applications require materials with very refractory grain boundary phases having low creep rates.

Microwave annealing of dense silicon nitride-based ceramics can result in further $\alpha$-to-$\beta$ Si$_3$N$_4$ transformation accompanied by grain growth. Improvements in the high temperature creep properties by increasing the crystallization of the grain boundary phases have been observed. Thus, microwave annealing is applicable to AGT materials that require good high temperature creep resistance where densification has been previously performed.

SRBSN is a cost-effective method to fabricate silicon nitride ceramics. Raw materials costs are less than about 1/4 those for high-purity silicon nitride materials, which improves the cost-competitiveness of these materials with metal parts. Conventional SRBSN requires long nitridation times and two-step firing. By using microwave heating, nitridation times are reduced and all firing is performed in a one-step continuous process, simplifying the operation. The current materials produced by this fabrication method have strength appropriate for numerous applications at temperatures up to approximately 1000°C which again limits their use to low temperature AGT applications.

**REFERENCES**


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