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# CERAMICS IN GAS TURBINE: POWDER AND PROCESS CHARACTERIZATION

by Sunil Dutta
Lewis Research Center
Cleveland, Ohio 44135


TECHNICAL PAPER presented at the
Conference on Composites and Advanced Materials
sponsored by the American Ceramic Society
Cocoa Beach, Florida, January 17-19, 1977

# CERAMICS IN GAS TURBINES:

# POWDER AND PROCESS CHARACTERIZATION

by Sunil Dutta

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

## ABSTRACT

The role of powder and process characterization in producing high quality silicon nitride and silicon carbide components, for gas turbine applications, is described. Some of the intrinsic properties of various forms of $Si_3N_4$ and SiC are listed and limitations of such materials' availability have been pointed out. The essential features/parameters to characterize a batch of powder have been discussed including the standard techniques for such characterization. In process characterization, parameters in sintering, reaction sintering, and hot pressing processes are discussed including the factors responsible for strength limitations in ceramic bodies. It is inevitable that significant improvements in material properties can be achieved by reducing or eliminating the strength limiting factors with consistent powder and process characterization along with process control.

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## INTRODUCTION

The high temperature ceramic gas turbine is a candidate power plant because it offers potential solutions to some of the problems of energy, air pollution, and materials resources. The high efficiency ceramic gas turbine with its smaller volume and weight, has significant potential for use in aircraft and automobile engines, and in electric power generating systems. Advanced ceramics such as silicon nitride and silicon carbide have been widely considered for gas turbine components. Their material properties such as high strength, and good thermal shock, oxidation resistance, and phase stability make them well suited for gas turbines. Because of their high use temperatures these ceramics offer the gas turbine important advantages including reduction in cooling air requirements and in specific fuel consumption, and may permit the use of lower grade fuels.

The need for ceramics in gas turbines has been well recognized. However, the lack of consistent methods of powder and process characterization and the lack of consistent materials sources, in addition to the problems of designing with brittle materials, inhibit their use. The objective of this paper is to describe the material and process characterization required for process control in the manufacture of gas turbine components.

## PROPERTY REQUIREMENTS

The material requirements for high temperature gas turbines vary for each component depending on the exact nature of the operational environment (mechanical, thermal, chemical, etc). For example, Table 1 shows the ceramic materials considered for components of a vehicular gas turbine[1], and gives the maximum operating temperature for each component.

TABLE 1

Ceramic Materials for Vehicular Gas Turbine Components[1]

| COMPONENT | MAXIMUM OPERATING TEMPERATURE°C (F) | CERAMIC MATERIAL |
|---|---|---|
| Combustor | 1648 (3000) | SiC |
| First Stage Stator | 1315 (2400) | $Si_3N_4$ |
| First Stage Rotor Shroud | 1093 (2000) | $Si_3N_4$ |
| First Stage Rotor | 1280 (2300) | $Si_3N_4$,SiC |
| Second Stage Stator | 1150 (2100) | $Si_3N_4$ |
| Second Stage Rotor | 1093 (2000) | $Si_3N_4$,SiC |
| Regenerator | 982 (1800) | LAS/MAS* |

As noted in the introduction, the essential properties for gas turbine components are high temperature mechanical strength, good oxidation, thermal shock resistance, and phase stability.

Table 2 indicates some important properties of some forms of $Si_3N_4$ and SiC ceramics which are under investigation for gas turbine components.

*LAS - Lithium Aluminum Silicate
MAS - Magnesium Aluminum Silicate

TABLE 2

Typical Properties of $Si_3N_4$ and SiC Ceramics

| Material | Density g/cc | Strength (MOR) $MN/m^2$ (ksi) R.T. | H.T. 1370°C (2500°F) | 1370°C(2500°F) Thermal Coeff. of Expansion in./in./C | 1370°C (2500°F) Thermal Conductivity cal/sec/$cm^2$/C |
|---|---|---|---|---|---|
| $Si_3N_4$ | | | | | |
| Hot Pressed | 3.18 | 690-828 (100-120) | 345-414(50-60) | $3.28 \times 10^{-6}$ | 0.033 |
| Reaction Sintered | 2.7 | 276-324 (40-47) | 345 (50) | 3.15 | 0.012 |
| Pressureless Sintered | 3.06 | 552-621 (80-90) | 276-345(40-50) | - | - |
| SiC | | | | | |
| Hot Pressed | 3.29 | 669 (97) | 345-379(50-55) | 4.8 | 0.076 |
| Pressureless Sintered | 3.08 | 607 (88) | 607 (88) | 5.0 | 0.058 |
| SiC/Si/C | 2.9 | 483 (70) | 483 (70 up to 1200°C (2200°F) | 5.1 | 0.053 at 1090°C (2000°F) |

Among the properties discussed, thermal expansion and thermal conductivity, along with the modulus of elasticity, control the thermal stresses developed. Thus they determine the thermal shock exposure a material of a given strength can tolerate. Of the numerous ceramics available, $Si_3N_4$ and SiC have lower thermal expansion and higher thermal conductivity, and consequently higher thermal shock resistance. In addition, these ceramics have low densities and possess excellent mechanical strength, at room and high temperatures. Therefore, the selection of $Si_3N_4$ and SiC as candidates for gas turbines was made on the basis of strength and resistance to thermal shock. However, these properties are very sensitive to processing history such as powder preparation, fabrication conditions, and fabrication techniques, which are responsible for porosity, foreign inclusions, low melting phases, stoichiometry etc., all of which limit the strength. Therefore, further improvements in material properties remain to be achieved by consistent powder and process control.

## MATERIALS AVAILABILITY

Presently, materials costs and availability of silicon nitride and silicon carbide are problem areas. Since no large and continuing market exists for these materials, their present cost is high and their availability is quite limited. Table 3 shows a list of manufacturers, who have been engaged in synthesizing or manufacturing high purity, micron and sub-micron $Si_3N_4$ and SiC powders.

TABLE 3

Potential Sources of High Purity, $Si_3N_4$ and SiC Powders

| Silicon Nitride ($Si_3N_4$) | Silicon Carbide (SiC) |
|---|---|
| Kawecki Berylco/Advanced Materials Engineering | Pittsburgh Plate Glass |
| General Telephone & Electronics | General Electric Co. |
| Norton Co./Lucas Ltd. | Carborundum Co. |
| Indussa Corporation | Sonneborn Refractories & Chemicals Corporation |

Silicon nitride materials are in such an early stage of development that they are undergoing constant changes in methods of manufacturing, processing, additives etc., thus resulting in different chemistries in the final synthesized powder, from one batch to another.

Sinterable silicon carbide powder is less available than silicon nitride powder. No high purity, sub-micron SiC powder is available commercially. Although Pittsburgh Plate Glass was a source of β-SiC powder, this powder was withdrawn from the market. General Electric does not manufacture β-SiC for sale. Carborundum has announced a fine grained α-SiC powder, but it is not yet commercially available. In any case, progress is hindered by a lack of powders having reproducible characteristics.

## POWDER CHARACTERIZATION

The essential features to characterize in a batch of powder either in research and development programs or for quality control in production are shown in Table 4.

Table 4

Characterization Features of Silicon Nitride and Silicon Carbide Powder

| |
|---|
| X-ray Density |
| Chemical Composition/Stoichiometry |
| Trace Cation and Anion Impurities |
| Surface Area |
| Average Particle Size |
| Particle Shape |
| Particle Size Distribution |
| Phase Composition |
| Unreacted Phases (Si,C) |

Silicon nitride and silicon carbide powders from different vendors have wide compositional variations with respect to impurities, stoichiometry, chemistry etc. They can also vary from batch to batch in material prepared at different times. Therefore, a quantitative characterization of these features (Table 4) is very important to understand the cause and effect relationships in material properties.

Some of the standard techniques of characterizing ceramic powders are listed in Table 5.[2]

TABLE 5 [2]

Standard Techniques for Ceramic Powder Characterization ($Si_3N_4$ and SiC)

| Technique | Characterization Features |
|---|---|
| Wet Chemistry | Quantitative Elemental Analysis |
| X-ray Fluorescence | Trace Elements |
| Emission Spectroscopy | Cation Analysis 1-10 ppm |
| Mass Spectroscopy | Cations & Anions below 10 ppm |
| Vacuum fusion | Nitrogen |
| Neutron Activation | Oxygen less than 0.3 percent |
| Non-dispersive X-ray | (Elemental analysis) of particles > 1 um size |
| X-ray Diffraction | Phase Identification, Crystal structure |
| Electron Diffraction | Particles > 0.1 um size |
| Optical Microscopy | Particles > 0.5 um size |
| Screening/Sieving | Particles > 400 mesh |
| Sedimentation | 0.05 - 100 um size range |
| Electron Microscopy | 0.001 - 5 um size range |

Of these techniques, wet chemical analysis, X-ray diffraction, optical microscopy, electron microscopy, and screening/sieving are most routinely used while others are less commonly used due to inadequate laboratory facilities and an excessive time and cost required. However, their use is increasing. For example, more and more researchers are using the neutron activation technique for quantitative estimation

of oxygen[3] in silicon nitride, aluminum nitride etc., instead of the vacuum fusion technique.

Effort is underway to improve chemical analyses because of anomalies in analysis of the same starting powder. To illustrate the problems, Table 6[(4)] shows chemical analyses of two silicon nitride powders performed in different laboratories.

TABLE 6[(4)]

Wet Chemical Analysis Performed at Various Laboratories

SILICON NITRIDE POWDER (2-grades)

| | Controlled Phase 85/15* | | High Purity* | | |
|---|---|---|---|---|---|
| Element | AME(U.K.) Wt.% | NASA-Lewis Wt% | AME(U.K.) Wt% | KBI Wt% | NASA-Lewis Wt% |
| Oxygen | 1.3 | 2.29 | 0.55 | 0.55 | 1.8 |
| Fe | 0.5 | 0.78 | 0.63 | 0.40 | 0.27 |
| Ca | 0.2 | 0.40 | 0.25 | 0.02 | 0.05 |
| Al | 0.5 | 1.17 | 0.50 | 0.10 | 0.09 |
| Ti | -- | 0.036 | 0.042 | -- | 0.019 |
| Mn | -- | 0.015 | -- | -- | -- |
| C | 0.2 | 0.16 | 0.15 | -- | 0.55 |

-- Not analyzed
*Advanced Materials Engineering, U.K.

For example, in controlled phase 85/15 grade powder, the oxygen content analyzed at AME (Advanced Materials Engingeering Laboratory) was 1.3 wt percent, while Sanders at NASA-Lewis, obtained a higher value of 2.29 wt percent. Similarly, the aluminum content analyzed by AME to be 0.5 percent as compared to a higher value of 1.17 percent, reported by Sanders. In high purity grade $Si_3N_4$ powder, the major variations were found in the analysis of oxygen, aluminum, calcium and carbon contents. Although the variation in results could be due to errors in the specific experimental technique, a lack of accepted methods of analyses raises questions about correctness of the data, since there are no suitable ways to cross check results from one experimental technique to other among laboratories.

Characterization of ceramic powders such as silicon nitride and silicon carbide is an extremely time consuming and expensive task, and varies between one user to another. The manufacturers of such powders need to carry out extensive characterization on the powder to maintain quality. Several methods should be employed to cross check results, because the reliance upon one technique can lead to erroneous interpretations. With $Si_3N_4$ and SiC powders, an important parameter is residual oxygen, in the synthesized powder. Also, surface silica ($SiO_2$) and the increase in $SiO_2$ content during storage, should be determined quantitatively to understand the basic nature of the starting raw materials.

It is anticipated that when all the above features are determined accurately and correlated with the material properties, a suitable specification can be developed for a powder, with reproducible characteristics.

## PROCESS CHARACTERIZATION

The major role of process characterization is to identify the source of the strength limiting factors in ceramics. They are listed in Table 7.

Table 7

Strength Limiting Factors in Ceramics

| |
|---|
| Porosity |
| Inclusions |
| Agglomerates |
| Cooling Cracks |
| Unreacted Phase(s) |
| Phase Transformation |
| Large Grain Size |
| Surface Defects |

For example, inclusions, agglomerates etc, are usually introduced during powder handling and processing; while porosity, coarse grains and pores etc, result during densification. All of these defects can be randomly distributed throughout the material and cause wide scatter in strength, resulting in a low Weibull "m" value. Therefore, in order to have maximum reliability, and to produce material of consistent quality, careful characterization of each processing step is essential. For example, during milling, characterization of milling media, milling contaminants, particle distributions etc, to determine the quality of mixing, and the nature and level of impurities introduced during the milling operation are essential.

Similarly, during cold forming such as injection molding processes, parameters of the injected mix such as viscosity of organic binder, particle distribution, particle shape, etc, should be characterized in order to control the molding behavior (flow characteristics) of a particular composition and the resulting quality of the molded product.

Sintering, reaction sintering, and hot pressing are the major hot forming processes. The parameters that need careful characterization in these processes are shown in Table 8. In all three processes, characterization of various parameters are crucial for process control, to produce high quality products. For example, time, temperature, and atmosphere are common to all three processes. In reaction sintering of silicon, the relation of temperature and pressure of the nitriding cycle must be controlled to achieve high density products with homogeneous microstructures and uniform porosity distribution. Similarly, in hot pressing, control of parameters, e.g. die material, die liner, spacer material along with the hot pressing pressure are essential. The pressure may be applied at various stages of sintering, which could affect the density, grain size, microstructures and strength. Fig. 1 shows three different temperature-pressure profiles. Fig. 1A indicates that a small pressure is being applied during the early stage of hot pressing until the compact reaches the selected sintering temperature, where the maximum pressure is applied. On the other hand, in Fig. 1B, maximum pressure is applied at an intermediate stage before maximum temperature is achieved, while in Fig. 1C, both pressure and temperature are increased simultaneously such that the compact reaches maximum hot pressing pressure at maximum sintering temperature.

TABLE 8

Characterization Parameters in Sintering, Reaction Sintering and Hot Pressing Processes

| Features | Sintering | Reaction Sintering | Hot Pressing |
|---|---|---|---|
| Sintering Aids | X | X | X |
| Binder (vol %) | X | X | X |
| Binder Removal | X | X | |
| Green Density | X | X | X |
| Die Material | | | X |
| Die Liner | | | X |
| Spacer | | | X |
| Sintering Temperature | X | X | X |
| Sintering Time | X | X | X |
| Sintering Atmosphere | X | X | X |
| Gas Pressure | X | X | |
| Hot Pressing Pressure | | | X |

Dutta and Rubin [5] observed the effect of these temperature-pressure profiles on density, grain growth and microstructures in hot pressed alumina. For example, profile 1C yielded comparatively the highest density at a given intermediate temperature, compared to 1(A) & 1(B), although there was very little difference in density

values at the very final stage of sintering. Also, profile 1C produced the most uniform microstructures with no exaggerated grain growth, while profile 1A, resulted in maximum exaggerated grain growth. However, it is difficult to anticipate which one of these temperature-pressure profiles would yield best results during hot pressing of $Si_3N_4$ and SiC although it is noteworthy that profile 1C is more conventional in commercial practice.

## CONCLUDING REMARKS

Powder and process characterization are critically important to the production of high performance $Si_3N_4$ and SiC ceramics for gas turbine applications. It is absolutely essential to correlate powder and process characterization data with material property data, to develop specifications for material with reproducible characteristics, in order to make the use of $Si_3N_4$ and SiC ceramics practical for gas turbines.

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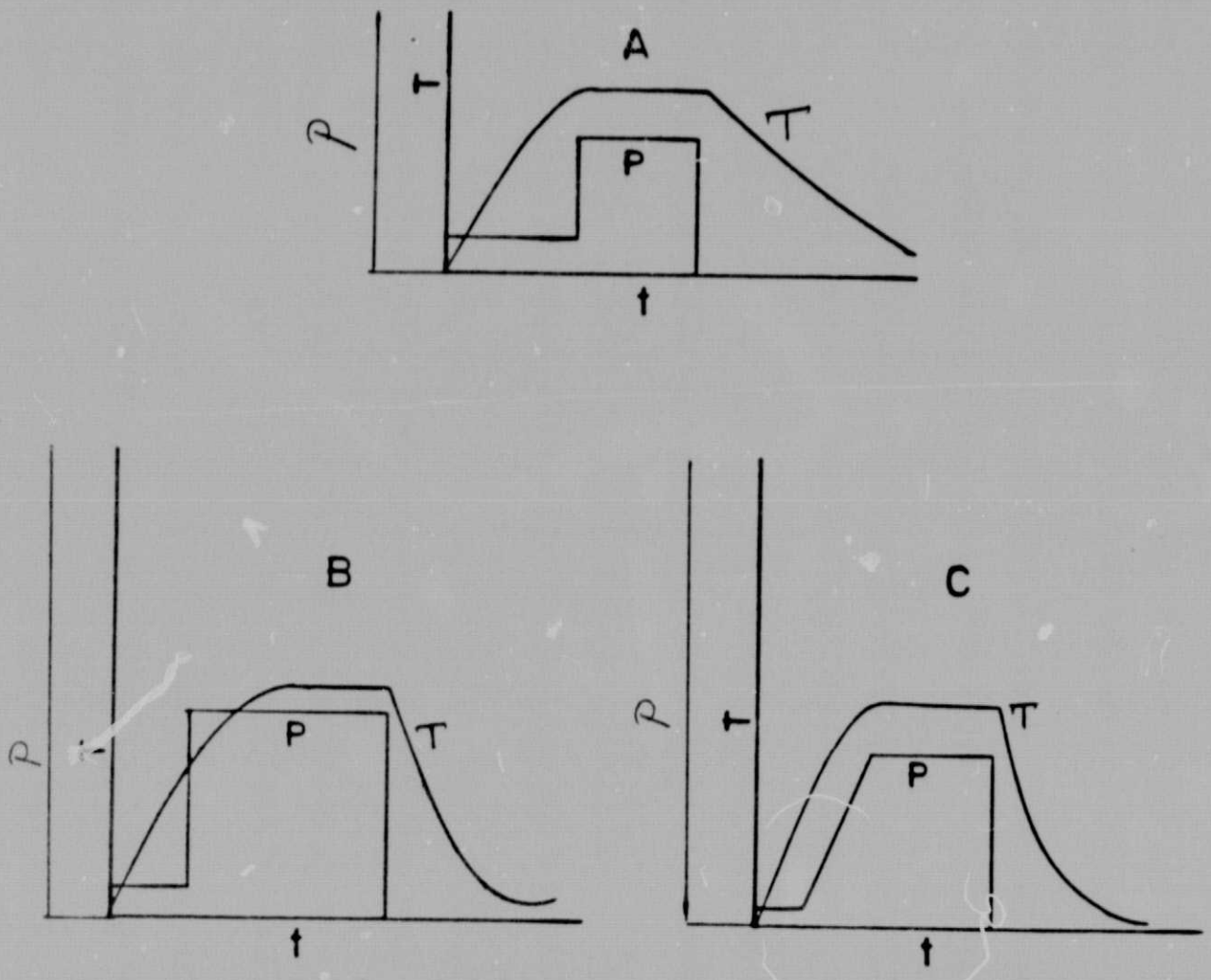


FIGURE 1. TIME-TEMPERATURE-PRESSURE PROFILE IN HOT PRESSING OF CERAMICS