Development of silicon nitride substrates with high thermal conductivity for heat sink applications based on economic technologies

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Abstract

This study illustrates novel approaches to manufacture high thermal conductive Si_3N_4 substrates by near-net-shape and low cost tape casting techniques. It is important to systematically investigate the effect of sintering additives on the material properties, especially on thermal conductivity. To optimize material characteristics, a new developed microstructure-property-simulation using the finite element method of the Fraunhofer-Institut für Silicatforschung ISC was applied. This investigation presents the possibility of assembling a Si_3N_4-AMB-substrate with a three times higher thermal conductivity as usual for heat-sink applications and thus makes it possible to increase the life cycle of electronic assemblies.

1. Introduction

Commercial applications for silicone nitrides include constructional elements in mechanical engineering/turbine manufacturing and cutting tools. These applications profit on characteristical properties like high strength at high temperatures, low density, corrosion resistance against fused metals (especially non-ferrous metals), high hardness, low friction coefficient, wear resistance, a good thermal shock behaviour and spalling resistance. Especially the thermal characteristics and mechanical strength makes Si_3N_4 suitable for applications in power electronics. Tab.1 shows typical values of gas pressure sintered Si_3N_4 (GPSSN) characteristics.

Tab. 1. Typical characteristics of GPSSN [1]

	Si_3N_4
density ρ [g/cm³]	3,2
bending strength σ_B [MPa]	900-1200
Young's modulus E [GPa]	300-310
fracture toughness K_{1c} [MPam$^{1/2}$]	8,0-9,0
thermal conductivity λ [W/mK]	20-24

However, silicon nitrides aren't yet competing with established materials in substrate technologies because of its comparable low thermal conductivity, which lays about 20-24 W/mK and its high manufacturing costs especially for the hot pressing process and the complex and expansive finishing by hard machining.

The main focus of this investigation is on increasing the thermal conductivity value by testing different sintering additives. To manufacture silicon nitride substrates the development of a castable suspension is necessary. Sintering conditions are set to achieve a dense as possible ceramic which is based on phase building due to thermal treatment. The optimization of the microstructure is provided by a new microstructure-property-simulation developed by the Fraunhofer-Institut für Silicatforschung (ISC). Continuous measurements verify the properties and identify relationships between characteristics and microstructure. Coating the substrate with copper by active metal brazing technique completes the assembly and makes it suitable for heat-sink applications.

Thus the possibility of assembling a Si_3N_4- AMB-substrate with the use of low cost shape forming and sintering methods and three times higher thermal conductivity as usual is shown.

2. Experimental procedure

2.1. Compounding the slurry

The creation of slurry is the first step of the production process. The slip consists of the silicon nitride powder, the necessary sintering additives, solvents, plasticizer, dispersant and binder. Each one has to meet several demands. Powder and additives are the only components that remain after thermal treatment. Their particle characterization (e.g. size, distribution, surface, impurities) has a great influence on sintering behaviour, microstructure and so on the achieved properties. For sintering additives, different mixtures of rare earth oxides like Y_2O_3, La_2O_3 and other oxides like MgO, SiO_2, and Al_2O_3 have been tested. Binder (polyvinyl butyral) and plasticizer (benzoic acid) obtain a flexible, dimensionally stable green tape. Solvents, in this case an aceotropic mixture of alcohol and ketone, make sure, that all components can be dispersed and the slurry can be processed by tape casting. Organic solvents have the advantage of a high drying rate. A dispersant (fatty acid ester) avoids sedimentation, segregations and the building of agglomerates. To compound all parts a ball mill is used. Due to their size the grinding balls have only a mixing not a milling effect. This well-considered choice of the components is a basic requirement for castable and sinterable slurry.

2.2. Tape casting process

The best possibility to form extensive, plain ceramic parts with low thickness is the tape casting process. Fig. 1 shows the basic principle. The slurry is poured into a reservoir on a polymer carrier behind a pre-blade. The gap of the pre-blade is larger than the gap of the doctor-blade. The gap of the doctor blade defines the wet thickness of the casted tape. Because of two blades a second reservoir is built. The two-blade design allows better control of the slurry level, which also has an impact on the wet thickness. Another variable is the speed carrier. The slurry passes the doctor blade and comes to a drying zone. The solvents are evaporated over the surface and a dry tape remains on the polymer carrier. The casted tapes have a sufficient green strength so that they can easily be resized by punching for example.

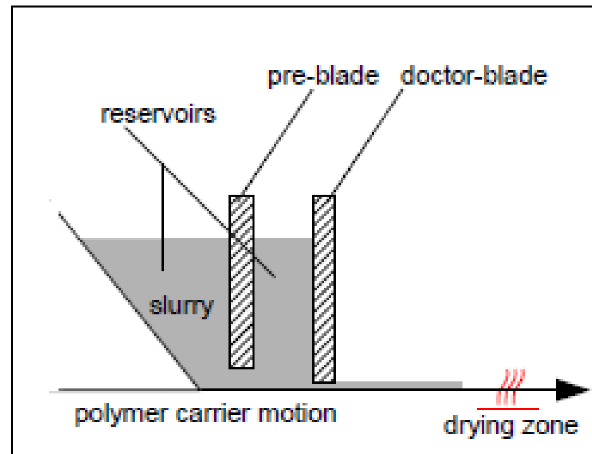


Fig. 1. Basic principle of tape casting

2.3. Sintering method

The casted tapes can subsequently be sintered by gas pressure sintering, which is a quite cost efficient method. The low diffusion coefficient of nitrogen makes the sintering of Si_3N_4 a sophisticated issue as it inhibits solid-state sintering and thus requires a liquid phase. Therefore, it is important to investigate systematically the effect of sintering additives on the material properties, especially on thermal conductivity. Fig. 2 shows a pilot gas pressure sintering furnace.

Fig. 2. Pilot gas pressure sintering furnace

The furnace can be operated with temperatures up to 2000 ℃ and nitrogen pressure up to 20 bar.

2.4. Active metal brazing technique

The Si_3N_4 substrates are soldered with copper using active metal brazing (AMB). Screen-printing the brazing paste (e.g. AgCuTi) is done on ground surface. After drying copper foils can be applicated. Brazing can be carried out either under a protective atmosphere or in vacuum at temperatures between 900-1000 ℃. If desired, an etch resist pattern may be printed to get a structured copper layer after chemical etching. Fig. 3 shows such a ceramic unit.

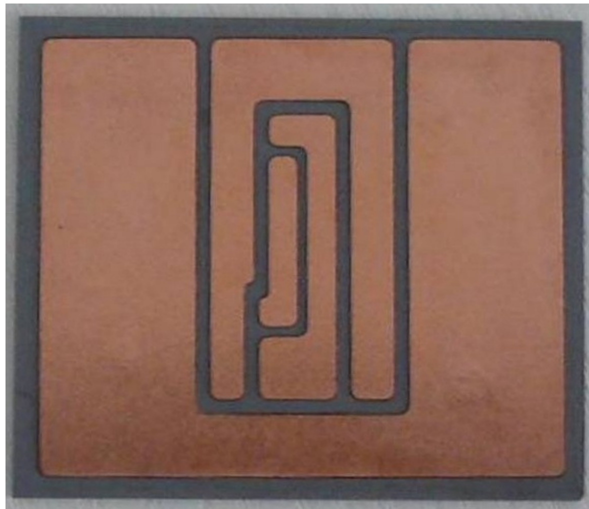


Fig. 3. Si_3N_4-AMB-substrate with structured copper layer

3. Property measurements

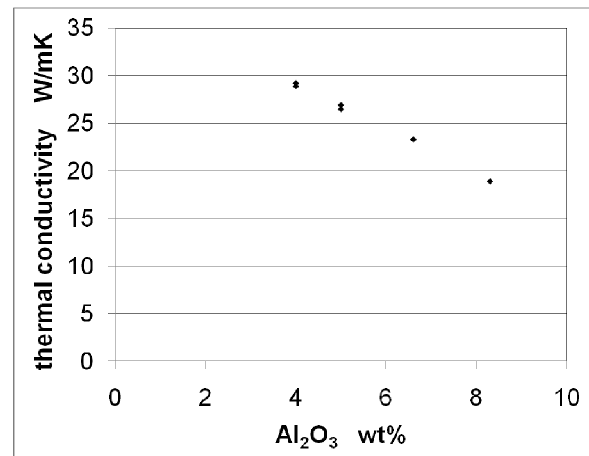
3.1. Mechanical and thermal characteristic

The focus is on the bending strength σ_B, density ρ and thermal conductivity λ. To specify the bending strength a 3-point bending test is used. Defects like porosities cause decreasing strength. Density is measured by buoyancy-flotation method. The thermal conductivity is indirectly determined by laser flash technique. It depends on conductibility of temperature, heat capacity and density. Therefore a dense Si_3N_4 is necessary to increase the strength and the thermal conductivity. Tab. 2 shows three batches with different sintering additives. Batch A contains Al_2O_3 and Y_2O_3, batch B a mixture of rare earth oxides and batch C a mixture of earth and rare earth oxides as sintering additives.

Tab. 2. Properties of different batches

Batch	Th. density ρ	λ [W/mK]	σ_B [MPa]
A	98 %	28	520
B	91 %	85	180
C	95 %	63	220

The Theoretical density is defined by the combination of fractions of Si_3N_4 and sintering additives. The insufficient density has a great negative effect on the bending strength because porosities exceed the critical defect size.
Different amounts of Al_2O_3 in batch A show a direct influence on the thermal conductivity (diag. 1).

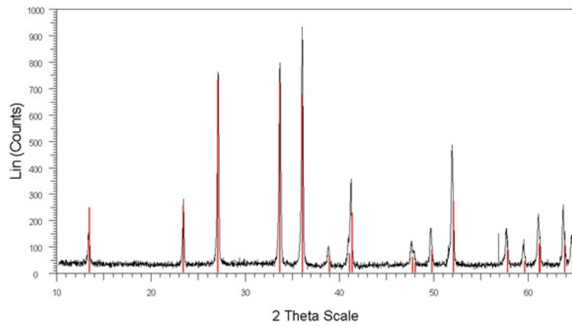


Diag. 1. Relationship between the thermal conductivity and value of Al_2O_3

An increasing of Al_2O_3 tends to result in lower thermal conductivity.
The difference between batch A and B, C in thermal conductivity should be examined by scanning electron microscopy and crystal phase analysis.

3.2. Microstructure and Phase analysis

Phase analysis is accomplished by X-ray diffraction (XRD). In this way only the crystalline fraction can be detected. Every crystalline substance has a well-defined X-ray diffraction pattern like a „fingerprint“, so the position of the peaks is characteristic for each material. Diag. 2 shows a phase diagram of Si_3N_4. Only β-Si_3N_4-cristallites can be detected, all other additives are amorphous.



Diag. 2. Phase analysis of Si_3N_4 [2]

The phase diagrams of the batches A, B and C exhibit Si_3N_4 only in the modification of β, so all α-Si_3N_4 in the powder has turned into the stable state. Batch A contains SiAlON-phases. Additionally the position of the Si_3N_4-peaks differs slightly from its regular location. That indicates a lattice imperfection of the Si_3N_4. Because of the Al^{3+} ionic radius 0,57 Å, they can be located either in the lattice or substitute a Si^{4+}-ion. Both cause a deformation of atomic structure and lead to reduced thermal conductivity. That's why Al_2O_3 is excluded as sintering additive for heat sink applications.
Batches B and C contain undefined phases with structure like SiAlON-phases. But in this batches no aluminous substance are used, that's why they have to be another structures, which cannot be easily detected by comparison with international database. This study will be continued.

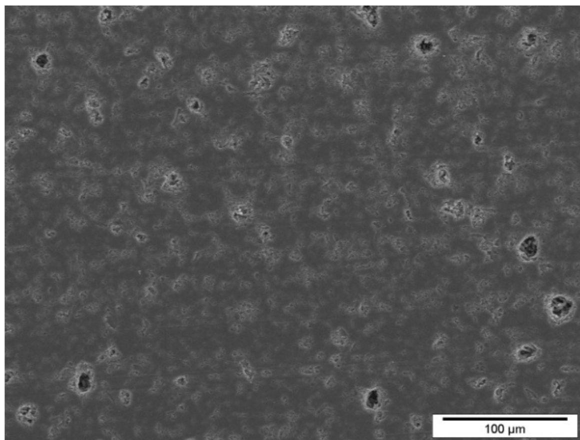


Fig. 4. Texture of batch C before development of sintering conditions

The modification of thermal treatment is observed by scanning electron microscopy. The texture at the beginning of the development is shown in Fig. 4. The batch has 95% of theoretical density and a lot of pores range from 1 µm to 5 µm exist. Additionally a few greater pores between 9 µm and 15 µm are detected too. A quantity analysis is disclaimed because of irregular pores and grown β-Si_3N_4-cristallites, which extend in the pores.

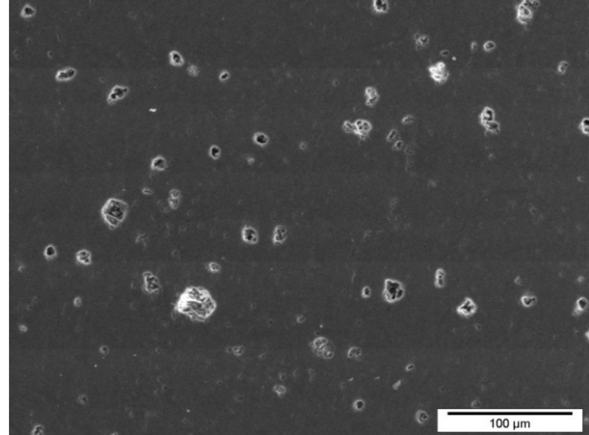


Fig. 5. Texture of batch C after development of sintering conditions

After development of sintering conditions the little pores almost disappear and a few pores between 9µm and 15 µm remain (Fig. 5). The material has now 98% of theoretical density, the bending strength increase to about 620 MPa.

Plasma etched samples present a secondary phase, which completely encloses the grains. Its enlargement is only up to 20 nm between the grains and 55 nm in the triple grain junctions. In comparison to that β-Si_3N_4-cristallites grow up to 15 µm. The influence of the secondary phase and grain size/form on the thermal conductivity and bending strength will be the main purpose of further studies.

4. Outlook

With that database of different batches it will be possible to create the necessary parameters to take advantage the new developed microstructure-property-simulation using the finite element method of the Fraunhofer-Institut für Silicatforschung ISC. Accordingly a direct relationship between microstructure (like secondary phases, grain shape/size/boundary) and properties can be discovered. So a further improvement of thermal conductivity will be probable. Fig. 6 shows the microstructure of sintered Si_3N_4 with sustained, hexagonal β-crystallites without preferred orientation and grain boundaries. Compared to real structure the simulated microstructure of Si_3N_4 by microstructure-property-simulation of the Fraunhofer-Institut für Silicatforschung ISC in Fig. 7 presents similar random β-crystallites.

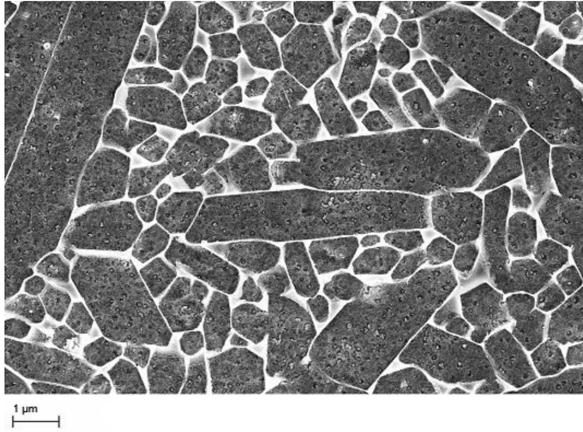


Fig. 6. Microstructure of sintered Si_3N_4 [2]

Fig. 7. Simulated microstructure of Si_3N_4 [2]

5. References

[1] Kollenberg, W. (ed.): Technische Keramik. 1. Aufl., Vulkan Verlag Essen, 1994.

[2] Courtesy of Fraunhofer-Institut für Silicatforschung ISC, Würzburg.