ADVANCED MATERIALS

High-Performance Silicon Nitride Materials

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Pressureless Sintering
Hot Isostatic Pressing
Sintering Aids
Powder Processing
Reinforced Ceramics
Silicon Slips

Dedicated to Professor Wolfgang Hilger on the occasion of his 60th birthday

The past decade has seen greatly increased interest in ceramic materials with special combinations of properties. Their hardness, high resistance to abrasive and erosive wear, and their good corrosion resistance when used under extreme mechanical and thermal conditions have made ceramics increasingly attractive for applications in mechanical and apparatus engineering. Silicon nitride (Si_3N_4) in particular, is suitable for the development of a high-performance, high-temperature material for vehicle engine construction. Although the properties of Si_3N_4 materials have been consistently improved in the last few years, they are still not adequate to allow these materials to be used in series production parts, for example as valves in automotive engines. One of the main reasons for this is the wide scatter and low reproducibility of the property parameters, which means that component reliability does not yet meet market requirements. Hence, one aim of Si_3N_4 materials development is to reduce the structural flaws resulting from physical and chemical inhomogeneity. This objective can only be achieved through a fundamental understanding of all the processing steps, from powder production to the final processing of the components.

1. Introduction

Silicon nitride materials can be distinguished from one another by their composition and manufacturing technologies. Hot pressed (HPSN), pressureless sintered (SSN), reaction-bonded and post-sintered (SRBSN), hot isostatically pressed (HIPSN) and hot isostatically pressed post-densified reaction-bonded silicon nitride (HIPRBSN) all contain very small quantities of a second phase, which must be added as a sintering aid because of the high proportion of covalent bonding in Si_3N_4. In contrast, pure reaction-bonded silicon nitride (RBSN) is single-phased but still contains a residual porosity. This material is used successfully where chemical stability, rather than high strength, is of prime importance. If small amounts of sintering aids were added, the porous RBSN material then offers the possibility of post-densification and an increase in strength by means of hot isostatic pressing. On the other hand, dense silicon nitride materials are used wherever high strength is required, especially at high service temperatures.

However, the manufacture and utilization of ceramic materials can lead to difficulties. The thermal expansion, which is very low in comparison with that of metals, and the brittleness, i.e. the fact that it is impossible to reduce stresses by plastic deformation, require the especially careful design and handling of the manufactured parts. In brittle fracture, failure originates at defects that can arise during manufacture, processing, and also during application. The strength of the components is determined by the sizes and positions of the defects and by the fracture toughness and load. Consequently, strength is a probabilistic quantity that depends on the stressed volume. Failure always originates at a critical flaw in the specimen or component. These flaws in ceramics can be considered to be cracks, microcracks, pores, inclusions, grain boundaries or grain boundary phases and also structural inhomogeneities.

In developing high-performance Si_3N_4 materials it is necessary to avoid structural flaws ≥ 30 µm.[1] To achieve this goal, high-quality raw materials must be used and advanced processing applied where the optimization of each individual processing step is crucial. It must be assumed that the overall distribution of flaws in ceramic parts is the sum of different flaw distributions, each of which in turn represents a distribution with a specific physical content. Thus, the distribution of inherent flaws with small dimensions can adjoin or overlap processing, handling or randomly induced flaws, yielding the total observed technical distribution of structural flaws, and therefore the resulting technical range of strengths.[1] Consequently, to determine the probability of

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failure of an engineering part, it does not suffice to test specimens of only one geometry and size (which is usually very small). Hence, efforts are now being made to test larger specimens and to replace the customary four-point bending test by the more suitable tensile test, because the stress distribution in the specimen is more uniform, and at the same time substantially larger volumes are involved.[2] To clearly show the possibilities for a further quality increase the following discussion will examine the especially promising Si_3N_4 materials SSN, RBSN and HIPRBSN more closely.

2. Pressureless-Sintered Silicon Nitride (SSN)

Because of the high proportion of covalent bonding in silicon nitride, and the associated low self-diffusion coefficient, and owing to its dissociation to silicon and nitrogen at relatively low temperatures, Si_3N_4 cannot be densified in the conventional way without the addition of sintering aids. Through the addition of certain sintering aids (see Section 2.3) a liquid-phase sintering process can be initiated, producing dense ceramic bodies.[3] Densification is strongly affected by the purity and fineness of the initial powders, processing methods, type and amount of sintering aids and sintering parameters.

The glass phase in the ceramic resulting from the liquid phase sintering process is responsible for the strength reduction at high temperatures (> 1000 °C), and therefore, the proportion of additives should be kept as small as possible.[4] In order to minimize the quantity of the liquid phase, high pressures and temperatures must be used during the sintering process. In gas-pressure sintering, the process is carried out under, for example, 100 bar of nitrogen, which counteracts any tendency of Si_3N_4 to decompose. Furthermore, sintering processes under applied pressure mechanically effect the densification of the residual porosity[5] and under optimal conditions lead to a compaction of the grains and hence high mechanical strength. However, the appearance of pronounced internal stresses due to this process must be regarded as critical.[6] The pressureless sintering process, on the other hand, has the major advantage that even large-volume and highly complex components can be produced in virtually their final form, meaning that no expensive finishing is required.

2.1. Powder Synthesis

The quality of the Si_3N_4 powder has a decisive influence on the properties and quality of the ceramic materials. The development of optimal powders requires the most comprehensive knowledge possible of the powder properties. Powders are characterized chiefly by their morphology, chemical composition and phase content. Table 1 shows the degree to which the properties of the powders affect their processing.[7] Sinterable Si_3N_4 powders of the type required for the production of high-performance ceramics must meet the following main requirements:

- mean particle size in the submicron range (0.1 µm < d < 1 µm)
- narrow grain size distribution (but not equal-sized particles)
- equiaxial particle shape
- $\alpha/(\alpha + \beta)$-Si_3N_4 ratio > 95 vol.-%
- low oxygen content (< 1.5 wt.-%)
- low carbon content (< 0.2 wt.-%)
- low metallic impurities content (< 0.1 wt.-%)

Table 1. Features of powder characterization.

Category	Characteristic	Dependent properties
Morphology	Grain size	Powder density
	Grain form	Free-flowing properties
	Agglomeration	Specific surface
	Grain size distribution	Homogeneity
Chemical composition	Main constituents	Surface properties
	Impurities	Dispersibility
Phase content	Degree of crystallization α/β phase ratio	Densification behavior

There are four ways of obtaining Si_3N_4 powders: direct nitridation of silicon (A), carbothermal nitridation (B), thermal decomposition of silicon diimide (C) and gas-phase reaction (D). While the production routes A to C are already being exploited industrially, the gas-phase reaction has so far been carried out only on a laboratory scale. Very pure powders can be produced especially by the diimide process. Examples of typical grain size distributions of powders produced via routes A, C and D are shown in Figure 1.

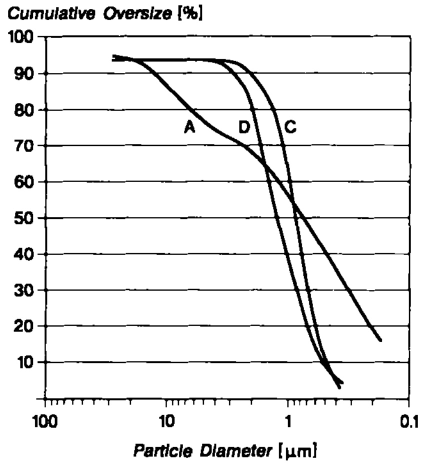

Fig. 1. Grain size distribution of silicon nitride powders produced by different methods: A: direct nitridation; C: diimide process; D: gas phase reaction.

The range between 0.1 and 1 µm for the average particle size is chosen in order to ensure a maximum green density[3] and low electrostatic forces.[7] The strength of the electrostatic attaction is determined by the synthesis process and the post-treatment of the powders. However, the type of powder determines not only its agglomeration behavior but also its "deagglomeration" behavior in solution (dispersing behavior) which is important for molding by slip casting. Powder synthesized via route A can be very readily dispersed while it is considerably more difficult to disperse powders resulting from route C.

Figure 2 shows the mechanical strengths of sinter compacts composed of powders produced by different routes. Parts formed by cold isostatic pressing gave high strength at room temperature when powder C (diimide process) was used, which is characterized by high purity and very regular, equiaxial particles. In regard to the molding of parts from the powders, the powder type, the preparation methods and the molding processes must be very carefully adapted to one another.[8]

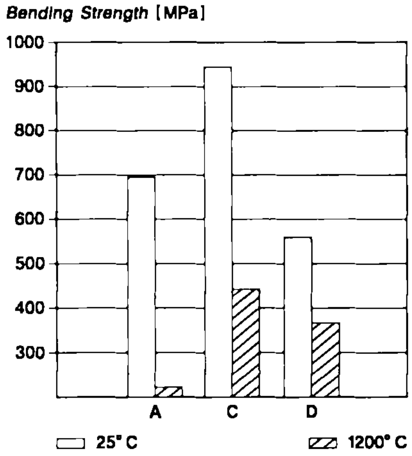

Fig. 2. Bending strength of ceramics composed of Si_3N_4-powders produced by different routes. A: direct nitridation; C: diimide process; D: gas phase reaction. α-Si_3N_4 powders were mixed with the sintering additives Y_2O_3, and Al_2O_3 in the ratio of Y_2O_3: Al_2O_3 of 2:1, and cold isostatically pressed and sintered in nitrogen at atmospheric pressure at 1800 °C. Strength was determined by the four-point bending test at 25 °C and 1200 °C.

2.2. Powder Processing

During powder processing, the incorporation and homogeneous distribution of sintering aids, and the adjustment of a suitable grain size distribution of the mixed powders has to be achieved.

This is accomplished especially successfully by attritors or annular-gap ball mills. After the mixing and milling process, the preparation of agglomerates with a homogeneous particle distribution and appropriate shape follows. The drying and agglomeration of the mixture takes place in the spray dryer. After molding, either by cold isostatic pressing, slip casting or injection molding, any organic binder that may have been added must be removed. Finally, the high-temperature sintering process yields the densified ceramic component, which normally must be subjected to finishing work because of shrinkage imperfections and adhering firing skins. As an example of this production procedure, Figure 3 presents a typical processing sequence for the production of SSN components.

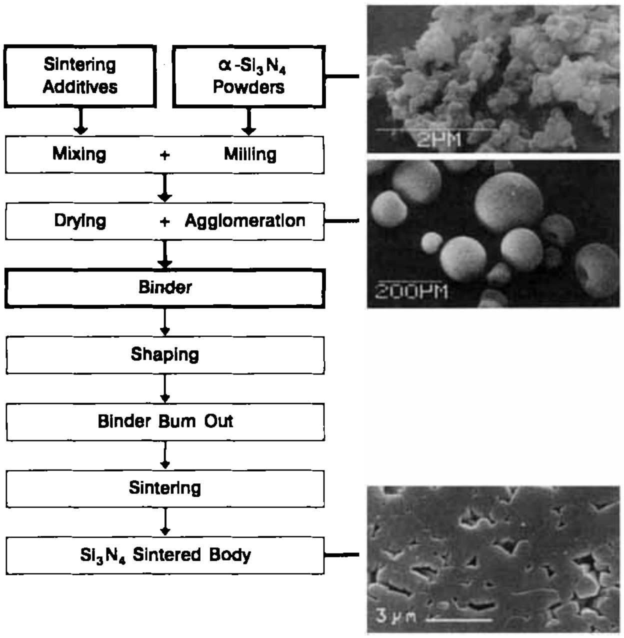

Fig. 3. Powder preparation and production of silicon nitride ceramics. (The introduction of raw materials is indicated by bold lines).

The experience of the last few years has shown that one of the major causes of failure of a ceramic component is the presence of foreign inclusions with diameters ≥ 30 µm. An analysis of these inclusions shows that even grains of dust can lead to the failure of ceramic components. Consequently, considerable efforts have been made to prepare the powder under cleanroom conditions in order to prevent contamination of the ceramic powder mixture with oversized dust particles. These facts are illustrated in Figure 4 with a typical structural flaw that is attributable to environmental contamination.

It must be pointed out in this connection that the results discussed in the following sections were obtained largely on materials that were produced under cleanroom (Class 3) conditions.

2.3. Reinforcement Concepts

The brittleness of ceramics is primarily caused by crack propagation. The objective of reinforcement concepts is, therefore, to increase the resistance of the microstructure to crack propagation.

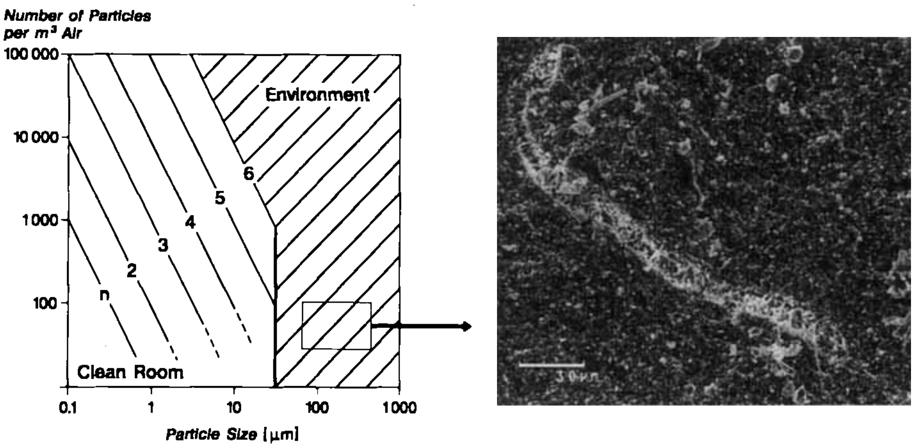

Fig. 4. Number and size of dust particles in different clean room classes. On the right, a fracture surface with a failure-initiating fault in a Si_3N_4 ceramic flaw can be seen. The flaw was caused by a dust particle of the kind found under normal environmental conditions.

The microstructure is determined essentially by the sintering aids which form a liquid phase during sintering. There are two possible types of sintering aids. First, oxides such as MgO, Y_2O_3 and Al_2O_3, which form amorphous or partially crystalline grain boundary phases because of their insolubility in Si_3N_4, and second, those which at suitable anion/cation ratios in Si_3N_4 lead to solid solutions (e.g. Be, Al).[9] In any case, the softening point, the viscosity and the amount of liquid phase are critical for densification and microstructural development. High viscosities always mean high aspect ratios of the precipitating β-Si_3N_4 grains.[4] This in turn acts to oppose good densification, meaning that these two mechanisms are frequently concurrent with each other. From the morphological point of view, good mechanical properties are best achieved by developing materials with high aspect ratios, with small mean grain sizes, low porosity and a minimal proportion of grain boundary phases. Below 1000 °C crack propagation under stress is influenced by different structural characteristics than at higher temperatures. Whereas at high temperatures strength is determined by the properties of grain boundary phases, at room temperature it is mainly the grain shape and size of Si_3N_4 that are decisive.[10]

In addition to specific structural development, two mechanisms essentially contribute to a reduction in crack propagation behavior at room temperature: first, crack deflection by mixed-in whiskers or fibers, or growth of in-situ whiskers or uniformly distributed micropores, and second, energy absorbtion by stress-induced phase conversion.[11] Most importantly, at high temperatures, the grain boundary slippage must be reduced by changing the chemical composition of the glassy phase and by the development of crystalline grain boundary phases.

Our own studies will therefore be presented below as typical examples of the reinforcement of SSN materials.

2.3.1. In situ reinforcement by glass-forming additives

Y_2O_3 and MgO have been the most often used sintering aids in the past. More recent work[12-14] has shown that the high-temperature properties in particular can be substantially improved by the use of oxides of the rare earth elements (RE*s*) as sintering aids. Therefore, Si_3N_4-powders have been mixed with various rare earth oxides and Al_2O_3 in a molar ratio of 2:1 (RE_2O_3: Al_2O_3 = 2:1).[15] The amounts used were chosen in such a way that in each trial the oxygen content contributed by the sintering additive was the same. In this way the influence of the rare earth oxides alone could be investigated. These powder mixtures were cold isostatically pressed and sintered under atmospheric pressure at 1800 °C.

In Figure 5 it can be seen that at room temperature as well as at high temperature the bending strength increases as the ionic radius of the rare earth oxides decreases.[16] Here the viscosity of the glass phases and the structural morphologies influenced by the rare earth oxides tend to counteract one another.[15] As a rule, densification can be improved by in-

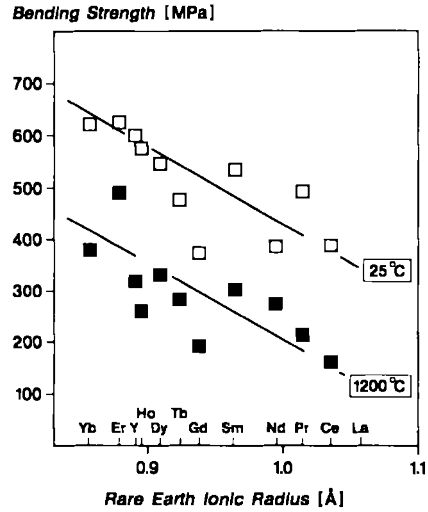

Fig. 5. In-situ reinforcement by the glass-forming intergranular phase. The Si_3N_4-powders were mixed with RE-oxides and Al_2O_3 as sintering aids (RE_2O_3:Al_2O_3 = 2:1). For specimen preparation compare the caption of Figure 2.

creasing the amount of additives with a lower melting point and lower viscosity[17] although exaggerated whisker growth can oppose densification. On the other hand, pronounced growth of elongated grains (Fig. 6) is very desirable in view of its reinforcement effect.

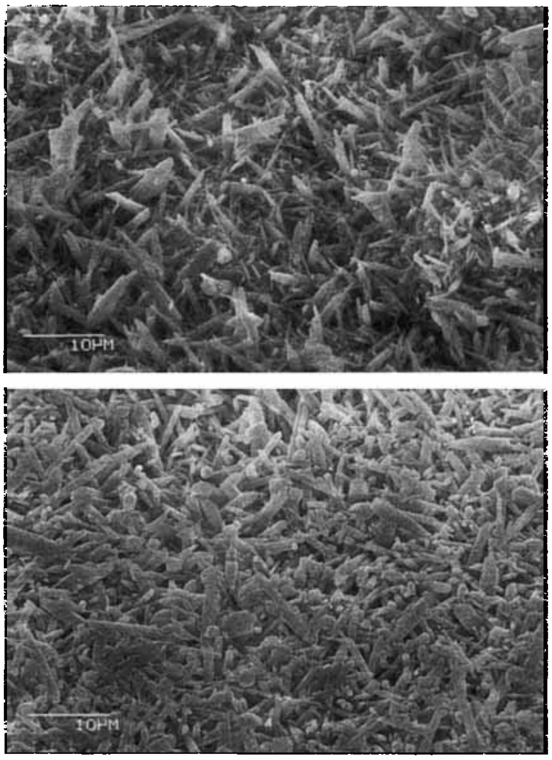

Fig. 6. Influence of the rare earths gadolinium (top) and dysprosium (bottom) on the growth of β-Si_3N_4 grains.

The higher the softening point of the glasses in the intergranular region, the more the grain boundary slippage will be prevented and the high-temperature strength improved. The exact composition of the glasses is not generally known. Probably, some nitrogen is dissolved in the glass phase. Studies of the Gd-Si-Al-O-N[18] and Nb-Si-Al-O-N[19] systems have shown that increasing substitution of nitrogen for oxygen in the glass network causes an increase in the glass transition temperature and a decrease of the thermal expansion coefficient. Possibly, the substitution of nitrogen is promoted by the incorporation of rare earth elements in the glass. Detailed studies with the help of advanced microanalytical and surface analytical techniques,[20] are essential in verifying this interpretation.

2.3.2. *Crystallization of the amorphous grain boundary phases*

One further way of increasing the high-temperature strength is to crystallize the amorphous intergranular phase by tempering under nitrogen. Numerous investigations have been carried out on the Si_3N_4-SiO_2-Y_2O_3 system in order to study the crystallization of the glassy phase and its characterization,[21, 22] but rare earth oxides have also been investigated.[13, 14, 23] In further studies, the initial composition was again chosen in such a way that the ratio RE_2O_3:Al_2O_3 was exactly 2:1, i.e so that $RE_4Al_2O_9$ could crystallize. In practice, it was found that instead of $RE_4Al_2O_9$, mainly apatites RE_5 $(SiO_4)_3N$, garnets $RE_3Al_5O_{12}$ and various silicate phases such as RE_2SiO_5 and $RE_2Si_2O_7$ crystallized at 1350 °C. When apatite was formed from any of the rare earth oxides the high-temperature strength was improved, while the crystallization of garnet and the silicate phases brought about only a slight improvement in strength.[16]

2.3.3. *Addition of dispersed crystalline phases*

The use of ZrO_2 as a sintering aid is known to improve the bending strength of Si_3N_4.[24] Apart from a minute glass phase fraction, ZrO_2 is present in the sintered structure as a crystalline intergranular phase. The strengthening mechanism of this Si_3N_4-ZrO_2 composite is based on a phase transformation mechanism, i.e. on the stress-induced change in the ZrO_2 from the tetragonal to the monoclinic modification, whereby the fracture energy can be absorbed.[25]

Since these mechanisms are effective only at temperatures below 1000 °C, trials were conducted with fully stabilized, cubic ZrO_2 and HfO_2. In these trials Al_2O_3 and Y_2O_3 were mixed with different proportions of HfO_2 and sintered at 1800 °C at atmospheric pressure. The proportion of Y_2O_3 was chosen to be so large that the cubic modification of HfO_2 is fully stabilized and, consequently, does not undergo a phase conversion on cooling.

Phase development during sintering is shown in Figure 7. The difference from a pure liquid-phase sintering process becomes very clear. The velocity of shrinkage is characterized by two maxima at about 1200 °C and 1400 °C (Fig. 7a). This shrinkage is accompanied by reaction of the sintering aids, formation of the glassy phase, and the phase transformation of Si_3N_4. The main shrinkage is associated with glass phase formation and α-β conversion of Si_3N_4.

Pure liquid-phase sintering is illustrated using the example of Y_2O_3/Al_2O_3 as the sintering aid (Fig. 7b). As soon as the additives react with one another, intergranular phases are formed which finally, at higher temperatures, are present only as a pure glassy phase. The α-β conversion of Si_3N_4 is associated with the formation of this glassy phase. After sintering, the original α-Si_3N_4-material has become β-Si_3N_4 with an oxinitride glass.

In contrast, the sintering aid HfO_2 remains crystalline but undergoes a phase conversion from the monoclinic to the cubic modification (Fig. 7c). It appears remarkable that this phase conversion is already concluded before the α-β phase conversion of Si_3N_4 takes place but seems to exert no influence on it. Thus, in addition to the β-Si_3N_4 grains and the glass phase with the constituents yttrium, aluminum, oxygen, silicon and nitrogen, the structure of the sinter compact

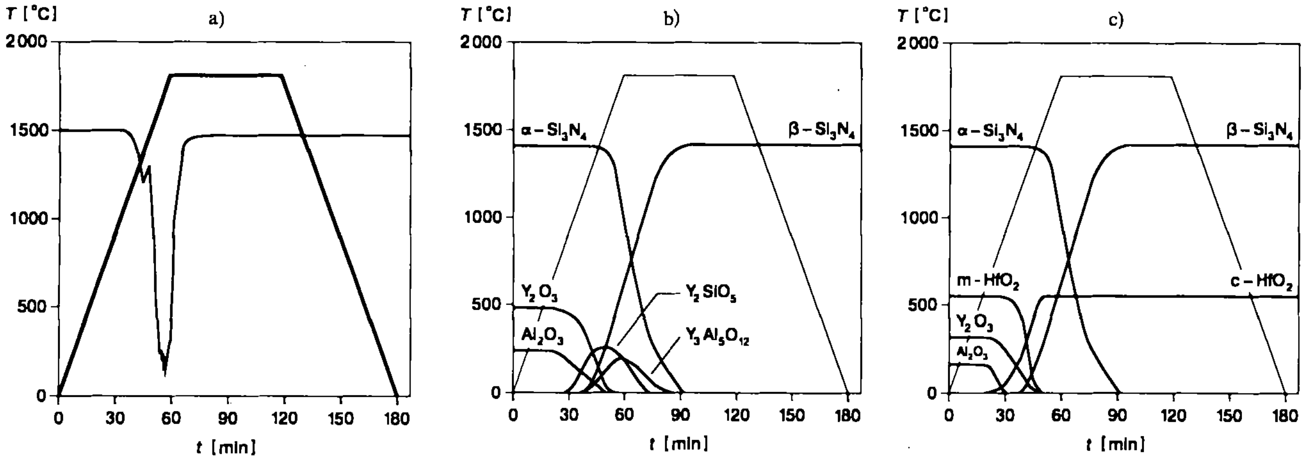

Fig. 7. Sintering behavior of Si_3N_4 with various sintering additives. The velocity of shrinkage is showin in (a) along with the sintering program (bold line): in 1 hour to 1800 °C, maintain for 1 hour; cool for 1 hour. Phase development with the glass-forming additives Y_2O_3 and Al_2O_3 (b) and additionally dispersed crystalline HfO_2 (c). The quantity and the quality of the crystalline phases were estimated by X-ray studies and are given schematically in the diagram.

consists additionally of cubic HfO_2. Corresponding micrographs of the structure are presented in Figure 8.

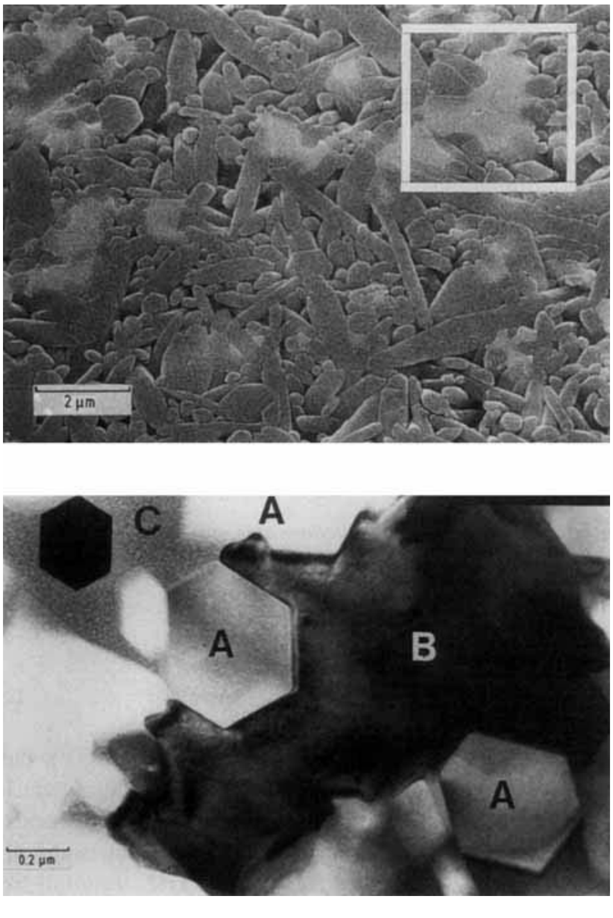

Fig. 8. Microstructure of ceramics that are reinforced with crystalline HfO_2; top, scanning electron micrograph, bottom, transmission electron micrograph (A: β-Si_3N_4; B: HfO_2; C: glass).

3. Reaction-Bonded and Hot Isostatically Pressed Reaction-Bonded Silicon Nitride

In contrast to the liquid-phase sintering process, in which the use of silicon nitride powders leads to a dense ceramic,.in RBSN the ceramic is sintered making use of a gas-solid reaction between silicon and nitrogen. Ceramics which are produced in this way can be further densified by subsequent hot isostatic pressing.

3.1. Reaction-Bonded Silicon Nitride (RBSN)

Reaction-bonded silicon nitride is produced by the nitridation of moldings formed from silicon powder as shown in Equation 1.

$$3\,Si + 2\,N_2 \rightarrow Si_3N_4 \qquad (1)$$

The reaction in accordance with this equation can yield both the α- and the β-modifications. The accompanying volumetric expansion of approximately 22% leads in this reaction to a decrease in the overall porosity without any appreciable alteration in the outer dimensions of the specimen. The molding methods used include various pressing processes, slip casting, film casting and plastic processes such as extrusion and injection molding. After the molding aids are burned out, frequent presintering under an inert gas atmosphere follows. Following this step, the parts are strong enough to be worked (as graphite is worked) and in this way given their final shape. The moldings are then usually heat treated under nitrogen at atmospheric pressure and at temperatures between 1000 and 1450 °C. The attractiveness of this method lies in the minimal dimensional change which occurs during nitridation (< 0.1 %), which means that no, or only minor machining of the final product is required. However, the components have a residual porosity of about 12%

to 30%, which has a strong influence on the mechanical properties.

The reaction between silicon and nitrogen is an exothermic process. The heat thus released can, because of an improperly programed temperature control, lead to excessive reaction rates and consequent local overheating. The result may be a melting of the silicon, which can bring the reaction to a standstill. No general rules governing the programing of temperature over time can be given for nitridation. However, the program depends on the furnace size, the amount of material being fired, the wall thickness of the parts, and the initial silicon grain size. The time required for complete nitridation can range from a few hours to several weeks, depending on the wall thickness. The maximum wall thickness that can be completely converted to silicon nitride is only approximately 30 mm, regardless of the length of the reaction time. For larger wall thicknesses the diffusion of nitrogen through silicon nitride becomes the rate-determining step, which causes the reaction rate to drop sharply.

In addition to the temperature control program, other nitridation conditions such as gas composition, gas pressure, temperature, time, and heating rate influence the course of the reaction and hence the structure and properties of this material.[4, 26] Whereas the molding process influences the packing density of the particles, the mean grain size and grain size distribution of the silicon powder, and the type and distribution of contaminants also affect the course of the reaction, and the structure and properties of RBSN.[27]

3.2. Hot Isostatically Pressed Reaction-Bonded Silicon Nitride (HIPRBSN)

Because of the relatively large shrinkage occurring during the densification of powder compacts, difficulties may appear during this process (contraction cracks, deformation), especially during the production of parts with complex shapes. For this reason RBSN with suitable sintering aids is also used as the starting material for hot isostatic pressing. In comparison with silicon nitride powder compacts the linear shrinkage here amounts only about 5–10%. The densification mechanisms are similar to those operating during the sintering of silicon nitride powder compacts. Pressure is applied to densify the material during the sintering process in order to accelerate the mechanisms responsible, such as particle rearrangement, diffusion, and plastic deformation. Pressure allows the amount of sintering aids to be reduced and improves especially the high-temperature strength. A reduction in the amount of sintering aids can also be achieved by crystallization of the amorphous grain boundary phase. Figure 9 shows a high-resolution micrograph of HIPRBSN, taken with a transmission electron microscope (TEM), showing a fully crystallized grain boundary phase: Y_2O_3 and Al_2O_3 were used as sintering aids.

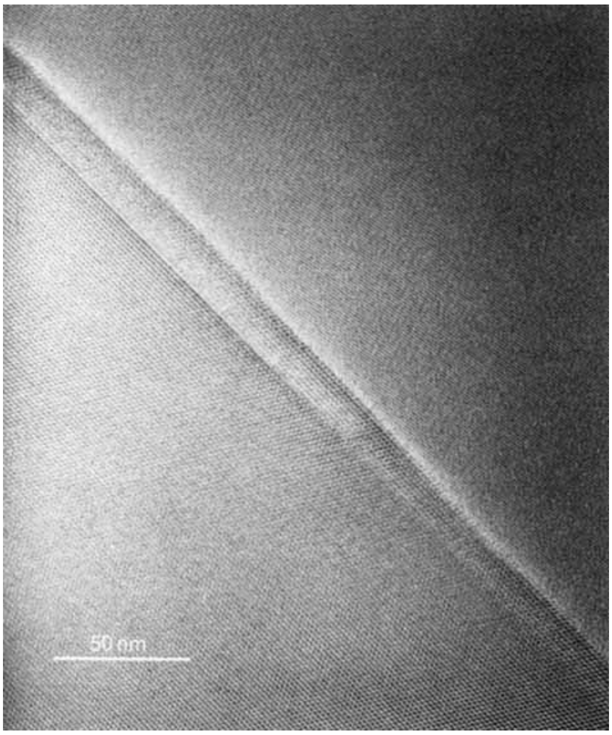

Fig. 9. TEM image of HIPRBSN with crystallized intergranular phase.

The densification of RBSN by hot isostatic pressing permits the production of parts with narrow tolerances without, or with only minor machining being required. Furthermore, in comparison with conventional hot pressing, the uniform transmission of pressure results in isotropic material properties. Through the application of pressures up to more than 3000 bar, influence can be exerted on the densification behavior and grain growth and hence the optimization of material properties.[27] Below, the production of parts made of HIPRBSN is described in detail, with the slip casting of silicon powder in an aqueous system being used as the molding method, on which detailed reports have already been published.[28] In the first stage of slip development the silicon-water and silicon-sintering aid-water phase systems were investigated.

3.2.1. Hydrolysis in the silicon-water system

The addition of silicon powder to water should lead to intensive hydrolysis due to the normal electrode potential of the reaction shown in Equation 2.

$$Si + 2\,H_2O \rightarrow SiO_2 + 2\,H_2 \qquad (2)$$

The potential is strongly negative (E = – 0.875 V), but silica is formed on the powder particle surface which produces a passivation layer which is insoluble in acids, thus preventing corrosion in acid media. Alkaline solution, however, can destroy the passivation layer according to Equation 3.

$$SiO_2 + 2\,OH^{\ominus} \rightarrow SiO_3^{2\ominus} + H_2O \qquad (3)$$

To characterize silicon hydrolysis, the amount of hydrogen formed was measured as a function of time at different pH values (Fig. 10).

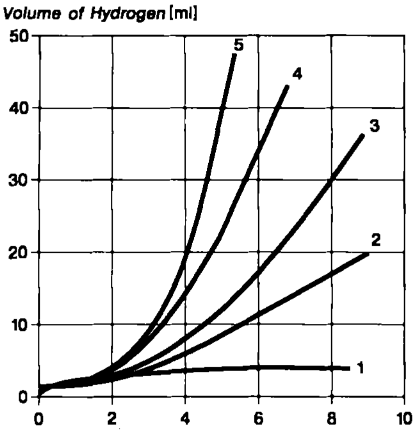

Fig. 10. Generation of hydrogen by the hydrolysis of silicon powder (50 wt.-%) in aqueous suspension plotted vs. time at different pH values: (1) pH = 2.4; (2) pH = 6.2; (3) pH = 10.0; (4) pH = 11.0; (5) pH = 12.0.

The higher the pH of the dispersion, the greater is the volume of hydrogen formed per unit time. Under strong alkaline conditions and at higher temperatures, the silicon is quantitatively decomposed, a reaction that is also used analytically for the determination of free silicon in SiSiC. In practice, it has been found that pH values above 9 are needed for the production of silicon slips.

3.2.2. Viscosity of silicon slips

Whereas at higher pH values hydrolysis of silicon powder can be observed, the usability of silicon slips under acid conditions is limited by a strong pH dependence of the slip viscosity. Towards the lower pH values the viscosity of the silicon powder dispersions increases sharply (Fig. 11).

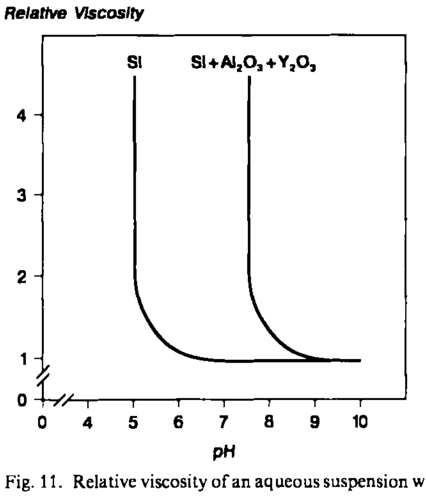

Fig. 11. Relative viscosity of an aqueous suspension with and without sintering aids as a function of pH (66.7 wt.-% solids; viscosity using Lehmann viscometer at pH 7).

Accordingly, below a certain pH-value the viscosity is too high to measure and therefore such dispersions are totally unsuitable for casting. The pH value at which the viscosity sharply rises depends on the powder concentration. At 75% powder content in the suspension it lies at pH 6, at 66% powder content at pH 4.5, while at 50% no such rise in viscosity can be observed down to a pH value of 2. To explain this phenomenon, reactions on the surface of the powder particles in the aqueous medium must be more closely examined (see 3.2.3.).

In summary, the pH range for preparing highly concentrated, chemically stable silicon slips of sufficiently low viscosity is limited to between 5 and 9.

3.2.3. Surface reactions

An analysis of silicon powders shows a silica content of about 1.5–2.0%. The silica forms a thin layer on the silicon particles and therefore the chemical behavior of the surface of silicon powder in water should be comparable with that of silica.

This behavior can be described as follows. Exposure to water leads to surface hydroxylation, enabling acid or base reactions to take place as shown in Equations 4 and 5.

$$\text{Si-OH} + H_3O^{\oplus} \rightarrow \text{Si-OH}_2^{\oplus} + H_2O \qquad (4)$$
$$\text{Si-OH} + OH^{\ominus} \rightarrow \text{Si-O}^{\ominus} + H_2O \qquad (5)$$

Silica is an acidic oxide, the reaction according to equation (5) can be expected to be dominant over a substantial range of pH values. That is the reason for the observation of a marked decrease of the pH when silicon powder is added to a basic solution. The reaction of the hydroxide ions with the silanol groups of the silicon surface reduces the $OH^{\ominus}$ concentration. The extent of this pH decrease depends on the specific surface of the dispersed particles and the degree of surface hydroxylation.

The following experimental finding can also be explained with equation (5). Over a wide range of pH values the zeta potential and hence the surface charge of the silicon particles is negative. For all powders examined, the particles were charged negatively at a pH greater than 2; this value represents the so-called "isoelectric point". At pH values higher than 2 the negative surface charge increases steadily, reaching its maximum at ca. -60 mV at a pH of around 7 (Fig. 12), and then remains constant up to higher pH values.

The zeta potential has an important influence on the state of particulate dispersion in suspensions.[30] Increasing surface potential generates an electrostatic barrier which prevents both contact between the individual particles and the formation of larger agglomerates of particles. The higher surface charge and the resulting electrostatic repulsion between the dispersed particles improves the properties of the dispersion, the viscosity is lowered and sedimentation decreases.

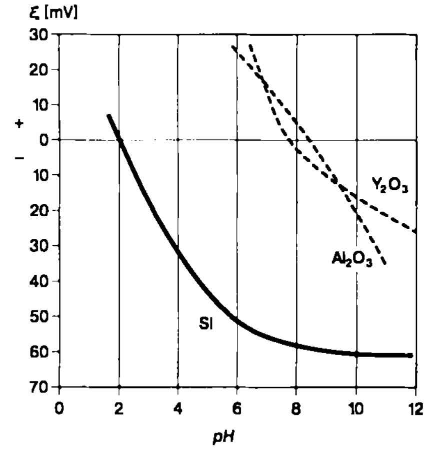

Fig. 12. Zeta potential (ξ) of silica, alumina and yttria powder particles in aqueous suspension as a function of pH.

3.2.4. Addition of sintering aids

The addition of the sintering aids Y_2O_3 and Al_2O_3 to an aqueous silicon suspension substantially influences the properties of the slip. Considering the importance of the surface charge to the sedimentation behavior, the viscosity, and the state of powder dispersion, the zeta potential of these powders was measured as a function of the pH value of the suspension (Fig. 12). For yttria the isoelectric point lies at a pH of ca. 8, the surface being charged positively at lower and negatively at higher pH values. Qualitatively the same result is observed for alumina powder dispersions with an isoelectric point at a pH of 8.5. Since the analogous point for silicon powder dispersions lies at a pH of 2, opposite signs of the surface charge of the components are observed in the pH range between 2 and 8.5 in aqueous suspensions of a mixture of these powders. This should lead to a higher viscosity of the slips because of the forces of electrostatic attraction. This assumption has been confirmed by experiment. For example, it is not possible to obtain a dispersion that contains all three powder types in an adequate concentration through mixing of the powders in distilled water (pH = 6.5). Because the silicon powder lowers the hydroxide ion concentration in alkaline dispersions, the initial pH must be chosen about three units higher than the desired final pH. The dependence of the relative viscosity of the sintering aid slip on pH has already been shown in Figure 11. The limit for the preparation of low-viscosity slips lies at pH 7.5.

3.2.5. Material properties

On the basis of the studies presented above, castable, low-viscosity and chemically stable slips can be prepared and cast. Depending on the silicon powder used, the densities of the slip cast and completely nitrided components lie between 2.40 and 2.65 g/cm³. Subsequent densification is carried out in a high-pressure autoclave using nitrogen as the pressure transmission medium. For gas pressures at around 200 MPa the densification temperature lies at about 1800 °C. Holding times at the final temperature and the maximum pressure depend on the properties of the starting material. The linear shrinkage of the densified components is between 7 and 10 %, depending on the initial density, much smaller than for other comparable sintering processes.

Figure 13 shows the distribution of four-point bending strengths in specimens cut from HIPRBSN sheets that had been produced by slip casting. The high Weibull modulus of $m = 23.42$ indicates that a structure with a very homogeneous distribution of flaws that could initiate failure can be achieved by the slip casting technique. Its strength exhibits a value of $\sigma_0 = 651$ MPa. It is possible to raise the strength of these materials through improvements in powder preparation that are especially designed for the purpose. A strength of 750 MPa with a Weibull modulus of 12 for isostatically pressed specimens could be achieved.

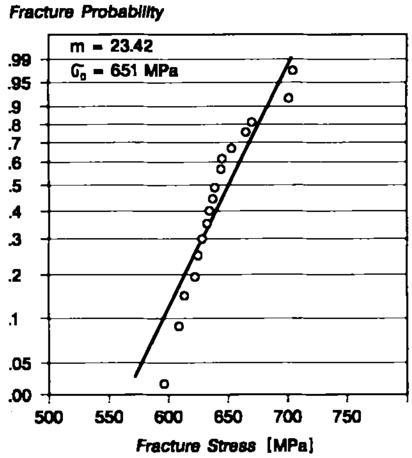

Fig. 13. Strength distribution of HIPRBSN slip cast moldings.

4. Conclusions

The results discussed in this report have revealed concepts that enable a fundamental improvement in the material properties of silicon nitride, such as the crystallization of the glass phase or the reduction in flaw frequency by using slip casting as the molding method. Additionally, these results demonstrate the different possibilities provided by the various processing methods for controlling material properties, component dimensions, shape, and production costs, etc. Although the process techniques for SSN and RBSN are fundamentally different, basic knowledge about the influence of the type and amount of sintering aids or the crystallization of the glassy phase can be applied to both types of material. Examples have been given here in order to show how basic knowledge can be expanded from findings in one subarea. These findings also clearly show that the powder preparation, the molding process or the sintering method cannot be considered in isolation. In contrast, the individual steps of overall production must be adapted to one another. Thus the powder properties determine the suitability of the powder for a specific molding technique. That means that the developer of high-performance ceramics must be given the opportunity, as early as possible, to scale up his work in order to be able to incorporate the processing steps into the materials development with the help of parallel (and particularly nondestructive) testing methods.

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[1] R. Danzer, *Proc. 12. Int. Plansee-Seminar 2* (1989) 183–198.
[2] G. Grathwohl, *Int. J. High Techn. Ceram.* (1988) 123–142.
[3] M. Mitomo, N. Yang, Y. Kishi, Y. Bando, *J. Mater. Sci. 23* (1988) 3413–3419.
[4] G. Ziegler, J. Heinrich, G. Wötting, *J. Mater. Sci. 22* (1987) 3041–3086.
[5] J. Heinrich, E. Backer, M. Böhmer, *J. Am. Ceram. Soc. 71* (1988) C28–C31.
[6] G. R. Terwilliger, F. F. Lange, *J. Am. Ceram. Soc. 57* (1974) 25–31.
[7] G. Schwier, G. Nietfeld, *Werkst. Konstruktion 2* (1988), 149–154.
[8] F. Aldinger, H.-J. Kalz, *Angew. Chem. Int. Ed. Engl. 26* (1987) 371; *Angew. Chem. 99* (1987) 381–391.
[9] K. H. Jack in F. L. Riley (Ed.): *Nitrogen Ceramics*, Noordhoff-Leyden, Leyden 1977, 109–128.
[10] G. Wötting, B. Kanka, G. Ziegler in S. Hampshire (Ed.): *Non-Oxide Tech. Eng. Ceram.*, Elsevier, London 1985, 83–96.
[11] N. Claussen, J. Jahn, *J. Am. Ceram. Soc. 61* (1978) 94–95.
[12] Y. R. Xu, S. R. Fu, D. S. Yan, *Physica 150* (1988) 276–282.
[13] K. Ueno, *Yogyo-Kyokai-Shi 94* (1986) 702–705.
[14] B. Saruhan, M. J. Pomeroy, S. Hampshire in S. Hampshire (Ed.): *Non-Oxide Tech. Eng. Ceram.*, Elsevier, London 1985, 69–82.
[15] M. Peuckert, C. Boberski, P. Selgert, *Proc. 3rd. Int. Symp. Ceram. Mater. Compon. for Engines*, Elsevier, Amsterdam 1989, in press.
[16] C. Boberski, M. Peuckert, P. Selgert, *Proc. 1st Eur. Cer. Soc. Conf.*, Elsevier, Amsterdam 1989, in press.
[17] G. Wötting, G. Ziegler, *Ceram. Int. 10* (1984) 18–29.
[18] J. Rocherulle, P. Verdier, Y. Laurent, *Mater. Sci. Eng. 2* (1989) 265–268.
[19] J. Lang, P. Verdier, R. Pastuszak, R. Marchand, *Ann. Chim. (Paris) 5* (1970) 663.
[20] R. Hamminger, *Surf. Interface Anal. 12* (1988) 519–526.
[21] W. E. Lee, C. H. Drummond, G. E. Hilmas, J. D. Kiser, W. A. Sanders, *Ceram. Eng. Sci. Proc. 9* (1988) 1355–1366.
[22] L. J. Gauckler, H. Hohnke, T. Y. Tien, *J. Am. Ceram. Soc. 63* (1980) 35–37.
[23] W. A. Sanders, D. M. Mieskowski, *Am. Ceram. Soc. Bull. 64* (1985) 304–309.
[24] F. F. Lange, *J. Am. Ceram. Soc. 63* (1980) 38–40.
[25] K. Terao, Y. Miyamoto, M. Koizumi, *J. Am. Ceram. Soc. 71* (1988) C167–C169.
[26] J. A. Mangels, *Am. Ceram. Soc. Bull. 60* (1981) 613–617.
[27] J. Heinrich, D. Munz, G. Ziegler, *Powder Metall. Int. 3* (1982) 153–159.
[28] R. Dillinger, J. Heinrich, J. Huber, *Mater. Sci. and Eng. A109* (1988) 373–378.
[29] I. Meisel: *Diploma Thesis*, Universität Bayreuth, 1987.
[30] M. D. Sacks, G. W. Scheiffele, *Ceram. Eng. Sci. Proc. 7–8* (1985) 1109–1123.

Communications

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Spatially Selective Conducting Patterns in Transparent Films Derived from Ladder Type Polymers**

By *Igal Belaish, Dan Davidov*, Heny Selig, Malcolm R. McLean,* and *Larry Dalton*

Conducting patterns can be created in the insulating pristine ladder type polymer films BBL and BBB (see Fig. 1) by spatially selective heating using laser annealing. The conducting regions consist of cross-linked, stable, ladder polymers. Subsequent fluorination leads to conducting patterns embedded in a completely *transparent* film. These features may lead to a variety of possible applications.

In the last decades there has been significant progress in the synthesis, processing, and characterization of rigid rod polymers.[1] A few examples of such polymers are shown in Figure 1. These polymers have exceptional properties such as high tensile strength and modulus.[2,3] They are stable at elevated temperatures (which may exceed 600 °C) and may be processed into fibers or highly packed films with excellent planar arrangements.[2] The conductivity of these rigid rod polymers can be controlled by thermal pyrolysis.[4]

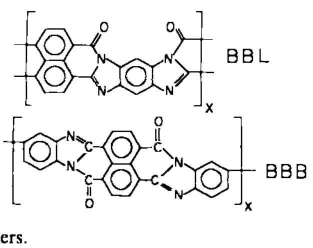

Fig. 1. Examples of ladder type polymers.

Particularly, BBB polymer undergoes a phase transformation at a temperature T_{p} of 680 °C to a new ladder type polymer with high intrinsic conductivity.[4] Exposure of

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