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EFFECT OF THE POWDER CHARACTERISTICS OF Si_3N_4 ON THE MICROSTRUCTURE OF SINTERED BODIES

G. Woetting, H. Hausner

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16. Abstract

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EFFECT OF THE POWDER CHARACTERISTICS OF Si_3N_4 ON THE MICROSTRUCTURE OF SINTERED BODIES

G.Woetting and H.Hausner**

ABSTRACT: Si_3N_4 powders have been sintered with addition of 2 wt.% MgO to 95% theoretical density after attrition milling and subsequent purification. A homogeneous distribution of the small amount of sintering additive has been obtained by the use of soluble magnesium salts and spray drying.

INTRODUCTION

In the last years investigations have been conducted to an increasing degree of direct or pressure-free sintering of silicon nitride. The reaction sintering technology used till now in many cases led to products with only 80% to 85% of the theoretical density. Although the pressure sintering technology made possible density values ≥96% of the theoretical density, difficulties arose, however, during the production of complicated shapes. The development of a "normal" sintering process with materials having primarily covalent bonds, which also include silicon nitride, was spurred by the successful work of Prochazka [1] with silicon carbide who succeeded in sintering this material by proper powder preparation and by certain additives to high densities without the use of external pressure.

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** Institute for Nonmetallic Materials at the Technical University Berlin

The first authors who published papers concerning the pressure-free sintering of Si_3N_4 were Terwilliger and Lange [2-5]. They sintered Si_3N_4 under a pressure of 0.1 MPa of nitrogen with the addition of 5wt.% MgO at 1700°C and achieved densities up to 95% whereby, however, a loss in weight of up to 16wt.% occurred. These density values were also achieved by Oda [6] who employed a mixture of MgO and BeO as sintering-assist material under otherwise similar conditions. In our own work [7] we investigated, among others, the sintering behavior as a function of the MgO concentration and the type of the Mg-compound added. These additives react, as is also well known from pressure-sintering technology, with the SiO_2 located at the surface of the Si_3N_4 [8,9] particles with the formation of a melt phase whereby liquid-phase sintering takes place. The material transport is favored by a solution- again precipitation mechanism whereby the preferred solution of α-Si_3N_4 and a repeat precipitation of the thermodynamically more stable β-Si_3N_4 occurs [10,11].

The room temperature strengths of the pressure-free materials sintered in this way are considerably higher than those of reaction-sintered Si_3N_4; however, they exhibit a strong decrease in strength from 1200°C on which can be attributed to the presence of a gradually softening vitreous grain boundary phase, similar to that of pressure-sintered Si_3N_4.

In order to be able to utilize higher sintering temperatures, the decomposition of Si_3N_4, becoming increasingly stronger from 1750°C on, must be suppressed. This can be done by increasing the ambient nitrogen pressure which was first accomplished successfully by Mitimo [12-14]. Since partial pressures of other gaseous compounds are also formed over Si_3N_4 [15], it is additionally necessary to impede the gas exchange with the surroundings in order to keep the losses in weight during sintering as low as possible. Mitomo was able to achieve this by encapsulating his samples in boro-nitride covered graphite crucibles. With a nitrogen pressure of 1 MPa and encapsulation he was able to hold the loss in weight, occurring at 1800°C and 30 minutes, to about 7wt.%, whereby he attained sinter densities of a maximum of 93%. In a large part of the other investigations a relatively high concentration of oxidic additives is used, such as by Rowcliffe [16] 4% to 17% of Y_2O_3, Priest [17] 20% of CeO_2, Buljan [18] up to 20% of MgO, La_2O_3, Y_2O3, ZrO_2, and either under atmospheric [18] or with increased nitrogen pressure [16-17].

Greskovich [19,20] and Prochazka [21] were the first authors who reported concerning the sintering of Si_3N_4 with the addition of small amounts of non-oxidic additives such as Be_3N_2, Mg_3N_2, $BeSiN_2$, $MgSiN_2$ etc. Here the mechanism seems to depend, similar to that for sialones, on a solution of these substances in the Si_3N_4 grid whereby the constitutional void concentration is increased and a mass transport, sufficiently high for densification, can occur by volume diffusion. This mechanism requires considerably higher energies than the liquid-phase sintering which is brought out by the requirements of 2000°C and $p_{N_2} \approx 8$ MPa necessary to achieve densities above 95%. The absence of a vitreous grain boundary phase will lead to improved high-temperature properties.

An improvement of the mechanical properties at high temperatures can also be expected through minimizing the amounts of added materials because of the reduction of the secondary phase concentration in the samples; in addition, those investigations seem to be meaningful which try to devitrify this secondary phase by the precipitation of refractory phases or, by changing the chemical composition during sintering try to effect a solution in the Si_3N_4 grid which is designated as "transient liquid sintering".

Within the framework of this work an effort is made to hold the amount of sinter-assist materials as small as possible whereby the effect of powder characteristics will be investigated.

EXPERIMENTAL

For the sinter tests described here we used exclusively the Si_3N_4-powder H 1 from H.C. Starck Berlin, Goslar which normally is used for hot pressing (table 1). The powder was ground once more in an agitation ball mill (Molinex PE075, Gebr. Netzsch, Selb) and the iron abrasion was removed after grinding by washing with hydrochloric acid. The individual powder charges were mixed with a solution of $Mg(NO_3)_2 \cdot 6H_2O$ corresponding to an amount of 2wt.% of MgO (and 2% of the polyethylene adduct KP 2500) in an Al_2O_3 drum grinder with pulverized reaction-sintered Si_3N_4 and were granulated by means of a spray dryer. The powders were compressed in a steel matrix with 100 MPa to 300 MPa to sample units of 8 mm diameter and 6 mm height and were subjected to subsequent densification in an isostatic press.

Table 1 Characteristic of the Si_3N_4 starting powder HCST-H 1

chemical composition

element	weight %	element	weight %
N	38.65	Fe	0.03
O	0.90	Al	0.10
C	0.42	Ca	0.01
		Si	remainder

phase state	wt.%
free Si	1
β-Si_3N_4	3
α-Si_3N_4	remainder

specific surface 8.42 m^2/g

The press density was about 65% of the theoretical density. The samples were sintered in boro-nitride crucibles equipped with lids in a mixture of 50% boro-nitride- and 50% Si_3N_4 powder.

The BN crucibles were positioned in a graphite sample carrier, the covers of the boro-nitride crucibles could be pressed down tightly with a graphite ram. This arrangement is intended to prevent that reducing, carbon-containing gases can react with the samples which could lead to great difficulties during sintering. The sintering was done in a graphite resistance -heated high-temperature furnace (Degussa VSP Gr 7/10). The sintering conditions were 1700°C, 10 min at heating-up and cooling-down speeds of 25K/min. The temperatures were measured with a pyrometer and with thermocouples.

For the sinter samples the density was determined with a Hg-hydrometer and metallographic as well as X-ray tests were made. The oxygen concentration was determined by photon activation (BAM Berlin).

RESULTS AND DISCUSSION

The specific surfaces of the silicon nitride powders, obtained after varying grinding times in the attrition device, the iron concentration remaining after cleaning with hydrochloric acid, and the oxygen contents of the powders are listed in table 2. Figure 1 shows the Si_3N_4 powder in the initial state and after four hours of grinding.

Figure 2 shows the density and the weight loss of the sinter bodies and figure 3 the phase state as a function of powder preparation.

From figure 2 it can be seen that an increase in the specific surface, combined with an increase in oxygen content, increases the sinter densities markedly which, in individual cases, even exceeded 95%.

Since the increase in sinter densities after more than four hours of grinding is still quite small, the conclusion suggests itself that specific surfaces of the order of magnitude of 20 m^2/g and combined with oxygen contents around 2wt.% are sufficient to sinter Si_3N_4 form bodies to ≥90%. The loss in weight, about equal for all samples, results primarily from the magnesium compound; with careful advance annealing values below 5wt.% can be attained even for these high-dispersion powders.

Table 2 Powder characteristics after varying grinding times

	spec.surface m^2/g	Fe content ppm	O content wt.%
starting powder H 1	8.42	400	0.9
powder after grinding times of			
4 h	20.0	50	2.1
8 h	28.2	70	2.9
12 h	31.8	90	3.9

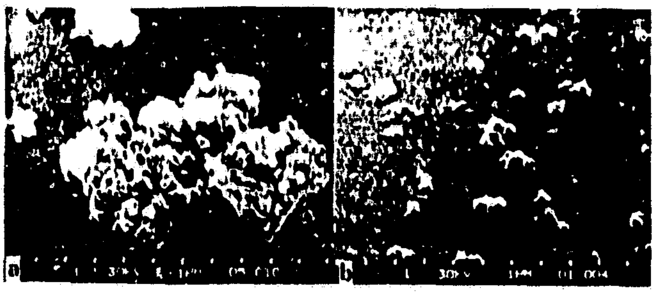

Figure 1 REM-pictures of the Si_3N_4 powder HCST-H1 in initial state (a) and after four hours of grinding (b)

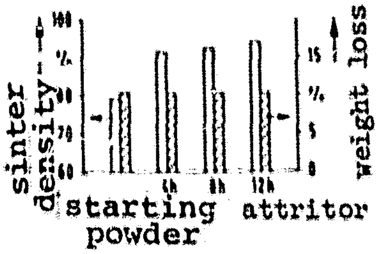

Figure 2 Density and weight loss of the sinter bodies as a function of powder preparation

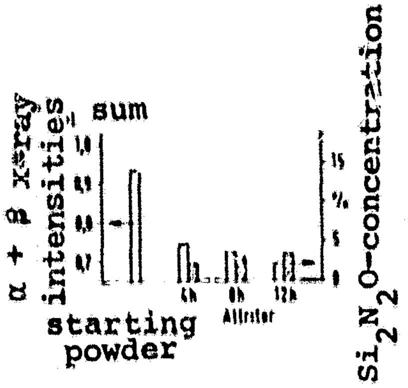

Figure 3 Phase state of the sinter bodies as a function of powder preparation

The oxygen additionally getting into the powder because of grinding or chemical purification increases, through reaction with the MgO, the amount of melt phase which causes the concentration of α- and β- Si_3N_4, determined by X-rays, to decrease compared to a sample which was produced from the initial powder, but without sinter-assist material. At the same time we were able to prove the existence, analogous to the oxygen concentration, of increasing amounts of Si_2N_2O in these sinter bodies, as shown in figure 3. Figure 4a-c lists raster-electron microscopic structure photographs of these samples. Figure 4a shows the rather coarse nature of sinter samples from untreated starting powder. Because of the low densification taking place, the secondary phase formed is quickly dissolved during etching. The samples shown in figures 4b and 4c exhibit a substantially lower attack after equal etching times.

Because of the greater fineness of the starting powder the glass phase formed is distributed over a considerably larger surface. On the one hand this causes the layer thicknesses to be /581 smaller, and on the other hand, the higher internal surface

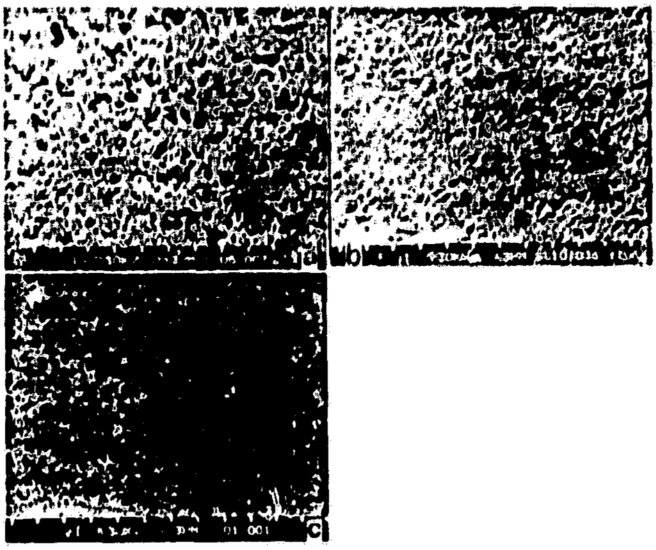

Figure 4 REM-photographs of Si_3N_4 sinter structures (+2% MgO) after varying powder preparation (etching with NaOH 420°C,20s) a) specific surface of the powder $8.4m^2/g$
b) specific surface of the powder $20m^2/g$,
c) specific surface of the powder $31.8m^2/g$

will allow an increased solution of Si_3N_4 in the secondary phase which can produce an improvement in the chemical and thermal properties. For example, Lohmann [22] has proven for glasses in the system Si-Al-Y-O-N that, among others, the chemical resistance and the transformation temperature increase unequivocally with the concentration of the dissolved nitrogen which he attributes to the formation of trivalent bonds by nitrogen in the glass structure.

Within the framework of these considerations additional investigations for the determination of the mechanical and thermal properties of the sintered materials are in progress.

CONCLUSIONS

The results obtained show that the pressure-free sintering of Si_3N_4 powders of conventional hot-press quality [23] to densities ≥90% is possible if the following conditions are satisfied:

- The Si_3N_4 powder has a specific surface of about 20 m^2/g and an oxygen content of about 2wt.%
- The MgO concentration is at least 2wt.%
- The additive is distributed uniformly in the Si_3N_4 powder
- During sintering an arrangement is selected which makes sure that the equilibrium partial pressures developing above the Si_3N_4 and the added materials are retained and that the admission of reducing, carbon-containing gases is made more difficult.

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