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High Temperature Properties of Si_3N_4 Materials

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Abstract

The gas pressure sintering of Si_3N_4 *is strongly influenced by the gas atmosphere in the sintering aggregate. During sintering a weight loss takes place. This is caused by the interaction of silicon nitride and the glassy phase with the sintering atmosphere. Carbon compounds such as CO promote these reactions. This leads to a reduction of the oxygen content. Additionally a decomposition process of* Si_3N_4 *takes place with formation of finely distributed free silicon. This process is accompanied by a crystallization of grain boundary phases during cooling from sintering temperature. This fact causes an increase of the bending strength of samples with high weight losses at high temperatures.*

Das Drucksintern von Si_3N_4 *wird sehr stark von der Gasatmosphäre im Ofen beeinflußt. Bei Anwesenheit von Kohlenstoffverbindungen, z.B. CO, treten Gewichtsverluste auf, die primär auf die Reduktion des Sauerstoffgehaltes zurückzuführen sind. Daneben kann es zum Abbau von* Si_3N_4 *unter Bildung von fein verteiltem freien Silizium kommen. Dabei tritt eine Kristallisation der Korngrenzenphasen während der Abkühlung der Sintertemperatur auf. Bei diesen Proben kommt es zu einer Steigerung der Biegebruchfestigkeit bei 1200°C.*

Le frittage sous pression de gaz du Si_3N_4 *est influencé de manière très forte par l'atmosphère du gaz règnant dans le four. En présence de composés carbonés comme par exemple le CO, on note des pertes de poids qui sont principalement causées par la réduction de la teneur en oxygène. On observe simultanément la décomposition de* Si_3N_4*, conduisant à la formation de silicium libre finement réparti. Ce phénomène est accompagné par la cristallisation de phases des joints de grains lors du refroidissement à partir de la température de frittage. Les échantillons ainsi élaborés présentent un accroîssement de la résistance mécanique à haute température (1200°C).*

1 Introduction

Silicon nitride is one of the most promising candidates for high-temperature materials. Dense silicon nitride bodies are usually sintered with the aid of oxide additives such as Al_2O_3, Y_2O_3, the rare earth or the alkaline earth oxides. Al_2O_3, Y_2O_3 and their combinations are the most intensively studied additives.[1] Because of the low sinterability of Y_2O_3-doped Si_3N_4 bodies without other additives, the use of Al_2O_3 is advantageous. The liquidus temperature of the silicate melt is lowered by about 100°C if Al_2O_3 is used in addition to Y_2O_3. This leads to a marked increase in sinterability. On the other hand, Al_2O_3 additions decrease the viscosity of the glassy phase, which has an adverse effect on the high-temperature properties of the material. The mechanical properties of Si_3N_4 ceramics at temperatures above 800°C are determined by the intensive subcritical crack growth in the glass phase of the grain boundary.[2] That is why the high-temperature bending strength depends on the homogenization, the type and composition of the grain boundary phase and its degree of crystallization.

The properties of the Si_3N_4 ceramics can also be influenced by the sintering conditions. There are only a few papers in the area of systematic correlation between green body sintering conditions, microstructure and mechanical properties.

The purpose of this work was to investigate some factors influencing the high-temperature mechanical

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properties of sintered silicon nitride (SSN) and sintered reaction-bonded silicon nitride (SRBSN).

2 Experimental

2.1 SSN sample preparation

The silicon nitride powder used in the present work was a commercial one (BET = 9·8 m^2/g; 96% α-Si_3N_4; 1·5 wt% oxygen; 0·1 wt% carbon). It was intensively mixed with the sintering additives Al_2O_3 (ALCOA A-16) and a mixture of rare earth oxides R_2O_3 (66% Nd_2O_3; 17·5% Pr_2O_3; 14·5% La_2O_3; 1% Sm_2O_3) in a planetary ball mill in ethanolic solution. The balls and the vessel were made from agate. The rare earth oxides were precipitated during mixing in the ball mill as acetylacetonates.[3] The resulting suspensions were dried, the powder mixture granulated and pressed (250 MPa) into bars measuring approximately 5 × 6 × 60 mm^3. The concentration of the sintering additives was 6·8% rare earth oxides and 1·7% alumina. Sintering was carried out in a two-step sintering regime at temperatures between 1850 and 1900°C, a pressure between 50 and 80 atm N_2 and a sintering time of 90 min. The different interactions between the samples and the atmosphere in the furnace were realized by different powder beds. More details of the sintering will be published elsewhere.[4]

The experiments for determination of high-temperature strength were conducted in vacuum. For every set of conditions 5–8 samples were tested. The oxygen content was measured by neutron activation.[5]

2.2 SRBSN sample preparation

A high-purity silicon powder (BET = 3·4 m^2/g; 0·95 wt% oxygen) was used for preparation of the SRBSN samples. The green bodies were prepared in the same way as the SSN materials. Nitridation was carried out in a nitrogen/hydrogen atmosphere. The temperature was gradually increased up to 1380°C over 22 h. The α/β ratio of the RBSN was 90 : 10, the degree of reaction was 96 ± 0·5%. The porosity in the RBSN state was 29·5 ± 0·5%.

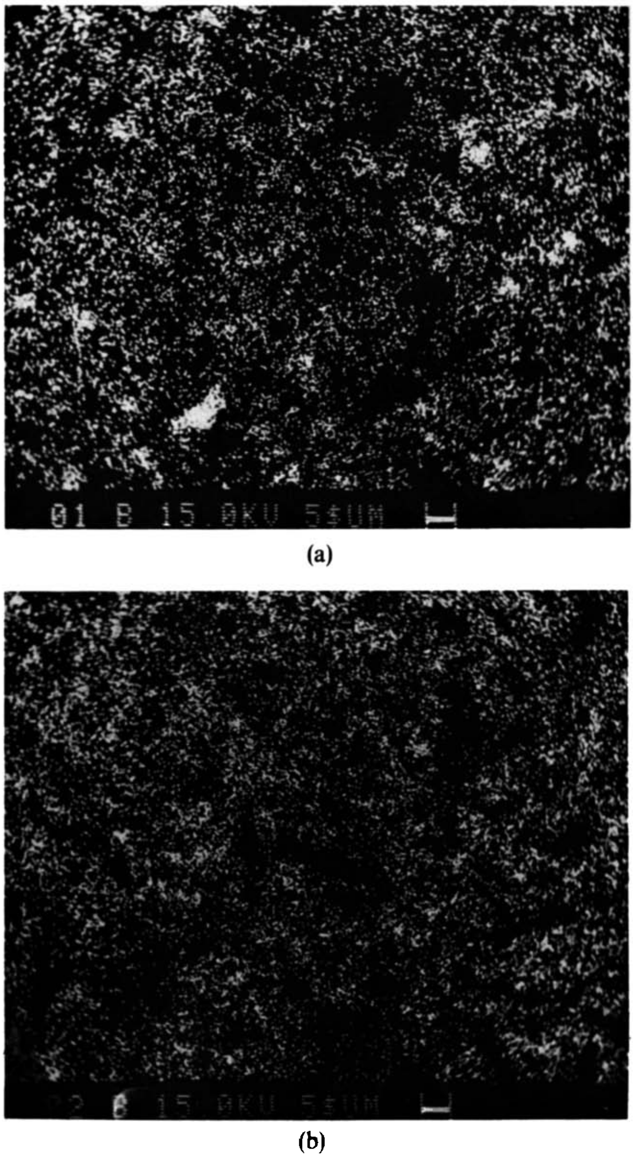

Fig. 1. SEMO analysis of the Nd distribution in sintered Si_3N_4 bodies (Nd $k\alpha$). (a) Prepared in a ball mill; (b) prepared by milling and precipitation.

3 Results and Discussion

The influence of homogenization of the additives is shown in Fig. 1. The powder mixtures were prepared by simple milling in a planetary ball mill or by chemical methods.[4] It is shown that with homogenization by chemical precipitation the distribution of the additives can be improved and therefore the high-temperature strength increases (Table 1). The better mechanical properties at high temperatures were also demonstrated for SRBSN (Table 1) and HPSN materials.[6]

The different interactions between the samples and the atmosphere in the furnace influence the composition of the grain boundary and the high-temperature properties. The interaction was

Table 1. Bending strength at 1200°C of SSN and SRBSN materials (sintering conditions: $T = 1850°C$; $t = 90\,\text{min}$; $P = 80\,\text{atm}$)

Preparation	σ_3 *(SSN) (MPa)*	σ_4*(SRBSN)(MPa)*
Milling	380 ± 40	458 ± 50
Milling with precipitation	460 ± 40	535 ± 40

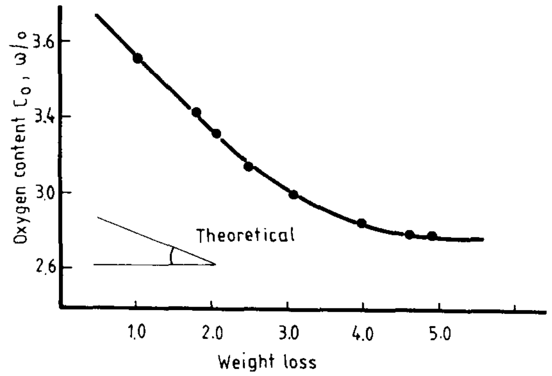

Fig. 2. Relationship between the weight loss and oxygen content. Sintering conditions: $T = 1900°C$; $P = 50$ atm; $t = 90$ min; theoretical ascent—according to eqn (1).

changed only by the variation of the powder bed. Samples with low weight losses were sintered in a closed crucible from RBSN. Samples with high weight losses were sintered in a low density powder bed. In all samples the carbon content remains at the level of the used silicon nitride powder.

The relation between the total oxygen content and the weight loss after sintering is shown in Fig. 2. This figure indicates that a linear dependence between oxygen content and weight loss only exists at low weight losses. The high ascent of the curve shows that the weight loss cannot be caused only by the mechanism:

$$3SiO_{2(melt)} + Si_3N_4 \rightarrow 6SiO + 2N_2 \qquad (1)$$

The expected ascent for this mechanism is marked as 'Theoretical' in Fig. 2. Carbon compounds (carbon heater, crucible) such as CO also take part in the reduction of the oxygen content.[7] When a high weight loss has been obtained the oxygen content in the samples after sintering reaches a nearly constant level. This fact indicates that a decomposition process of Si_3N_4 takes place. This decomposition leads to formation of free disperse-distributed silicon. The different colours of the sintered bodies are an indication of this. Samples with a high weight loss are black but with a low weight loss have only a grey colour. It was shown that disperse-distributed metallic inclusions are reponsible for the colour of oxynitride glasses.[8] Polished sections of the samples with high weight losses show a higher content of free silicon than that of samples with low weight losses.

In Table 2 the relations between the results of the X-ray phase analysis, the weight loss and the oxygen content after sintering are shown. In samples with a high weight loss a grain boundary phase crystallization was found. According to the phase diagrams of the systems Si, Nd/O, N and Si, Nd, Al/O, N,[9] the grain boundary phases cannot be crystallized at the sintering temperature. The crystallization of the grain boundary must take place during the cooling process from the sintering temperature. This is promoted by a low content of SiO_2. But this cannot be the only reason for the crystallization of the grain boundary because an increasing weight loss leads at constant oxygen level to a higher degree of crystallisation of the grain boundary phase (Table 2, Fig. 2).

If it is taken into account that with higher weight losses the free silicon increases and that the crystallization process in oxynitride glasses can take place by heterogeneous nucleation at silicides,[8] a possible explanation of the phenomenon is heterogeneous nucleation of the crystalline phases on the homogeneous distributed silicon. This assumption is supported because crystallization of the grain boundary phase has not been shown in samples with a weight loss as far as 3% which have the same composition of the grain boundary phase as the samples with a higher weight loss but a lower concentration of free silicon.

In Fig. 3 the bending strength at 1200°C in relation to the weight loss after sintering is shown. It is demonstrated that the bending strength is nearly constant at low weight losses. Only if partial decomposition of Si_3N_4 during sintering takes place the bending strength increases. That means the bending strength at 1200°C is especially influenced by the crystallization of the grain boundary phase and not by the oxygen content.

The results of X-ray analysis after crystallization of the grain boundary phase at 1350°C (24 h) have

Table 2. Results of X-ray phase analysis of different SSN samples (sintering conditions: $T = 1900°C$; $t = 90$ min; $P = 50$ atm)

Samples	ρ *(g/cm³)*	Δm (%)	*Oxygen content* (%)	*After sintering*	*Crystalline phases after heat-treatment (1350°C/24 h)*
1	3·26	1·8	3·43	β-Si_3N_4	β-Si_3N_4, $R_2Si_2O_7$
2	3·25	3·0	2·95	β-Si_3N_4	β-Si_3N_4, N-Apatite
3	3·25	4·0	2·80	β-Si_3N_4, N-Apatite (0·10)	β-Si_3N_4, N-Apatite (0·32)
4	3·25	4·7	2·80	β-Si_3N_4, N-Apatite (0·25)	β-Si_3N_4, N-Apatite (0·32)

The relation of the X-ray intensities of the peak with $d = 0·286$ nm (the most intense peak of the phase $R_5(SiO_4)_3N$ with apatite structure), and of the peak with $d = 0·266$ nm (β-Si_3N_4) are given in parentheses.

Table 3. Four-point bending strength of SSN materials at 1200°C after sintering and after crystallization (sintering conditions: $T = 1900°C$; $t = 90\,min$; $P = 50\,atm$)

Sample	*Material*	Δm (%)	σ_4 (*MPa*) (*at 1200°C*)	
			After sintering	*After heat-treatment (1350°C/24 h)*
1	SSN	1·8	380 ± 30	515 ± 78
3	SSN	4·0	454 ± 35	445 ± 35
5	SRBSN	1·8	458 ± 50	450 ± 50

shown that this phase has a high SiO_2 content when the weight loss is small. The bending strength at 1200°C increased after crystallization of the grain boundary phases of samples with a low weight loss during sintering. This effect is not observed by samples with high weight loss even though the degree of crystallization increased (Table 3).

In SRBSN materials sintered under the same conditions the grain boundary phase was partially crystallized also at low weight losses ($<1\%$). This low weight loss is attributed to an additional process, the nitridation of the residual silicon.

The partial crystallization of the grain boundary phase can be explained by the following effects. SRBSN sinter only at higher temperatures than SSN materials.[11] For that reason evaporation and decomposition are also higher and the colour is darker than for SSN materials. The thermal treatment of these materials does not result in a significant increase of the bending strength (Table 3).

4 Conclusions

The high-temperature properties of Si_3N_4 ceramics depend on different facts. Beside the quantity and homogeneous distribution of the glassy phase the degree of crystallization of the grain boundary phases influences these properties. The formation of the crystalline phase can be produced by controlled interaction of the samples with the sintering atmosphere. Heterogeneous nucleation on fine-distributed free silicon during sintering seems to be the reason for the crystallization of the grain boundary phase. Further investigation is necessary for a final explanation of the phenomenon.

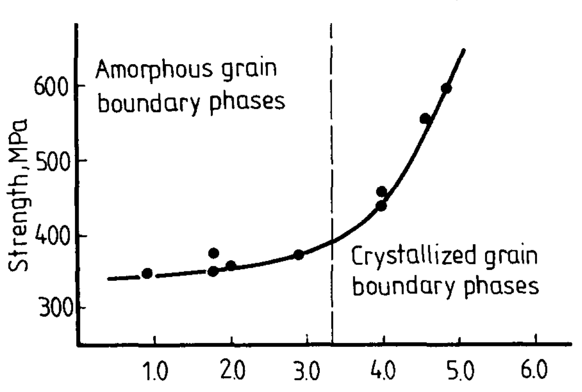

Fig. 3. Dependence of the four-point bending strength from weight losses during sintering. Sintering conditions: $T = 1900°C$; $P = 50\,atm$; $t = 90\,min$.

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