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α/β-Phase Transformation of Si_3N_4 without Sintering Additives

P. Šajgalík

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9,
CS-842 36 Bratislava, CSFR

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Abstract

Higher content of β-silicon nitride phase in green pellet results in a higher rate of α- to β-silicon nitride phase transformation when no sintering aids are applied during the isothermal firing of pellets at 1550°C. When the bed composition elevates the partial pressure of SiO, the phase transformation is significantly lower and the weight loss is stopped.

Si_3N_4-Grünkörper, die ohne Zugabe von Sinterhilfsmitteln bei 1550°C isotherm gesintert wurden, zeigten bei einem höheren Anteil der β-Phase eine höhere Umwandlungsgeschwindigkeit von α-Si_3N_4 nach β-Si_3N_4. Eine Pulverbettzusammensetzung, die einen SiO-Partialdruck aufbaut, hemmt die Phasenumwandlung und es tritt kein Gewichtsverlust auf.

L'accroîssement de la teneur en phase β dans le nitrure de silicium conduit à un taux de transformation $\alpha \rightarrow \beta$ supérieur lors du chauffage isotherme à 1550°C de pièces en cru ne contenant pas d'ajout de frittage. Lorsque la composition du lit de poudre élève la pression partielle de SiO, la transformation de phase est notablement plus faible et la perte de masse est interrompue.

1 Introduction

The importance of α- to β-phase transformation in the fabrication of high-strength silicon nitride ceramics has been recognized. The reconstructive phase transformation requires breaking of Si–N bonds and suitable liquid solvents.[1,2] The general conclusion is that oxide additives[3-10] or free silicon[11] accelerate the densification rate and formation of β-silicon nitride. Little information has been issued as to whether densification and α/β transformation occur in systems without sintering additives. Shimada and coworkers[12-14] studied densification, α/β-phase transformation and toughening of silicon nitride under high-pressure hot-pressing conditions (1100–1700°C, 1·5–5·0 GPa) without additives. They found a definite relation between densification and phase transformation in the latter stage of densification. Kuwabara *et al.*[15] and Haviar & Hansen[16] studied β'-sialon systems which contained very little grain boundary liquid phase. After removal of liquid phase they detected the presence of vapour transport of mass which contributed to phase transformation but not to densification. Greskowich & Rosolowski[17] pointed out that densification of silicon nitride during solid-state sintering is inhibited by formation of β-Si_3N_4 grains with high aspect ratios.

The present paper considers the possibility of α/β-phase transformation of silicon nitride without sintering additives and the possibility of influencing the transformation and thermal decomposition of silicon nitride by bed composition. The experimental results were compared with a computer simulation model of phase transformation.[18]

2 Experimental

Two powders labelled as A and B used for the present study contained 20 and 10 mass% of β-phase respectively. The powders were prepared by mixing the two silicon nitride powders H1 and SHS (Fig. 1 and Table 1). The mixtures were homogenized by ultrasonic agitation of appropriate amounts of powders H1 and SHS in dry acetone. Addition of 5–30 mass% of SHS powder to the powder H1 did not significantly influence the particle size distribution of α-particles, which are considered to be transformed to the β-phase and decomposed. That is why the particle size distribution of prepared powder mixtures was considered close to the

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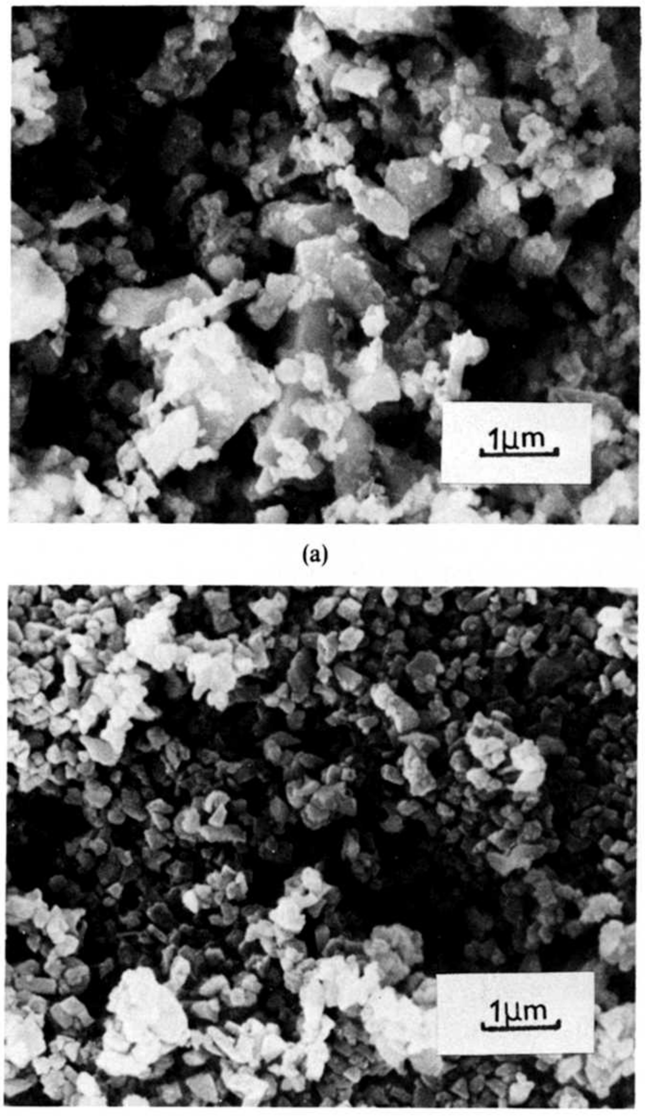


(a)

(b)

Fig. 1. Micrographs of (a) powder H1 and (b) powder SHS.

Table 1. Composition, surface area and purity of the starting powders H1[a] and SHS[b]

	H1	*SHS*
BET (m^2/g)	9·87	—
α-Content (mass%)	~93	~25
O (mass%)	1·61	0·80
Ni	—	0·05–0·1
C	0·48	—
Al	0·06	0·01–0·05
Fe	0·006	0·1–0·5
Mg, B, Ti, Cr	—	0·005–0·01
Cu, Ag	—	0·001–0·005
Ca	0·008	0·005–0·01

[a] H. C. Starck, Berlin, Germany.

[b] Prepared by self-propagation high-temperature synthesis at the Institute of Structural Macrokinetics ASci, Chernogolovka, USSR.

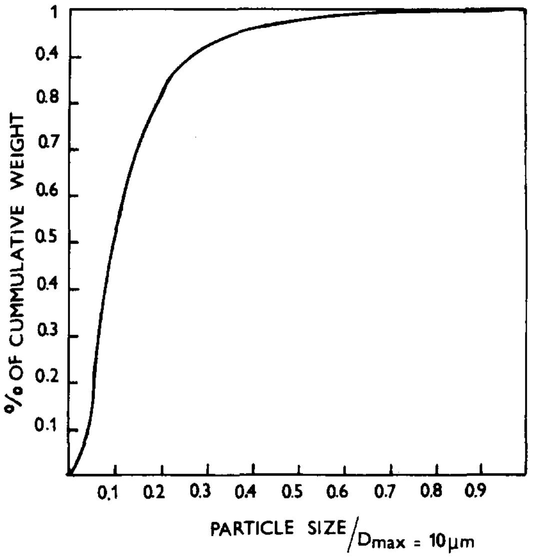


Fig. 2. Particle size distribution of Si_3N_4 powder (H1 grade, H. C. Starck, Berlin, Germany).

powder H1 (93 mass% of α; Fig. 2). The green pellets with a diameter of 6 mm and a thickness of 2 mm were pressed with 200 MPa in a conventional steel die. The relative green densities were in the range 0·53 to 0·56. The pellets were embedded in two different powder beds. Bed composition I consisted of SHS powder and bed composition II consisted of the mixture SiO_2 and carbon black powder in the mass ratio 1:1. The pellets were isothermally fired at 1550°C in a graphite furnace under nitrogen pressure of 1 MPa. Temperature was measured by optical pyrometer (Ircon-Modline) at the surface of the graphite crucible. The silicon nitride α/β-phase ratio was determined by X-ray powder diffraction analysis[19] and densities were determined by the mercury immersion method.

3 Results

3.1 α/β-Phase transformation

The changes in β-phase content during isothermal firing of pellets of A and B powders in bed composition I are shown in Fig. 3. Curve AI corresponds to the β-silicon nitride content of pellets of powder A and curve BI corresponds to the pellets of powder B isothermally fired at 1550°C. Figure 3 indicates that the conversion rate (slope of curves) and the final β-content depend on the starting α/β ratio. The conversion rate decreases after a firing period of 5 and 10 h, for powders A and B, respectively. The rate of α/β transformation was significantly reduced when the bed composition II was applied in the case of powder A (Fig. 4).

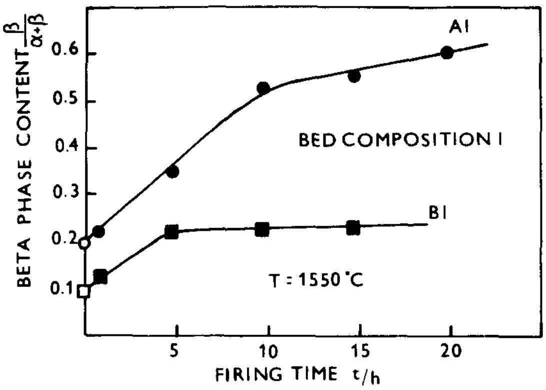


Fig. 3. Effect of starting content of β-Si_3N_4 on the α/β transformation during isothermal firing at 1550°C in powder bed composition I. Empty symbols correspond to the phase composition of green body compacts.

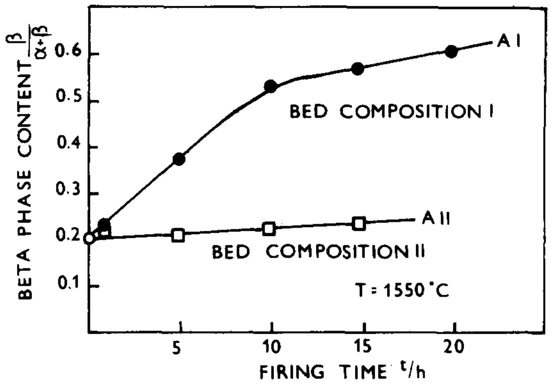
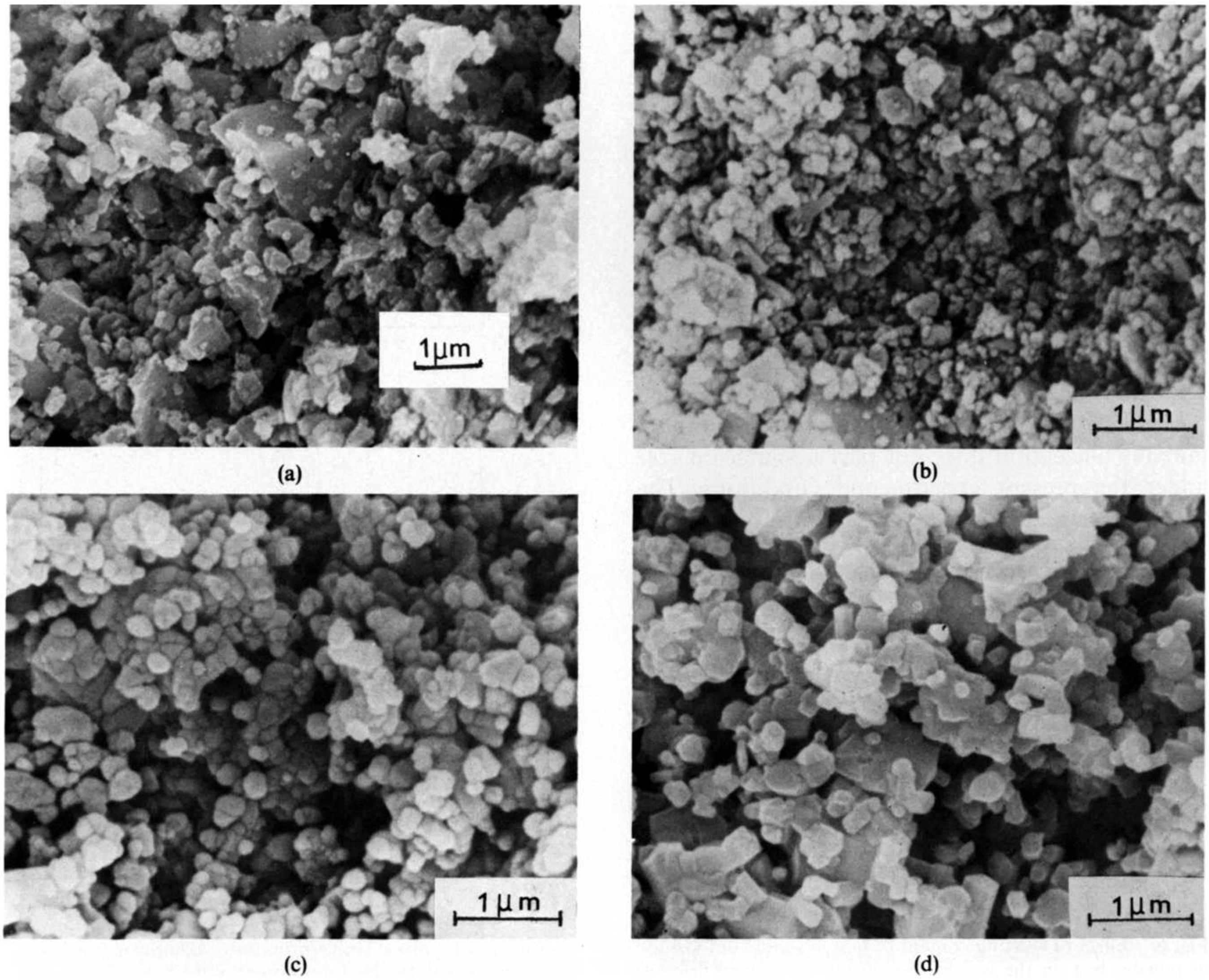


Fig. 4. Effect of composition of bed powder on the α/β transformation during isothermal firing at 1550°C.

3.2 Microstructure

The change in microstructure of powder A during isothermal firing at 1550°C is shown in Fig. 5. The microstructure of the pellet after 1 h firing, Fig. 5(b), is not significantly changed in comparison to the green pellet, Fig. 5(a). Figure 5(c) indicates that the particle size distribution is more homogeneous after 5 h firing. The grain growth is evident and the fine particles have disappeared. Reshaping of grains after 15 h of firing is illustrated in Fig. 5(d), the particles becoming prismatic. The changes in microstructure and the changes in α/β ratio are not accompanied by densification.



(a) (b) (c) (d)

Fig. 5. Changes in microstructure of pellet of powder A fired in bed composition I. (a) Green pellet; (b) 1 h; (c) 5 h; (d) 15 h.

Table 2. Difference between green (ρ_0) and final (ρ_f) relative densities of pellets of powder A fired in bed composition I

Firing time (h)	$\rho_0 - \rho_f$
1	−1·8
5	−2·8
10	−4·8
15	−6·0
20	−4·6

3.3 Thermal decomposition

In the case of bed composition I the densities of pellets were always lower after the firing period than the densities of green pellets (Table 2). This indicates the presence of intensive thermal decomposition of silicon nitride not only from the surface of the pellets but also from the bulk of the pellets. Figure 6 shows the changes in weight loss during firing of powder A and B at 1550°C in bed composition I. At the same firing conditions powder A revealed a larger weight loss than powder B. The only important difference between A and B powders is the starting content of β-Si_3N_4. The weight loss curves for different β-silicon nitride contents, curves AI and BI shown in Fig. 6, are opposite to those for pellets fired with sintering additives.[20] Thermal decomposition was practically stopped (Fig. 6) when the bed composition II was applied during firing of powder A.

4 Discussion

4.1 Bed composition I

The fact that the transformation rate and the maximum level of β-content depend on the starting amount of β-silicon nitride indicate that spontaneous nucleation does not play a signficant role under the present experimental conditions. The shape of curves AI and BI (Fig. 3) seems to be similar to those shown in Fig. 7. These are the result of computer simulation of α- to β-silicon nitride phase transformation.[18] The model is based on the assumptions that:

—β-Si_3N_4 is a stable phase;
—growth (crystallization) of β-Si_3N_4 is the rate-controlling step;
—the growth rate of β-Si_3N_4 in the direction of the *c* axis is twice that in the perpendicular direction;
—no 'nucleation' of β-Si_3N_4 is taken into account;
—'weight loss' of α-Si_3N_4 is considered with a rate which is a fraction of the crystallization rate of β-Si_3N_4 needle-like particles;
—rearrangement of the particles during the simulation is not taken into account.

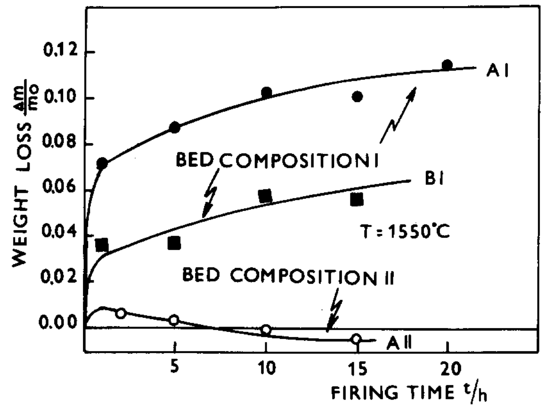


Fig. 6. Effect of starting content of β-Si_3N_4 and composition of powder bed on the weight loss during isothermal firing at 1550°C.

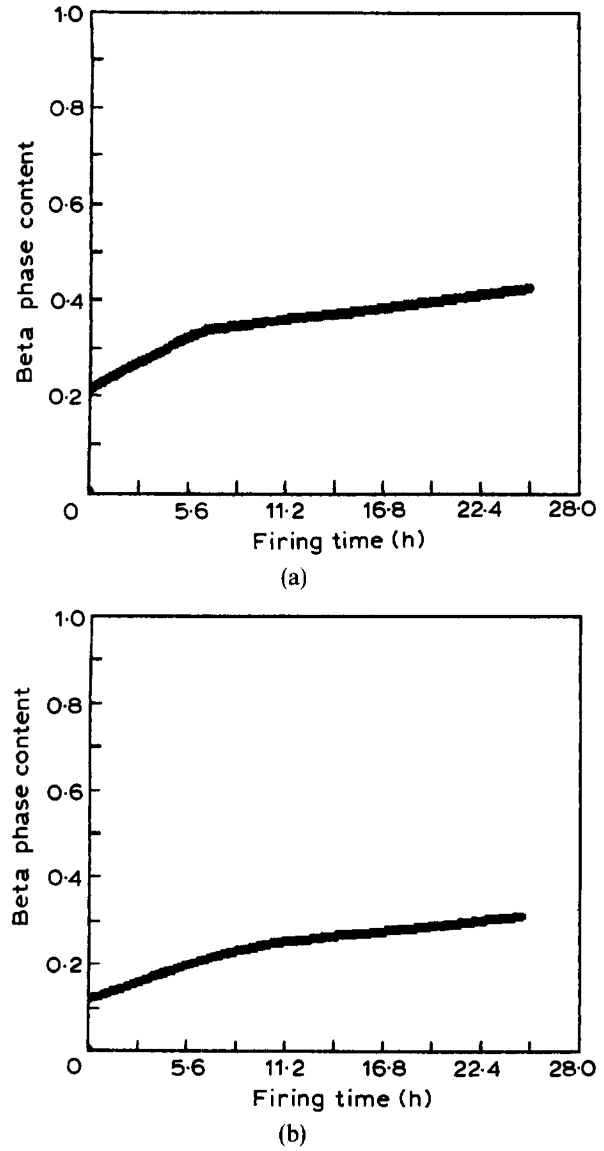


Fig. 7. Effect of starting content of β-Si_3N_4 on the α/β-silicon nitride phase transformation—computer simulation according to Ref. 18. Starting content of β-silicon nitride: (a) 20 mass%; (b) 10 mass%.

The difference in simulations between the cases of Fig. 7(a) and Fig. 7(b) is the starting content of prismatic β-silicon nitride particles. The higher rate of α/β transformation and the higher level of β-phase content in the case of 20 mass% of β-Si_3N_4 (Fig. 7(a)) is, according to the computer simulation, the result of higher free surface area of β-Si_3N_4 in the green pellet. This result is also pointed out in Ref. 18.

While the new phase can form only when there is enough free space for growth, the transformation rate is controlled by the pore size distribution. The grain growth is strongly reduced and the transformation rate decreased when the growing grains touch another grain. An example of such behaviour, when the grain is grown in presence of sintering additives, is shown in Fig. 8. The large β-silicon nitride grain grew to dimensions limited only by the dimensions of the pore. The highest growth rate of β-phase prismatic grains is in the direction of the *c* axis. When the grain growth in this direction is stopped, only the growth in the direction perpendicular to the *c* axis can proceed further, but of course with a significantly lower rate. In Ref. 10 it was pointed out that this rate of grain growth, perpendicular to the *c* axis, is the phase transformation controlling step in particular cases of α/β transformation. This is supposed to be the reason for the lower rate of α/β transformation (Fig. 3) after a definite firing time period.

Fig. 8. Large β-Si_3N_4 grain grown within the framework of the large pore.

The simulation of α/β-silicon nitride phase transformation (Fig. 7) is based on the presumption that all the β-Si_3N_4 grains grow in the direction perpendicular to the *c* axis even in cases when growth in the direction of the *c* axis is impossible. The shape of the curves shown in Fig. 7 is similar to the shape of curves measured experimentally (Fig. 3). Also in the case of simulation, the rate of α/β transformation is higher for a higher starting α/β ratio and after a definite time period this rate significantly decreases. A remarkable qualitative discrepancy between Figs 3 and 7 is the fact that the curve of experimentally measured rate of phase transformation for powder A in bed composition I conserves the higher value for a longer firing period than in the case of powder B. The opposite happens in simulation experiments, Fig. 7. This can be explained by results listed in Table 2. In reality, the porosity is increasing (i.e. the β-silicon nitride grains are growing to the pores which grow during the firing) while the simulation allows only stable 'pores' with constant size.

The weight loss curves (Fig. 6) show that the higher content of β-silicon nitride phase in the green compact results in a higher weight loss. The intensity of decomposition of silicon nitride depends mainly on the partial pressure of species over the surface of individual particles. From this point of view the pressure of external gas atmosphere and the size distribution of silicon nitride powder particles are important. Since the gas atmosphere and the pressure were the same in all experiments the decisive role is the development of the size distribution of the particles and pores during the firing, i.e. the microstructure. The simulation experiments show the difference in development of morphology of α-particles and also in weight loss during 'firing' of samples which differ in starting content of β-silicon nitride phase. Figure 9(a) and Fig. 9(b) show the weight loss in the case of 20 mass% and 10 mass% of β-Si_3N_4 in the 'green compact', respectively. Higher weight loss in the case of 20 mass% is obvious up to 15 h of simulation. All above-mentioned simulation experiments have to be considered only as qualitative criteria and there is no possibility of quantitative comparisons. The particle size distribution of both above-mentioned 'green compacts' used for simulation, i.e. compacts with 10 and 20 mass% of β-Si_3N_4, is very similar, and the representative cumulative distribution of simulated particles is shown in Fig. 10. The distribution is partially different in comparison to the particle size distri-

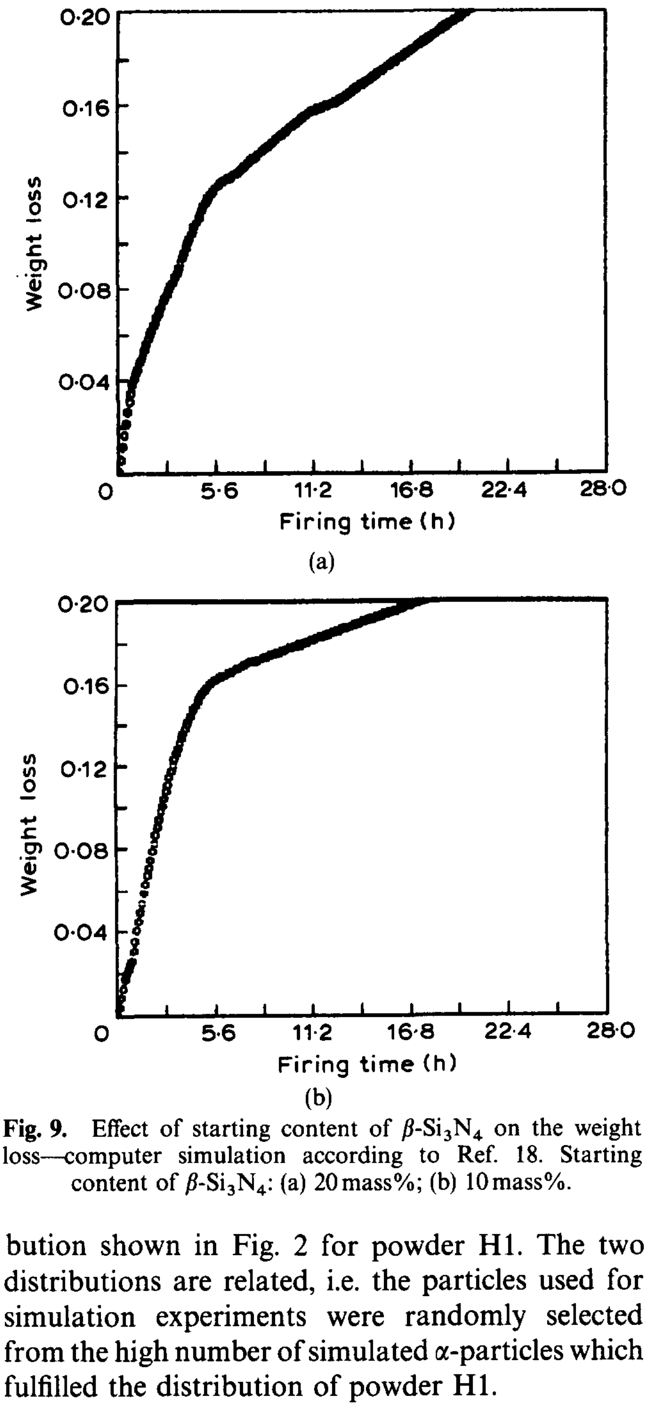


Fig. 9. Effect of starting content of β-Si_3N_4 on the weight loss—computer simulation according to Ref. 18. Starting content of β-Si_3N_4: (a) 20 mass%; (b) 10 mass%.

bution shown in Fig. 2 for powder H1. The two distributions are related, i.e. the particles used for simulation experiments were randomly selected from the high number of simulated α-particles which fulfilled the distribution of powder H1.

4.2 Bed composition II

In the case of bed composition II the α/β transformation was strongly reduced (Fig. 4). According to the equilibrium diagram presented by Blegen,[21] in the ternary system Si–O–N, five condensed phases are known at 1530°C: Si, SiO_2, Si_2ON_2, α-Si_3N_4 and β-Si_3N_4. The region of stability of these phases depends on the partial vapour pressure of N_2 and SiO. At an N_2 pressure of 1 MPa, corresponding to the conditions of present experiments, increasing SiO partial pressure increases the stability of particular phases in the order β-$Si_3N_4 > \alpha$-$Si_3N_4 > Si_2ON_2$, i.e. at high SiO partial pressures Si_2ON_2 is

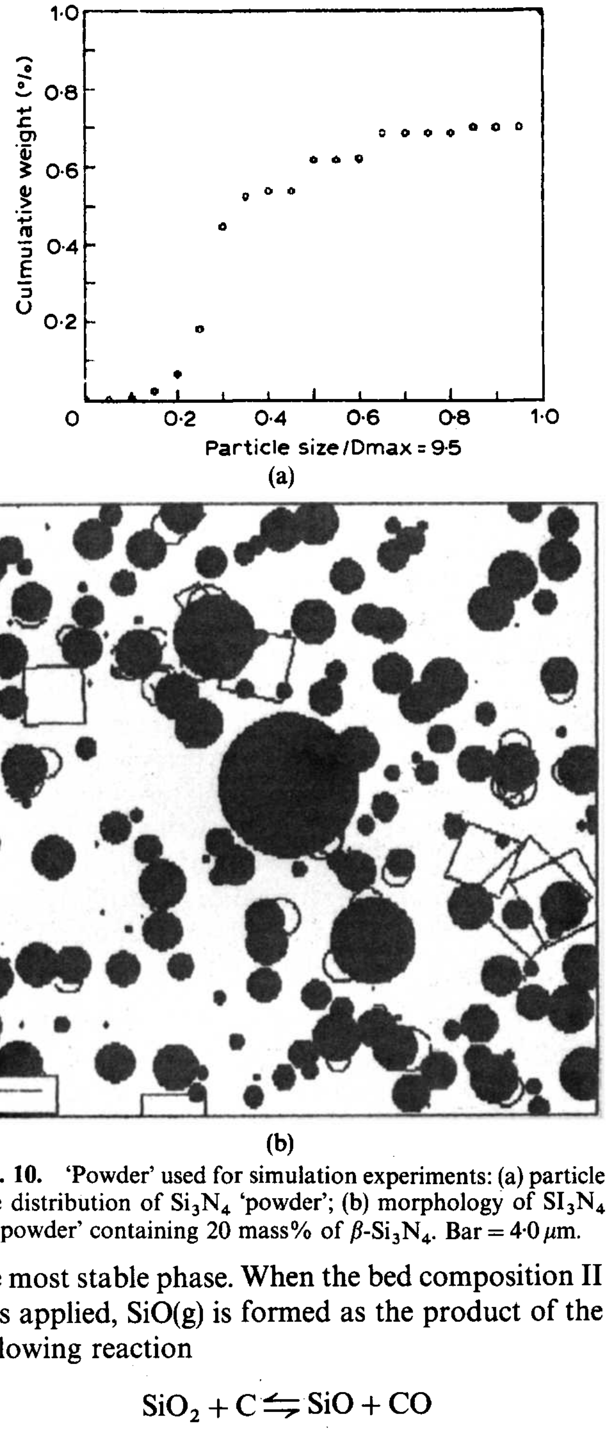


Fig. 10. 'Powder' used for simulation experiments: (a) particle size distribution of Si_3N_4 'powder'; (b) morphology of SI_3N_4 'powder' containing 20 mass% of β-Si_3N_4. Bar = 4·0 μm.

the most stable phase. When the bed composition II was applied, SiO(g) is formed as the product of the following reaction

$$SiO_2 + C \rightleftharpoons SiO + CO$$

proceeding in the bed composition at 1550°C. The partial pressure of produced SiO can be estimated in the range 1 to 10 kPa from the above-mentioned equilibrium and the data of CO concentrations as measured in Ref. 22. According to Blegen's diagram[21] the value of the partial pressure of SiO from this range shifts the stability of the system toward the oxynitride phase. The oxynitride phase was really observed on the X-ray pattern, in the pellet of powder A fired at 1550°C for 15 h. Weight loss of compacts fired in bed composition II is suppressed to a negligible level and after long firing times (15 h) a weight gain is observed. Under the experimental conditions (1 MPa of N_2, 1550°C) the bed composition II produces α-Si_3N_4 and, as was mentioned previously, SiO(g). An increased content of SiO is likely to lead to the following reaction:[21]

$$2\,SiO(g) + N_2(g) \rightarrow Si_2ON_2(s) + 1/2\,O_2(g)$$

so that the pellet will be 'infiltrated' with oxynitride. When the pellet was repeatedly fired in bed composition II at 1550°C for 1 h in each run, a weight gain of 4·2% and an increase in density of 5% were observed after the second cycle. The 'infiltration' is mainly realized on the surface of the pellet. This protection layer and also the change of partial pressure of SiO(g) over α-Si_3N_4 powder particles are considered as the reason for stopping of the weight loss. The facts that no sintering additives were used and that α to β phase transformation of Si_3N_4 was suppressed at elevated SiO partial pressure indicate that the phase transformation occurs via the vapour phase.

5 Conclusions

(1) α/β-Si_3N_4 phase transformation proceeds also in the systems fired without sintering additives in proper bed powders.
(2) The factor limiting the α/β transformation, when this proceeds in pure silicon nitride powder compacts, is the starting content of β-silicon nitride phase (i.e. free surface area of β-phase).
(3) This limitation indicates poor or no nucleation within such a system, i.e. the dominant mechanism is the crystallization of β-Si_3N_4.
(4) Elevated partial pressure of SiO significantly retards the α/β transformation and the weight loss of compacts of pure Si_3N_4 at 1550°C and 1 MPa of N_2.
(5) Elevated partial pressure of SiO results in creation of the oxynitride phase within the fired compacts of pure silicon nitride at 1550°C and 1 MPa of N_2, and after a long time of firing (10–15 h) at 1550°C densification and weight gain are observed.

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