CONF-970111--11

EFFECT OF POWDER CHARACTERISTICS ON THE α-TO-β Si_3N_4 TRANSFORMATION KINETICS

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ABSTRACT

β-phase nucleation and growth is an important step in the microstructure development of Si_3N_4 ceramics. Samples containing different powder types, sintering additives and α/β ratios were heated at intermediate temperatures and times to monitor the phase changes taking place. The rate of transformation was mainly dependent on the powder surface area and starting β-content. It was observed that additions of β-Si_3N_4 increased the rate of transformation.

INTRODUCTION

Silicon nitride materials are the leading ceramics for structural applications at elevated temperatures because of their excellent combination of properties. It is just being recognized how important the β-phase nucleation and initial growth stage of microstructure development are to the final properties of the silicon nitride, especially with all of the recent work involved in β-seeding of the starting materials.[1-7] In fact, the β-phase nucleation and initial growth is a key step to producing materials with high fracture toughness.[1-9] This microstructure development is directly related to the kinetics and morphology changes that occur during β-phase nucleation and initial growth. Understanding of the process variables in the initial stage of sintering and their control is essential for obtaining materials with high reliability and superior mechanical properties. Thus, a study was initiated to determine the interrelationships between the raw silicon nitride powders, the sintering additives as the liquid phase forms, β-phase nucleation and the kinetics of the α-to-β transformation. This is an area where there is a large body of fragmented data and observations, however, there is no systematic examination of the system. The present work examines the effects of the silicon nitride powders, the type of sintering additive and the use of β-Si_3N_4 seeds on the initial microstructure development.

Numerous studies have shown that the silicon nitride powder used in fabrication is an extremely important variable in the microstructural development and final properties of the materials.[1-7] Most of the early studies of silicon nitride powders were concerned only with either the densification behavior, the final mechanical properties or the high temperature properties produced by the various grades of powders available. None of the studies have done a comparative assessment of the effects of the raw materials on the microstructural development from a fundamental β-nucleation standpoint. Generally, the previous work found that high starting α-Si_3N_4 contents in the powders are preferable for densification and final material mechanical properties. However, β-phase starting powders have also been used to produce materials with good mechanical properties.[10]

Examination of the role of powders in the microstructure development is not only an academic exercise, but is of considerable engineering importance. Several studies have shown that the diimide-derived powders generally result in materials with the best mechanical properties. However, these powders are also the most expensive. Thus, there is a desire to use less expensive powders to fabricate materials with good mechanical properties.

EXPERIMENTAL PROCEDURES

Several powders will be examined in this research study that comprise a wide variety of characteristics, such as surface area, particle size, purity, and oxygen content (Table 1). All are high in α-phase content.

Table 1 - Characteristics of silicon nitride powders. Manufacturers' reported values.

Manu-facturer*	Grade	Fabrication Route	Mean Particle Size (μm)	Surface Area (m^2/g)	β-Phase Content (%)	Oxygen Content - Bulk/Lattice (wt. %)	Total Impurity Content (ppm)
Ube	E-10	Diimide[a]	0.2	11.7	2.6	1.40/0.63	100
Starck	M 11	Si Nitridation[b]	0.55	13.5	7.1	1.78/0.85	400
Starck	GP	Gas Phase[c]	0.55	10.9	3.8	1.12/0.38	100
Dow	EXP	Carbo. Red.[d]	0.84	9.3	0.5	1.7/0.91	500
Ube	E-05	Diimide[a]	0.4	5.1	N. D.	1.0/0.66	100
Ube	E-03	Diimide[a]	1.0	3.3	0.8	0.82/0.59	100

[a]Diimide decomposition. [b]Silicon nitridation. [c]Gas phase reaction [d]Carbothermal reduction.
*Ube, Tokyo, Japan: H. C. Starck, Berlin, Germany; Dow Chemical Co., Midland, MI.

To test the effect of raw materials on the initial stage microstructure development, the various powders were mixed with several different sintering additives that give a wide range of liquid properties. The intergranular phases chosen are shown in Table 2. The Y_2O_3-Al_2O_3 system (compositions 1 and 2) is one that has been studied extensively and has been used for most of the basic studies on grain growth and densification behavior and is included here for comparison with other studies. The choice of two different contents with provide some data on the effect of diffusion in the initial stage sintering process. The Y_2O_3-MgO system has also been studied previously and has been used to fabricate materials with high fracture toughness. It also represents a system with a lower eutectic temperature than the others. The $Y_2Si_2O_7$ (at 5 equivalent % oxygen) composition represents a very refractory grain boundary phase that will have a high liquid phase viscosity. The $Sr_2La_4Yb_4(SiO_4]_6O_2$ composition was included to examine a system with a very complex intergranular glass phase and its effect on the α-to-β transformation.

Table 2. Sintering additive compositions and approximate eutectic temperatures with Si_3N_4 and SiO_2.

Composition	Approx. Eutectic Temperature (°C)
1) 6 w/o Y_2O_3-2 w/o Al_2O_3	1280
2) 9 w/o Y_2O_3-3 w/o Al_2O_3	1280
3) 6 w/o Y_2O_3-1 w/o MgO	1200
4) $Y_2Si_2O_7$ (at 5 equivalent % oxygen)	1500
5) $Sr_2La_4Yb_4(SiO_4)_6O_2$ (at 8 equivalent % oxygen)	1400

The starting materials consisted of appropriate amounts of Si_3N_4, Al_2O_3, La_2O_3, Y_2O_3, Yb_2O_3, or SrO to form the desired intergranular phase.[a] The powders were milled for ~8 h (1.3 wt.% PVP[b] and 1 wt.% Darvan[c] were added as dispersants) to fully deagglomerate and mix the various constituents. The mixtures were dried, screened to -100 mesh and pressed at 100 MPa into discs approximately 2.5 cm in diameter and 3 cm thick. Binder burnout consisted of heating to 600°C in air for 1 h prior to sintering. Heat treatment was performed in a graphite element furnace with heating rates of 20°C/min to the hold temperature under nitrogen gas flow at ambient gas pressure. The heat treatment resulted in partial densification and α-to-ß transformation. The samples were then characterized by x-ray diffraction and the morphology examined by SEM.

RESULTS AND DISCUSSION

The α-to-ß Si_3N_4 transformation behavior between the different types of Si_3N_4 powders is summarized in Figs. 1 and 2 for two different sintering additive types. As shown, the kinetics are linear with time and the different powders exhibit quite different transformation behavior. For both of the sintering additive types shown, the Starck M11 Si_3N_4 powder generally exhibited the highest transformation rate, while the Dow EXP Si_3N_4 powder had the slowest. As will be shown below, the differences in the transformation rates for the different powders are dependent on the powder surface area and initial ß-Si_3N_4 content. In addition, other factors could possibly be involved, such as the silicon nitride lattice oxygen content or carbon content, which could affect the α-Si_3N_4 dissolution rate.

The effects of different sintering additive types on the transformation rate at temperatures of 1500°C and 1600°C are summarized in Figs. 3 and 4. Like the examples shown above, linear rate kinetics were observed for the various additives. The Y_2O_3-Al_2O_3 and Y_2O_3-MgO based materials had the highest transformation rates, which is not surprising since these additives also typically would have the lowest liquid phase viscosities during sintering which would enhance the transformation rate. The Y_2O_3-SiO_2 additive system would have the highest liquid phase viscosity and indeed, the slowest transformation rate is observed with these materials. The Y_2O_3-La_2O_3-SrO (La-Yb-Sr) system was intermediate in transformation kinetics compared to the other systems.

The different Si_3N_4 powders all contained different amounts of initial ß-phase. To determine the effect of the initial ß nuclei on the transformation behavior, several samples were fabricated with different amounts of ß-seeds in addition to what was initially present in the as-received powders. The effect of the ß-Si_3N_4 seed additions on the transformation behavior is shown in Fig. 5. The data is for one sintering additive type although the other systems exhibited similar behavior. As indicated, the ß-seed additions actually increase the α-to-ß transformation rate as shown in Fig. 6 and a linear relationship appears to exist between the transformation rate and the amount of initial ß-seeding. Such behavior of higher transformation rates with ß-seeding has been observed previously.[11-13] Recently, it has been speculated that the transformation rate is a function of the ß-seed nuclei density and surface area.[14]

Generally, it was observed that the highest surface area silicon nitride powders exhibited the highest transformation rates. The appropriate relationship between the transformation rate and surface area was estimated by examining the behavior of powders made by the same process. To insure that the powders made by the same process indeed behave in a similar fashion, an Arrhenius plot of α-to-ß Si_3N_4 transformation rate as a function of inverse temperature (1/T) for

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[a] Si_3N_4- Ube, Japan, E10; Al_2O_3- Reynolds, Malakoff, TX, RC-HP DBM; La_2O_3, Y_2O_3, Yb_2O_3- Molycorp, White Plains, NY; >99.9%; SrO as $SrCO_3$; Mallinckrodt, St. Louis, MO; Reagent Grade

[b] GAF Chemicals, Wayne, NJ: Polyvinylpyrrolidone K-15 [c] R. T. Vanderbilt, Norwalk, CT, 821A,

two silicon nitride powders (Ube E-10 and Ube E-03) was made (Fig. 7). The sintering additive for these samples was 6% Y_2O_3-2% Al_2O_3. The activation energies for the two powders are nearly identical in the range of 539-556 kJ/mol, which are similar to previous studies on silicon nitride transformation rate kinetics.[11-13] Since both of the powders were fabricated by the diimide process they should have similar initial lattice oxygen contents and carbon contents and small differences in total oxygen content and initial ß contents. So the only significant difference in the transformation rate is attributable to the surface area variation. A plot of the transformation rate as a function of silicon nitride powder surface area for the diimide powders is shown in Fig. 8. As indicated, there appears to be a linear relationship between the rate and the surface area for the data at 1500°C. Additional analyses at other temperatures are planned to confirm such a conclusion.

The results have established that the α-to-ß transformation kinetics for a particular sintering additive type are related to the initial ß content and the powder surface area. However, these factors alone do not explain all the differences in transformation behavior between the powders. In particular, the powder fabricated by carbothermal reduction (Dow EXP) displays a slower transformation rate than would be predicted based on the initial ß content and surface area. The difference is believed to be associated with the dissolution or melting behavior of the starting α-phase powder in the liquid phase upon which the transformation kinetics are directly dependent.

Possible influences on the dissolution behavior would include impurities (such as metallic cations, carbon and oxygen) and the bond strength in the crystal structure. In examining the data, the lower purity Si_3N_4 powders did exhibit the lower transformation rates, however, impurities, such as Ca and Fe would tend to increase the melting rate, not decrease it. Figure 9 shows the transformation rate as a function of the carbon content. While there is a definite trend to higher rates at the low carbon contents, the relationship is indeterminate at the higher carbon contents. This is probably due to the form in which the carbon is present. At the low carbon contents (<0.2 wt. %), the carbon is associated within the α-Si_3N_4 structure and consequently would have a direct effect on the dissolution rate. However, at the high carbon contents of the carbothermally produced powders, the carbon may be present as SiC or even free carbon which would not directly affect the α-to-ß transformation. The relationship between the lattice oxygen content and the transformation rate is shown in Fig. 10. As indicated, the transformation rate is observed to decrease with increasing lattice oxygen. Melting involves the breaking of bonds as the material enters the liquid phase. The effect of the lattice oxygen and carbon contents on the Si_3N_4 dissolution behavior may be associated with the differences in the bond strengths: Si-N of 335 kJ/mol, Si-O of 452 kJ/mol and Si-C of 318 kJ/mol.[15] The high lattice oxygen contents and the strengths of the Si-O bond could contribute to a decrease in the melting kinetics of the α-Si_3N_4 and a decrease in the overall transformation kinetics.

Results on the transformation rate with different sintering additive amounts are summarized in Figs. 11 and 12. Generally, the larger amount of sintering additive resulted in a slower transformation rate. If the additional sintering additive increases the liquid volume, a slower transformation rate would tend to indicate a diffusion controlled process for the α-to-ß transformation as compared to an interface controlled transformation.

CONCLUSIONS

The kinetics of the α-to-ß Si_3N_4 transformation are dependent on several characteristics of the starting silicon nitride powder. Most important, are the silicon nitride powder surface area and initial ß-Si_3N_4 content which both tend to increase the transformation rate. Other factors, such as lattice oxygen or carbon contents, appear to contribute to decreasing the transformation rate. In addition, the glass phase from the sintering additives also affects the transformation rate with higher viscosity and more refractory additives resulting in a decrease in the transformation rate. Larger volumes of the glass phase were observed to decrease the transformation rate.

ACKNOWLEDGMENTS

Research sponsored by the Propulsion System Materials Program, DOE Office of Transportation Technologies, under contract DE-AC0596OR22464 with Lockheed Martin Energy Research Corp.

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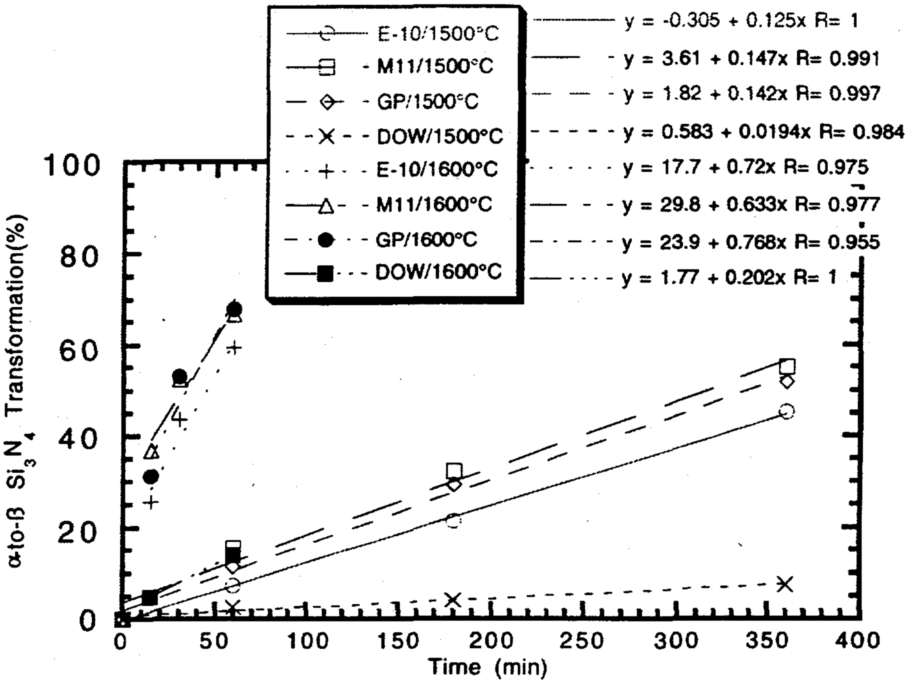

Fig. 1. α-to-ß Si_3N_4 transformation as a function of time for the various silicon nitride powders at 1500°C and 1600°C. The sintering additive was 6% Y_2O_3-2% Al_2O_3.

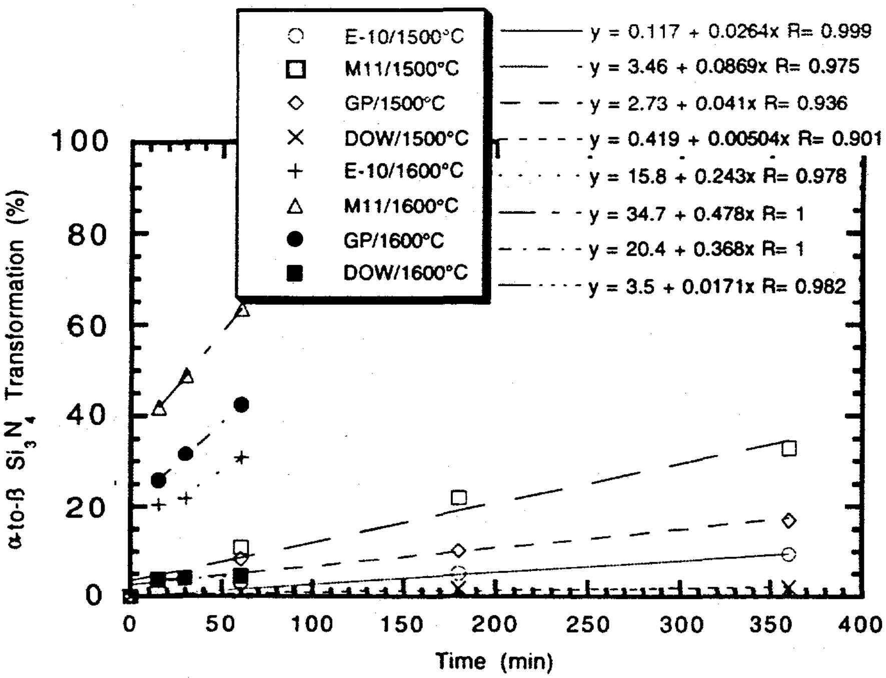

Fig. 2. α-to-ß Si_3N_4 transformation as a function of time for the various silicon nitride powders at 1500°C and 1600°C. The sintering additive was Yb_2O_3-La_2O_3-SrO.

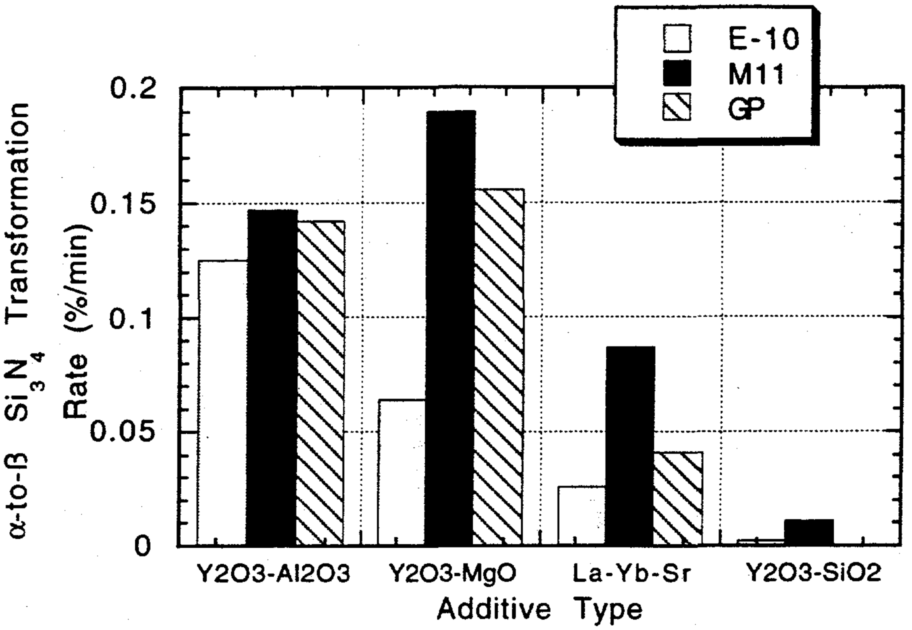

Fig. 3. α-to-ß Si_3N_4 transformation rate for the various types of sintering additives with the E-10, M11 and GP silicon nitride powders at 1500°C.

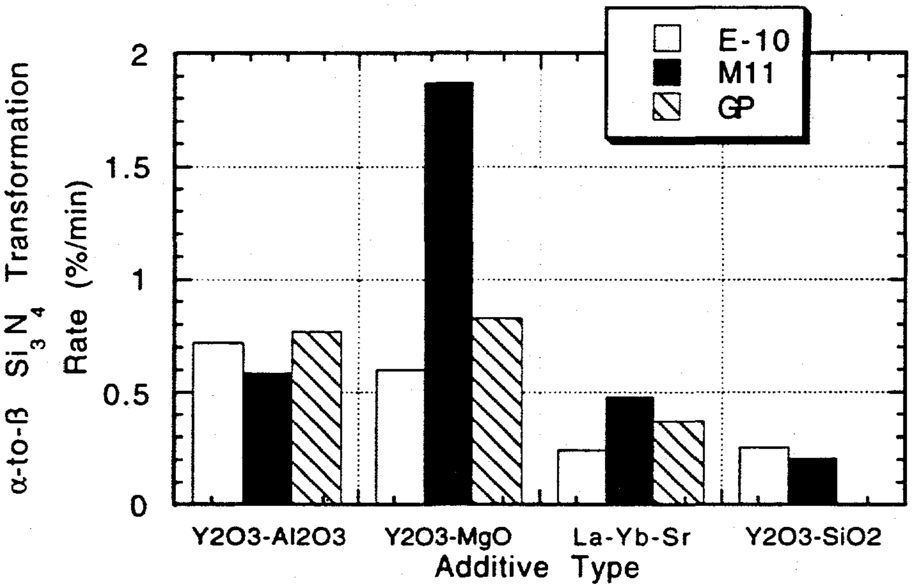

Fig. 4. α-to-ß Si_3N_4 transformation rate for the various types of sintering additives with the E-10, M11 and GP silicon nitride powders at 1600°C.

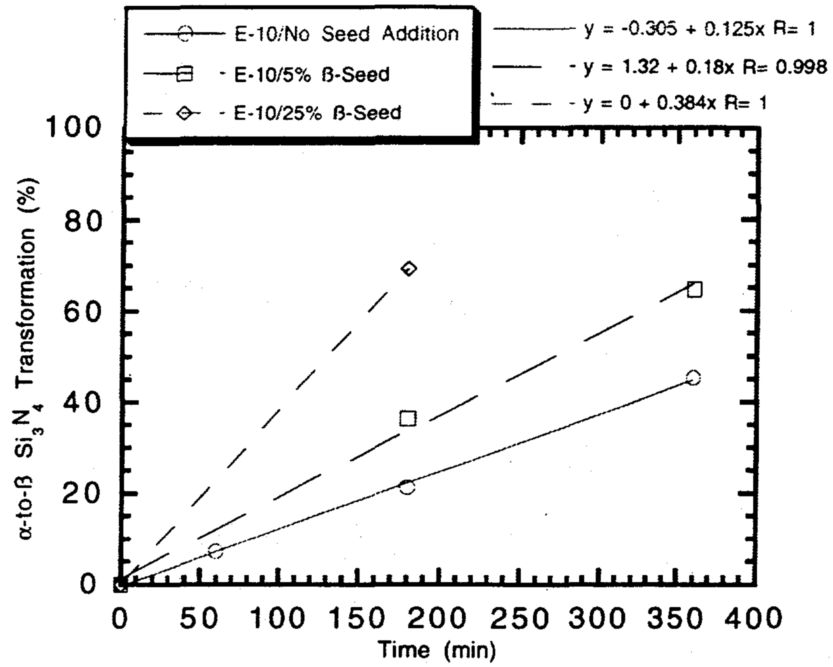

Fig. 5. α-to-ß Si_3N_4 transformation as a function of time for different amounts of ß-Si_3N_4 seed at 1500°C. The sintering additive was 6% Y_2O_3-2% Al_2O_3. The silicon nitride powder was Ube E-10 and the ß-seed was fabricated from Ube E-10 powder.

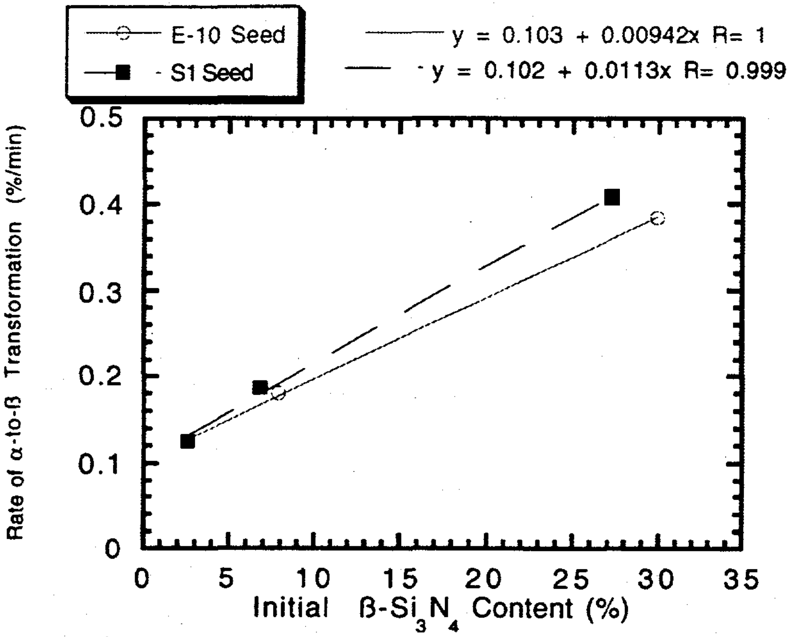

Fig. 6. α-to-ß Si_3N_4 transformation rate as a function of initial ß-Si_3N_4 content for two types of seed. The silicon nitride powder was Ube E-10, the sintering additive was 6% Y_2O_3-2% Al_2O_3 and the tests were at 1500°C.

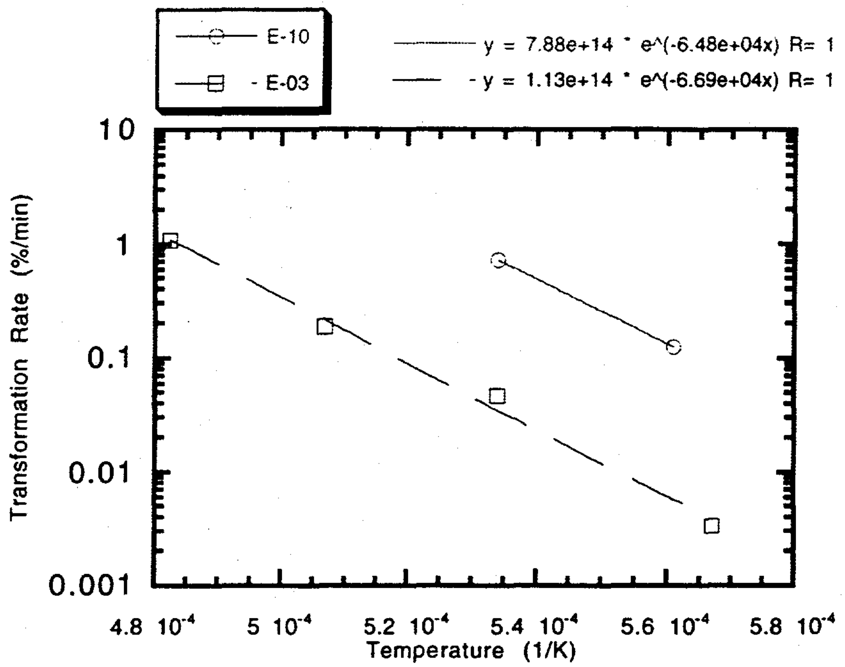

Fig. 7. Arrhenius plot of α-to-ß Si_3N_4 transformation rate as a function of inverse temperature (1/T) for two silicon nitride powders (Ube E-10 and Ube E-03). The sintering additive was 6% Y_2O_3-2% Al_2O_3.

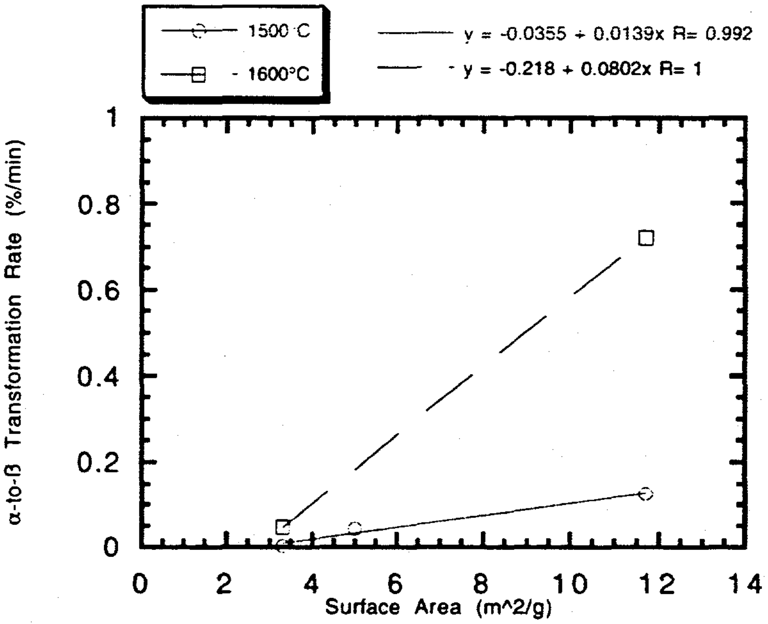

Fig. 8. α-to-ß Si_3N_4 transformation rate as a function of starting silicon nitride surface area for the various silicon nitride powders made by the diimide process (Ube E-10, E-05 and E-03) at 1500°C and 1600°C. The sintering additive was 6% Y_2O_3-2% Al_2O_3.

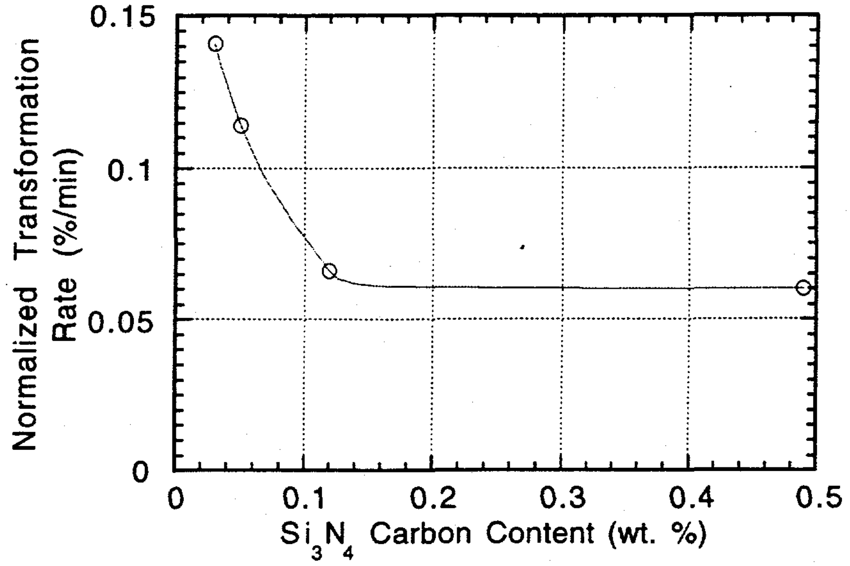

Fig. 9. Normalized α-to-ß Si_3N_4 transformation rate as a function of starting silicon nitride carbon content at 1500°C. The sintering additive was 6% Y_2O_3-2% Al_2O_3. The transformation rates were normalized to a powder surface area of 11 m^2/g and an initial ß-phase content of 2.5 %.

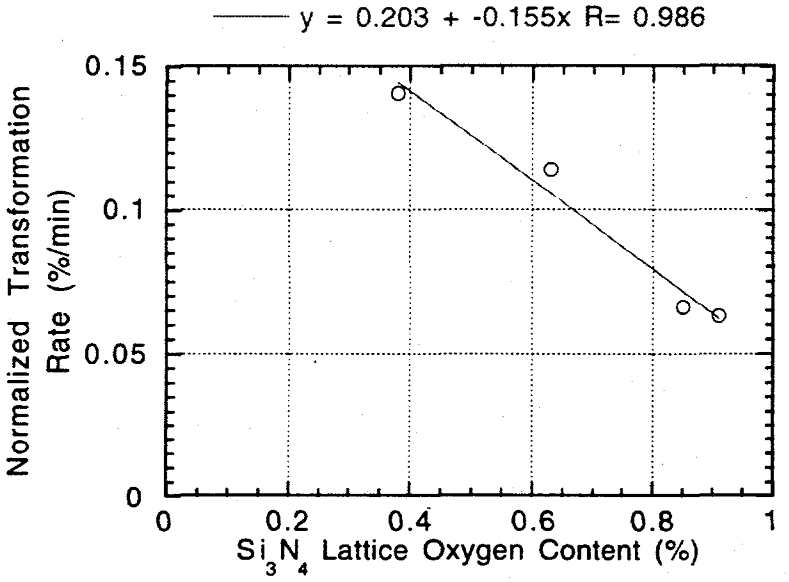

Fig. 10. Normalized α-to-ß Si_3N_4 transformation rate as a function of starting silicon nitride lattice oxygen content at 1500°C. The sintering additive was 6% Y_2O_3-2% Al_2O_3. The transformation rates were normalized to a powder surface area of 11 m^2/g and an initial ß-phase content of 2.5 %.

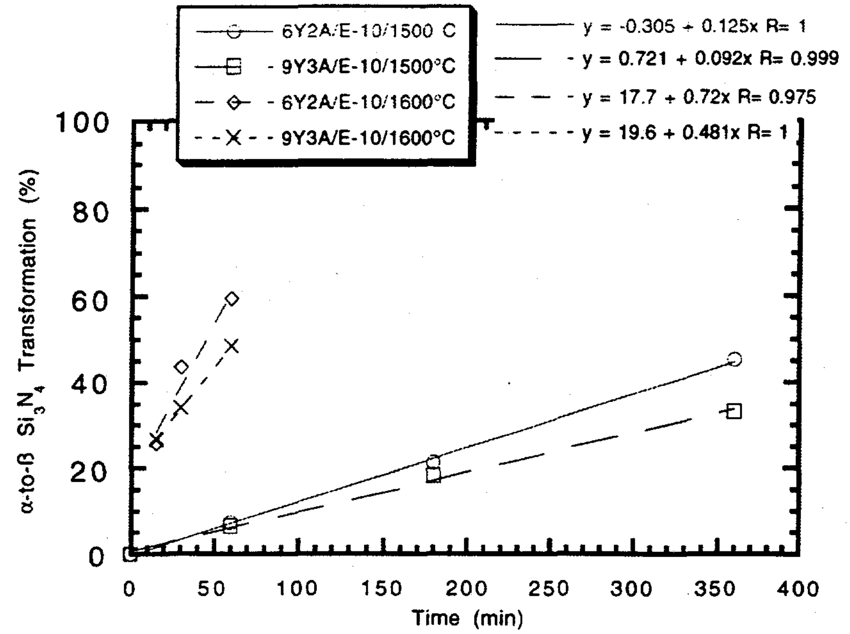

Fig. 11. α-to-ß Si_3N_4 transformation as a function of time for different amounts of sintering additive at 1500°C and 1600°C. The sintering additive was either 6% Y_2O_3-2% Al_2O_3 or 9% Y_2O_3-3% Al_2O_3. The silicon nitride powder was Ube E-10.

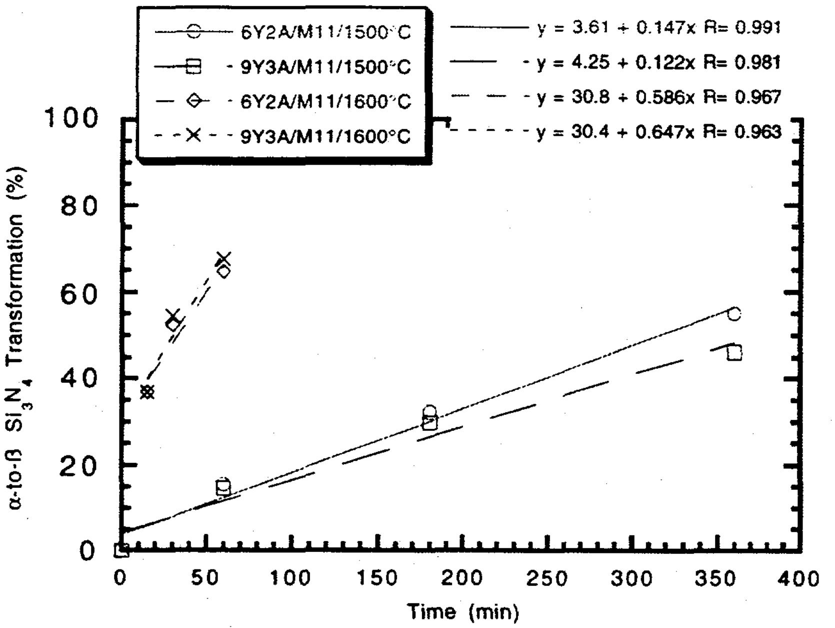

Fig. 12. α-to-ß Si_3N_4 transformation as a function of time for different amounts of sintering additive at 1500°C and 1600°C. The sintering additive was either 6% Y_2O_3-2% Al_2O_3 or 9% Y_2O_3-3% Al_2O_3. The silicon nitride powder was Starck M11.