

In situ Incorporation of Sintering Additives in Si_3N_4 Powder by a Combustion Process

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Abstract

A novel approach for *in-situ* incorporation of Al_2O_3 and Y_2O_3 additives into Si_3N_4 powder by a combustion technique is described. A suspension is made by mixing an alcoholic solution of Al/Y nitrates and citric acid with Si_3N_4 powder. The suspension forms a gray precipitate upon heating at 60°C. This precipitate undergoes a combustion reaction upon heating at 200°C and produces an amorphous phase of $\text{Al}_5\text{Y}_3\text{O}_{12}$ (YAG) on the Si_3N_4 powder. The amorphous YAG phase shows a homogeneous distribution on the Si_3N_4 powder. Pellets of the composite powder are fabricated by cold isostatic pressing and sintered at 1750°C for 2 h at 5 bar of nitrogen pressure. The microstructure of the sintered body prepared by this method reveals a high density, the fracture toughness (K_{1C}) is increased by 13.4%, compared to that of a sintered Si_3N_4 body formed with identical amounts of alumina and yttria additives prepared by planetary milling. © 1998 Elsevier Science Limited. All rights reserved

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1 Introduction

Increasing attention is being paid to the development of Si_3N_4 ceramics for structural applications due to its superior mechanical properties at high temperature. Pressureless sintering is a cost-effective method to fabricate complex-shaped Si_3N_4 ceramics into high density components.^{1,2} Sinterability of Si_3N_4 is limited by a low self-diffusion coefficient due to its strong covalent bonding. The

decomposition of Si_3N_4 around 1900°C under one atmospheric pressure of nitrogen creates an additional problem for sintering. Hence, addition of sintering additives are essential for densification. A combination of Al_2O_3 and Y_2O_3 powders as sintering additives markedly improves the sinterability and is used in many cases.^{1,3–6} Y_2O_3 and Al_2O_3 together with the SiO_2 layer on the surface of Si_3N_4 form a low viscosity liquid glass phase that apparently wets the solid completely and migrates rapidly throughout the microstructure.⁵

The degree of homogeneity of the sintering additives with the Si_3N_4 particles has a great influence on the sinterability and hence on the microstructure and mechanical properties of the sintered body. It is important that the additives are blended with the host particles as homogeneously as possible.

Conventionally, Al_2O_3 and Y_2O_3 powders are mixed with Si_3N_4 powder by either ball milling, planetary milling or attrition milling. These conventional techniques are time consuming and can make achieving homogeneity difficult. Non-conventionally, there are procedures of incorporating additives into Si_3N_4 powder using sol-gel coating techniques (alkoxide route),^{7–9} nitrate method,² etc. These improved techniques are reported to produce well homogenized powder, but involve an intermediate calcination step in the course of powder processing. The calcination is normally done at a temperature around 1000°C in order to decompose the anions of the additive salts. One way to avoid such a calcination step is to incorporate the sintering additives into Si_3N_4 powder *in situ* during processing.

Our recent studies^{10,11} demonstrated a low-temperature gel combustion technique for the synthesis of nano structured ceramic powders, using citrate and nitrate anions in the precursor. The process *in situ* generates ceramic powders as a

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combusted product from a precursor with a particular citrate–nitrate ratio. The purpose of this study is to incorporate Y_2O_3 - Al_2O_3 additives to Si_3N_4 powder by this technique and to fabricate a dense Si_3N_4 body by gas pressure sintering. The microstructure and mechanical properties of the sintered body are compared to conventionally prepared Si_3N_4 , with identical proportions of yttria and alumina additives.

2 Experimental

Sintering additives in the same amount of 8 wt% Y_2O_3 and 7 wt% Al_2O_3 were incorporated into the Si_3N_4 powder by conventional planetary milling and by a combustion route. The Si_3N_4 powder (M11, H.C. Starck, Germany) with a BET specific area of $12.7 \text{ m}^2 \text{ g}^{-1}$ and a mean particle size of $0.67 \mu\text{m}$ is used in both cases.

In the combustion process, a solution was made in isopropanol taking $Y(NO_3)_3 \cdot 6H_2O$ powder (99.9%, Aldrich, Germany), $Al(NO_3)_3 \cdot 9H_2O$ powder (98.5%, E. Merck, Germany) and hydrated citric acid ($C_6H_8O_7$, 99.5 %, E. Merck, Germany). A solution with a citrate–nitrate ratio $\gamma = 0.098$ was prepared (calculated according to the mole ratio of $C_6H_8O_7$ and NO_3^- in the solution). The reason for choosing the particular γ is that citrates and nitrates undergo a low-temperature combustion reaction and *in situ* generate their corresponding oxide powders at this ratio.^{10–12} Si_3N_4 powders were slowly added to the alcoholic solution of Al/Y-nitrate–citrates under constant stirring to form a suspension of about 10 vol%. The suspension was treated in an ultrasonic bath for 15 min and then placed on a hot plate at 60°C under constant stirring. The suspension became viscous after about 30 min at this temperature and yielded a paste. As soon as the paste formed, the temperature of the hot plate was raised to 200°C . The combustion reaction started and loose powders (powder A) were produced. The whole process took about 2 h, as schematically presented in Fig. 1. This powder was then ground in a mortar and sieved through a 150 mesh screen. The sieved powder was

cold isostatically pressed (200 MPa) into pellets of 1.4 cm diameter and 1.8 cm height using a CIP 500E cold isostatic press (Paul Weber, Germany).

A similar combustion experiment was also performed using water as solvent instead of isopropanol applying the same $\gamma = 0.098$. A gray paste consisting of Si_3N_4 powder and aqueous solution of $Y(NO_3)_3$, $Al(NO_3)_3$ and citric acid was resulted, which combusted similarly into loose powders at 200°C . Since the powders resulted from isopropanol were more homogeneous than that from water (will be discussed in the following section), the powder processed with isopropanol was used for further studies.

In the conventional processing, cubic Y_2O_3 (AKP 247, H.C. Starck, Germany) and α - Al_2O_3 (AKP 53, Sumitomo, Japan) powders with a mean particle size of 0.3 and $0.24 \mu\text{m}$, respectively, were used as sintering additives. Y_2O_3 , Al_2O_3 and Si_3N_4 powders were dispersed in isopropanol in a polyethylene container. The suspension was treated in a planetary ball mill (Fritsch, Germany) for 8 h using high density alumina balls. The milled suspension was first dried with a rotational evaporator and then taken into an oven (70°C) for further drying. The dried powder (powder B) was ground in a mortar, sieved through a 150 mesh screen and then cold isostatically pressed into pellets similar to that of powder A.

Isostatically pressed pellets (specimen A and B made from powder A and B, respectively) were sintered in a powder bed of Si_3N_4 and BN powders in a boron nitride crucible using a HTG 2400/5 furnace (Gero GmbH, Germany) under nitrogen atmosphere (at the pressure of 5 bar). The specimen A and B were sintered simultaneously at 1750°C for 2 h. The microstructure of the sintered bodies were examined by scanning electron microscope (DSM Gemini 982, Germany; and S200, Cambridge, UK), followed by polishing and plasma etching of the specimen. The plasma etching was performed with an O_2 : CF_4 ratio of 2:1 for 2 min in RF Plasma Barrel Etcher (RT 7150, UK). The density of the sintered specimen was measured following the Archimedes principle. Fracture toughness in *c*-axis (K_{IC}) and Vicker hardness (H_v) of the sintered body were measured by the indentation crack length method. The indentation load was 100 N with a loading time of 15 s. X-ray diffraction of the sintered bodies were taken by a diffractometer (D5000, Siemens, Germany).

3 Results and Discussion

In the combustion process as described above, the Al/Y oxides can be incorporated into the Si_3N_4 powder in either an aqueous or non-aqueous system.

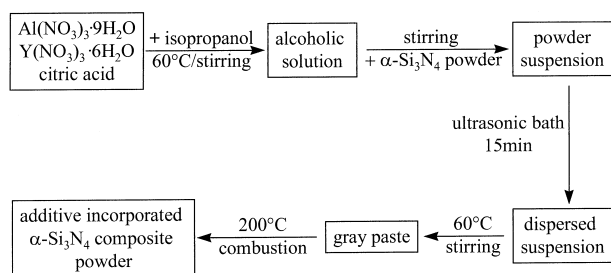
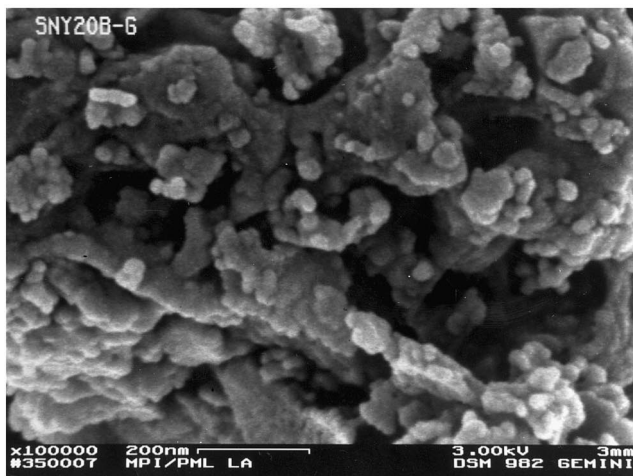
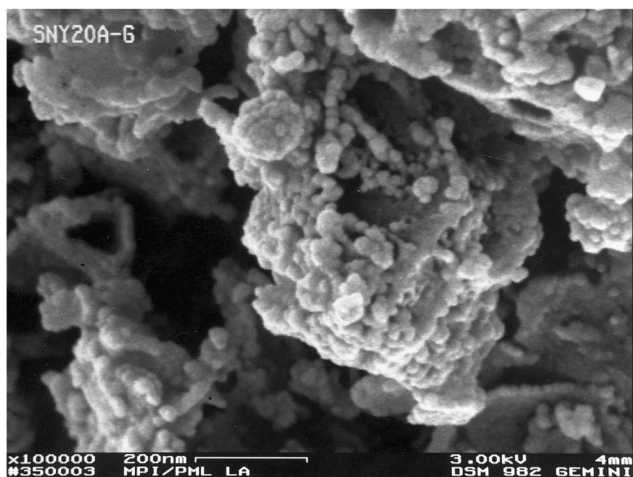


Fig. 1. Processing scheme for powder A.

Our experiments show that the alcohol system has advantages over the water system because the Al/Y oxides are more homogeneously distributed onto the surface of Si_3N_4 particles. Figure 2(a) presents the general morphology in the SEM for the composite powder A, made by the combustion method using isopropanol and Fig. 2(b) is that using water. The Al/Y oxide particles are about 10–30 nm in diameter. They are seriously agglomerated when water is used as solvent. Only the solvent is responsible for the difference. The reasons may be explained by the differences of the wetting ability and viscosity of aqueous and alcoholic gray paste. Although both solvents produce similar-sized additive particles which are seen in the Figures (bigger ones are Si_3N_4 particles), the powders made in isopropanol were more homogeneous compared to that of water. The possible hydrolysis reaction of Si_3N_4 powder in water may change the properties of the powders, e.g. increasing the amount of SiO_2 in the powder surface. Therefore, the powder processed with isopropanol was used for further studies.



(a)



(b)

Fig. 2. (a) SEM of the processed powder by combustion method using isopropanol, powder A. (b) SEM of processed powder by combustion method using water.

Citrates and nitrates in the composition undergo a redox reaction wherein citrate acts as reductant and nitrate as oxidant.^{10–12} It has been observed¹⁰ that yttria particles can *in situ* be generated from a precursor with $\gamma=0.098$. Once the exothermic reaction starts, aluminium nitrate and yttrium nitrate decompose to form amorphous particles of $\text{Al}_5\text{Y}_3\text{O}_{12}$.¹² It has also been observed¹² that this amorphous phase starts to crystallize at 800°C and completely transforms to the crystalline phase of $\text{Al}_5\text{Y}_3\text{O}_{12}$ (YAG) below 900°C. The transformation is followed via an intermediate phase [a mixture of YAG and $\text{Al}_2\text{Y}_4\text{O}_9$ (YAM)] phase in between 850 and 870°C.¹² The XRD pattern of the powder A (Fig. 3) shows only those peaks of $\alpha\text{-Si}_3\text{N}_4$. Hence, the amorphous $\text{Al}_5\text{Y}_3\text{O}_{12}$ particles formed upon combustion are homogeneously distributed on the surface of Si_3N_4 powder. Si_3N_4 powder does not seem to participate in the redox reaction. However, Si_3N_4 can act as dilutant reducing the heat effect and may dissipate the heat of the redox reaction.

The sinterability of Si_3N_4 is limited by a low self-diffusion coefficient. This is due to the high covalent bonding of Si_3N_4 . However, Si_3N_4 decomposes at 1900°C under atmospheric pressure of nitrogen. Therefore, the full densification of the nitride requires the addition of sintering aids and applying gas pressure. Thus, the proper amount of sintering additives were used and the samples were sintered at low nitrogen gas pressure in this study.

Table 1 presents mechanical properties of the sintered specimen fabricated from powder A and B, respectively. The sintered density of specimen A is slightly higher than that of B. This indicates a better sinterability of the combustion prepared powder than the powder conventionally prepared during sintering. The fracture toughness of specimen A is significantly higher (by 13.4%) than that of B. The properties of the sintered body are well

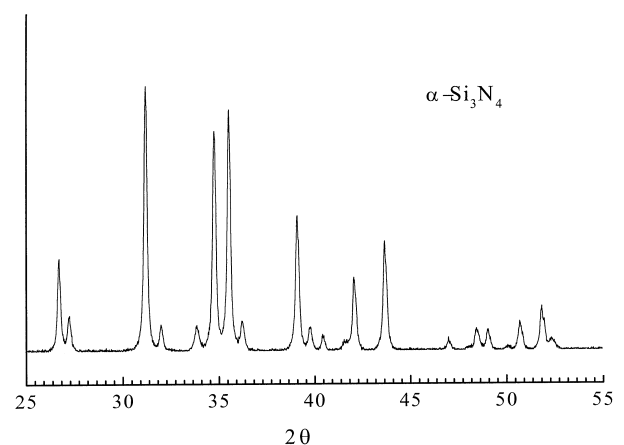
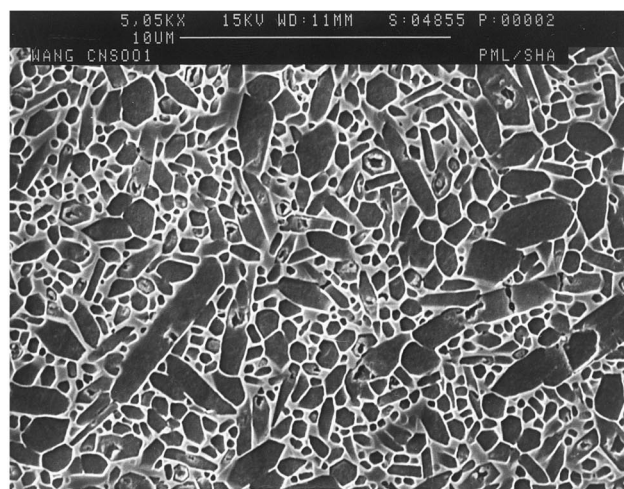


Fig. 3. X-ray diffraction pattern of the powder processed by the combustion process, powder A.

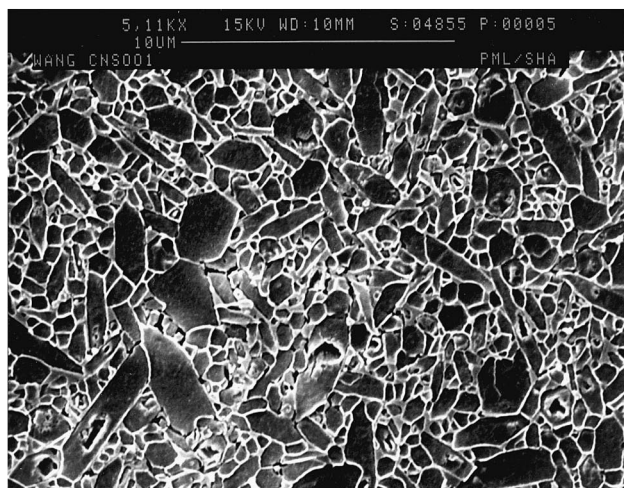
Table 1. Mechanical properties of the sintered bodies

Sintered body	Density ($g\ cm^{-3}$)	Fracture toughness K_{IC} (RT) ($MNm^{-3/2}$)	Hardness (H_v) (MNm^{-2})
Specimen A	3.28	7.2 ± 0.1 (average)	1440 (average)
Specimen B	3.26	6.3 ± 0.1 (average)	1400 (average)

correlated with the microstructure. Figure 4(a) presents the microstructural features of the sintered specimen A and B, respectively. Figure 4(a) shows a continuous glass phase with less sintering defects. The β - Si_3N_4 phase is rod-like (~ 2 – $5\ \mu m$) with an average aspect ratio between 5 and 10. The β - Si_3N_4 grains of specimen A are more homogeneous with elongated grains and a higher fraction of small grains compared to those produced with powder B. There are many cracks around the β - Si_3N_4 grains in specimen B, which may correspond to more crystalline grain boundary phase formed during cooling (see Fig. 5) because of the volume change



(a)



(b)

Fig. 4. (a) SEM of the combustion processed specimen A, after sintering. (b) SEM of the conventionally processed specimen B, after sintering.

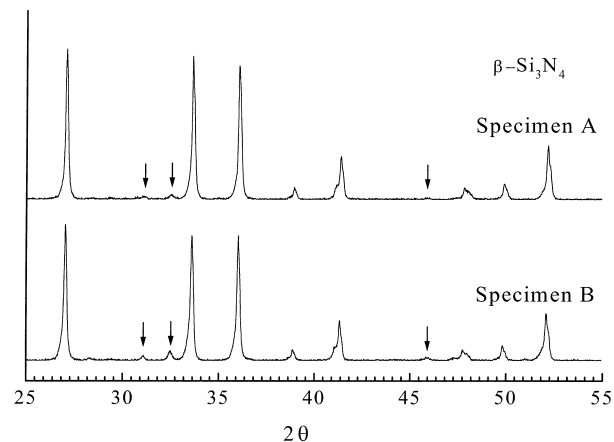


Fig. 5. X-ray diffraction of the sintered specimens from powder A and B (arrows indicate $Y_2Si_2O_7$).

between the liquid glass phase and the solid crystalline phase.

The densification of Si_3N_4 is described as a liquid phase sintering process. At higher temperatures, SiO_2 , which is always present at the surface of the Si_3N_4 particles, reacts with the oxide additives to form an oxide melt, and with increasing temperature, an oxynitride melt by dissolving Si_3N_4 . While the α - Si_3N_4 particles dissolve and supersaturate the liquid phase, β - Si_3N_4 is reprecipitated.¹³ The amount, distribution, chemical composition and phase content of the grain boundary phase formed by the oxynitride liquid phase determines the mechanical properties of the sintered body.

It is obvious that a more homogeneous distribution of sintering additives will accelerate the densification process. As mentioned previously, the crystalline phase of $Al_5Y_3O_{12}$ (YAG) is formed below $900^\circ C$ in the same combustion process without Si_3N_4 powder. But by using mixtures of Y_2O_3 and Al_2O_3 powders, the YAG phase can only be formed at temperatures above $1600^\circ C$.¹⁴ This means that although the same amount of sintering additives are taken, the behavior of Al/Y oxides in powder A and powder B is different. The nanometer size sintering additives allow the melt of Al/Y oxides at lower temperatures and the formation of the oxynitride liquid phase earlier. The advantage of earlier formation of liquid phase is obvious. This will accelerate the nucleation of β - Si_3N_4 phase and further the densification process. From Fig. 4 it is seen that the β - Si_3N_4 was well developed and the elongated β -grains were linked smoothly by the glass phase. The liquid phase during cooling is arranged at the grain boundaries in thin layers and at the grain boundary triple junctions. The elongated grain structure of the β -phase has a strong influence on the mechanical properties. The higher aspect ratio of the β -grains in specimen A against B results in higher fracture toughness, because the linked, elongated β -crystals

provide better resistance to crack growth due to the absorption of energy.¹⁵ Lange *et al.*¹⁶ also indicated that elongated grains increase the fracture toughness of materials.

The X-ray phase analysis after sintering (Fig. 5) showed that the transformation of $\alpha\text{-Si}_3\text{N}_4$ into $\beta\text{-Si}_3\text{N}_4$ is complete in both powders. The results indicate also that a second crystalline phase (as indicated by arrows) was present beside the $\beta\text{-Si}_3\text{N}_4$ phase. The identified secondary phases are mainly different modifications of $\text{Y}_2\text{Si}_2\text{O}_7$. This crystalline phase is much more obvious in the sample using powder B than that of powder A. This phase is formed during initial heating and remains stable until the end of sintering.¹⁷ The crystallization of $\text{Y}_2\text{Si}_2\text{O}_7$ reduces the amount of liquid phase and changes its chemical composition. The SEM photographs of the sintered body (see Fig. 4) illustrate this point. Usually the $\alpha\text{-}\beta$ phase transformation has already finished at a temperature of about 1700°C. From this temperature on the $\beta\text{-grains}$ are growing. If there is not enough or only a small amount of sinter activity left due to the reduced amount of liquid phase, the grain growth of Si_3N_4 becomes the dominating mechanism. As a consequence, the elongated $\beta\text{-grains}$ hinder each other and may cause the formation of cracks.

4 Conclusions

The present study shows that a combination of Y_2O_3 and Al_2O_3 sintering additives can *in situ* be incorporated with Si_3N_4 powder by a low-temperature combustion technique. The technique is rapid and avoids the intermediate calcination step, normally needed by conventional sol-gel techniques. Different levels of additives can be incorporated with Si_3N_4 and hence offer a method for modifying the microstructure of the sintered material.

The microstructure of the sintered body with this new combustion method is more dense and the fracture toughness (K_{IC}) is increased by 13.4%, compared to that of the conventional method in this work. The more homogeneously distributed and nanometer fine sintering additives introduced by the combustion process in Si_3N_4 powder accelerate the liquid sintering process and hence lead to improved development of microstructure without cracks.

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