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Effect of processing variables on synthesis of β-Si_3N_4 particles

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Abstract

Synthesis of highly anisotropic rod-like β-Si_3N_4 particles with different morphological characteristics was accomplished using commercial α-Si_3N_4. A number of powder mixtures were prepared with additions of various oxides ($Al_2O_3 + RE_2O_3$, being RE = Y, La or Yb) that were subsequently heat treated in a loose powder state in the temperature range of 1750–1950 °C and dwell times from 10 to 180 min under high pressure of N_2 (60 MPa) in a hot isostatic press. The obtained aggregated porous bodies were lightly crushed by hand using an alumina mortar and pestle and subsequently subjected to sequential chemical treatments to eliminate the glassy phases and possible residual crystalline compounds, and to separate the synthesized β-Si_3N_4 particles. Resulting β-Si_3N_4 particles were characterized by X-ray diffraction and examined by scanning and transmission electron microscopy. Morphological characteristics of the synthesized β-Si_3N_4 particles were determined through quantitative dimensional analysis. The effect of amount and chemical composition of oxide additives responsible for liquid phase formation as well as heat treatment parameters on β-Si_3N_4 particles size and morphology are established. Possible mechanisms of β-Si_3N_4 particles growth are discussed.

Keywords: Si_3N_4; Synthesis; Seeds; HIP

1. Introduction

In the last two decades considerable effort has been made to improve mechanical properties of silicon nitride-based ceramics, especially its fracture toughness. It has been established that improved fracture toughness is strongly related with the presence of highly anisotropic rod-like grains of β-Si_3N_4 in the microstructure of silicon nitride-based ceramics.[1–3] These elongated β-Si_3N_4 grains are formed *in situ*, during liquid phase sintering and additional heat treatments, due to anisotropic grain growth and act as reinforcing structural elements similar to whiskers in ceramic matrix composites, promoting thereby toughening mechanisms. Currently it has been established that the presence of such grains in the material is a necessary but not a sufficient condition for toughening or reinforcing the material. Several characteristics of these grains, such as size, aspect ratio and bonding energy of the grain/amorphous intergranular phase interface are determining factors for toughening of silicon nitride ceramics.[4–6] Strict microstructure tailoring enables production of silicon nitride-based materials with fracture toughness values of about 10 MPa $m^{1/2}$. This considerably broadens the application area for these materials.

Among the different methods of microstructure tailoring that have been developed for silicon nitride-based ceramics, the addition of β-Si_3N_4 particles with controlled morphological characteristics (“seeding”) to the initial α-Si_3N_4-based powder mixtures is considered to be the simplest and most effective approach.[7–16] During sintering, α-Si_3N_4 particles dissolve in the oxynitride liquid phase that forms from the sintering additives at the sintering temperature. Upon saturation of the liquid phase, β-Si_3N_4 precipitates on pre-existing β-Si_3N_4 particles, resulting in its growth. Therefore, controlled additions of β-Si_3N_4 particles increase the number of precipitation nuclei, and this strongly influences grain growth and overall microstructure formation.[17]

In this context, production of β-Si_3N_4 particles with tailored morphology takes on special significance. Various methods of synthesis of such β-Si_3N_4 particles have been described in the literature.[18–25] An interesting, simple and effective approach was initially proposed by Hirao et al.[18] and subsequently

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improved.[19,20] This paper presents the results of a thorough investigation of β-Si_3N_4 particle synthesis using different compositions and amounts of sintering aids and heat treatments. The results obtained are important to develop a processing method for β-Si_3N_4 particles with desired characteristics.

2. Experimental

In this investigation, the processing route to synthesis β-Si_3N_4 particles is based on the method developed by Hirao et al.[18] Both, the initial composition of the starting powder mixtures, and the heat treatment parameters were chosen as the processing variables to synthesis β-Si_3N_4 particles. Commercially available α-Si_3N_4 powder (M11, H.C. Starck, Germany), Al_2O_3 powder (Baikalox CR-10, Baikowski Chimie, France), Y_2O_3, La_2O_3 and Yb_2O_3 powders (with >99.9% purity, Aldrich Chemical Co., USA) were used in this investigation. The composition of powder mixture samples Y7, Y3, L7 and Yb7 (numbers 7 and 3 indicate the mol% of the additives) are shown in Table 1.

The powders were mixed in an attritor mill for 4 h, at 400 rpm with isopropyl alcohol as the milling media. The balls and jar of the mill were made of silicon nitride. The slurries obtained after milling were passed through an ASTM 325 sieve to separate the milling media and subsequently dried in a rotary vacuum evaporator. The dried powders were placed into BN crucibles in a loose powder state. The heat treatments were carried out in a hot isostatic press (QIH-3, ABB Autoclave Systems, Inc.) under 100 MPa of nitrogen at the following temperatures/dwell times: 1750 °C/60 min; 1850 °C/10 min; 1850 °C/60 min; 1850 °C/180 min; 1950 °C/60 min.

Identification codes of the synthesized powders were similar to those used for the starting mixtures and are shown in Table 1. The digits following the mixture identification correspond to the heat treatment temperature and dwell time, respectively. The first two digits, of the three digits, namely, 17, 18, and 19 correspond to the temperatures 1750, 1850 and 1950 °C, respectively, while the last digit, 1, 2, or 3 stands for 10, 60, or 180 min of dwell time. For example: the code L7-192 identifies β-Si_3N_4 particles synthesized from L7 sample mixture and heat treated at 1950 °C for 60 min.

After heat treatment, the resulting aggregated porous bodies were lightly crushed using an alumina mortar and pestle, and subjected to chemical treatment in order to dissolve the vitreous phase and to remove possible crystalline RE-containing phases formed from the oxide additives, to obtain loose, non-agglomerated β-Si_3N_4 particles. It should be specially noted that such chemical treatment could not cause any dissolution even of the fine Si_3N_4 particles. The main steps of the chemical treatment included:

- treatment in a concentrated 50% HF/50% HNO_3 solution at 60 °C for 24 h (dissolution of residual vitreous phase);
- treatment in concentrated H_2SO_4 at 80 °C for 24 h (dissolution of crystalline phases possibly formed from oxide additives);
- treatment in dilute NH_4OH at 60 °C for 24 h (removal of the surface SiO_2 layer from the Si_3N_4 particles).

Between the different steps of chemical treatment, the material was rinsed thoroughly with de-ionized water.

The resulting powders were analyzed using X-ray diffraction (XRD) and examined by scanning electron microscopy. Scanning electron micrographs were used for quantitative analysis to determine particle size and morphological characteristics of the β-Si_3N_4 particles.

3. Results and discussion

The heat treatments given to the mixtures resulted in complete α → β phase transformation, and this was confirmed by XRD analysis. Even after short dwell times at relatively low temperatures (1750 °C/60 min and 1850 °C/10 min) no peaks corresponding to α-Si_3N_4 were detected in the XRD spectra. This result indicates that even if α-Si_3N_4 was present in the composition after the heat treatment, its content was below the detection limit of the XRD technique. In Fig. 1 the XRD spectrum of the material treated at 1750 °C/60 min reveal only the β-Si_3N_4 reflections.

After heat treatment, the β-Si_3N_4 particles appear to be coalesced together with the vitreous phase forming aggregates in the shape of "colonies". A scanning electron micrograph of the starting Si_3N_4 powder (>96% of α phase, $D_{50} = 0.66$ μm) is shown in Fig. 2, and the aggregates of β-Si_3N_4 particles obtained after different heat treatment procedures from the various compositions are shown in Fig. 3.

Visual inspection clearly reveals the morphological differences in β-Si_3N_4 particles due to differences in processing parameters, i.e., composition and amount of additives as well as heat treatment temperatures and dwell time. After chemical treatment that resulted in removal of the vitreous phase and of the possible crystalline secondary phases from the aggregates, the β-Si_3N_4 particles were dispersed to permit SEM examination and quantitative evaluation of particle morphology and dimensions. Fig. 4 shows an example of the dispersed particles. Some

Table 1
Starting composition of the mixtures

Sample denomination	Si_3N_4 (wt.%)*	Al_2O_3 (wt.%)	Y_2O_3 (wt.%)	La_2O_3 (wt.%)	Yb_2O_3 (wt.%)
Y7	92.34	4.56	6.05		
Y3	95.16	2.08	2.76		
L7	87.05	4.44		8.51	
Yb7	85.51	4.36			10.13

* Corrected for the amount of 1.668 wt.% O_2 present in the form of SiO_2 surface oxide films on Si_3N_4 particles.

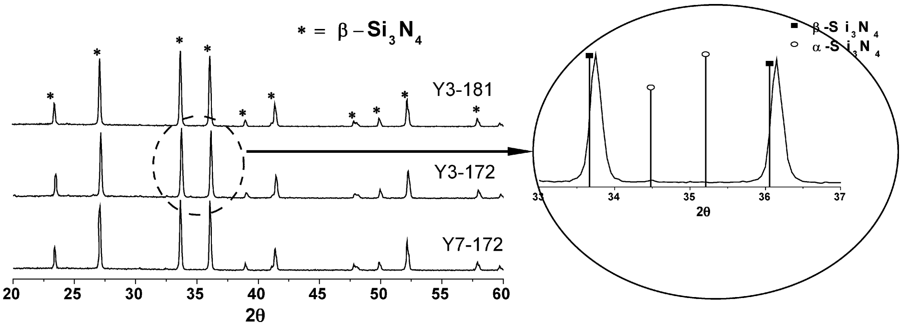

Fig. 1. XRD spectra showing β-Si_3N_4 as the only identified phase.

particles were studied using transmission electron microscopy (TEM). The transmission electron micrographs shown in Fig. 5 reveal the fine structure of the synthesized β-Si_3N_4 particles. It can be seen that their growth occurred epitaxially on the pre-existing β-Si_3N_4 particles that were present in the starting Si_3N_4 powder.

Pre-existing β-Si_3N_4 particles can be clearly seen in Fig. 5c. Some particles revealed a typical defect structure, with a network of stacking faults (see Fig. 5d) that were probably caused by orientation mismatch during grain growth.

Quantitative morphological analysis of the β-Si_3N_4 particles was carried out with software for quantitative image analyses, UTHSCSA Image Tool v.3. At least 600 particles were analyzed from each batch that was synthesized, to ensure reliability of experimental data.

Considering specific morphological features of synthesized β-Si_3N_4 particles that are characteristically rod-like with a hexagonal cross-section, their length (*L*) and diameter (*D*) were measured. From these values, the so-called aspect ratio (*L*/*D*), the parameter by which particles with such morphology are characterized, was derived. The data obtained are shown in Fig. 6. The figure shows the influence of synthesis temperature at a fixed dwell time (60 min) and of synthesis duration at a fixed temperature (1850 °C) on the dimensions and aspect ratio of the β-Si_3N_4 particles.

In the absence of published data on kinetics of β-Si_3N_4 particle growth under conditions used in this investigation, an attempt to determine the rate-controlling mechanism of the process has been made using traditional relations describing grain growth during liquid phase sintering of silicon nitride-based ceramics (Eq. (1)). The LSW theory (with reference to the Lifshitz and Slyozov[26] and Wagner[27] theory) indicates that the coarsening-rate-law exponent of $n = 2$ implies interface-reaction control, whereas $n = 3$ implies diffusion control. The grain growth in this case is described by the following relation:

$$G^n - G_0^n = Kt \qquad (1)$$

where G and G_0 are the grain size after sintering time t, and of the initial powder, respectively; K is a constant, $K = \exp(-Q/kT)$ where Q is the activation energy for grain growth, T is the absolute temperature and k is Boltzmann's constant. For Si_3N_4 that exhibits strong anisotropy during grain growth, the increase in diameter and length of β-Si_3N_4 particles is calculated separately.

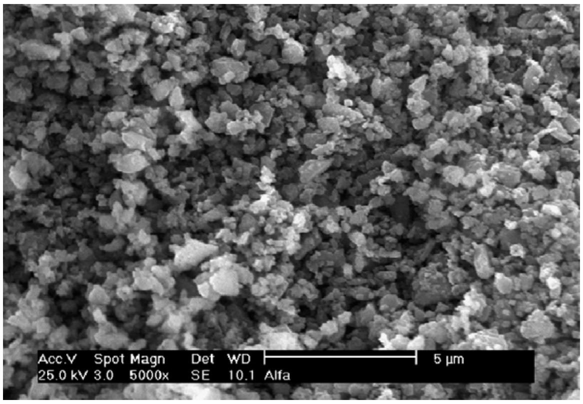

Fig. 2. Scanning electron micrograph of the starting α-Si_3N_4 powder.

In our case, calculations of particle growth using Eq. (1), for synthesis temperature of 1850 °C, gave n values for diameter and length of the β-Si_3N_4 particles equal 9 and 15, respectively. These abnormally high values are contrary to predictions of LSW theory and indicate extremely sluggish particle growth kinetics. One of the plausible explanations for such sluggish particle growth kinetics is that the process is occurring in a very porous system (loose powder mixture) that hinders continuous material transport to the solid–liquid interface (if "grain growth" is considered in terms of Ostwald ripening model, which is the most plausible approach) or prevents the mobility of "grain boundaries" (if "grain growth" occurs via coalescence, which is less plausible). Thus, the LSW theory that is commonly used for description and analysis of grain growth of β-Si_3N_4 under conditions of liquid phase sintering is apparently not adequate in our case, because it is unclear which mechanisms control grain growth under these exact conditions.

Recent studies on grain growth in dense Si_3N_4 bodies also suggest that the LSW theory is inadequate, due mainly to slow kinetics of β-Si_3N_4 grain growth.[28] An alternative approach to β-Si_3N_4 grain growth, based on the effect of the quantity of liquid phase in the sintering system was also introduced.[28] This approach suggested that if grain growth is controlled by lattice diffusion, increase in liquid phase content in the system during sintering resulted in slower grain growth rates. On the other hand, if the process is controlled by reactions at the liquid/solid interface, the grain growth rate is independent of the amount of liquid phase in the system. Analysis of β-Si_3N_4 particle growth rate in this investigation was carried out on the basis

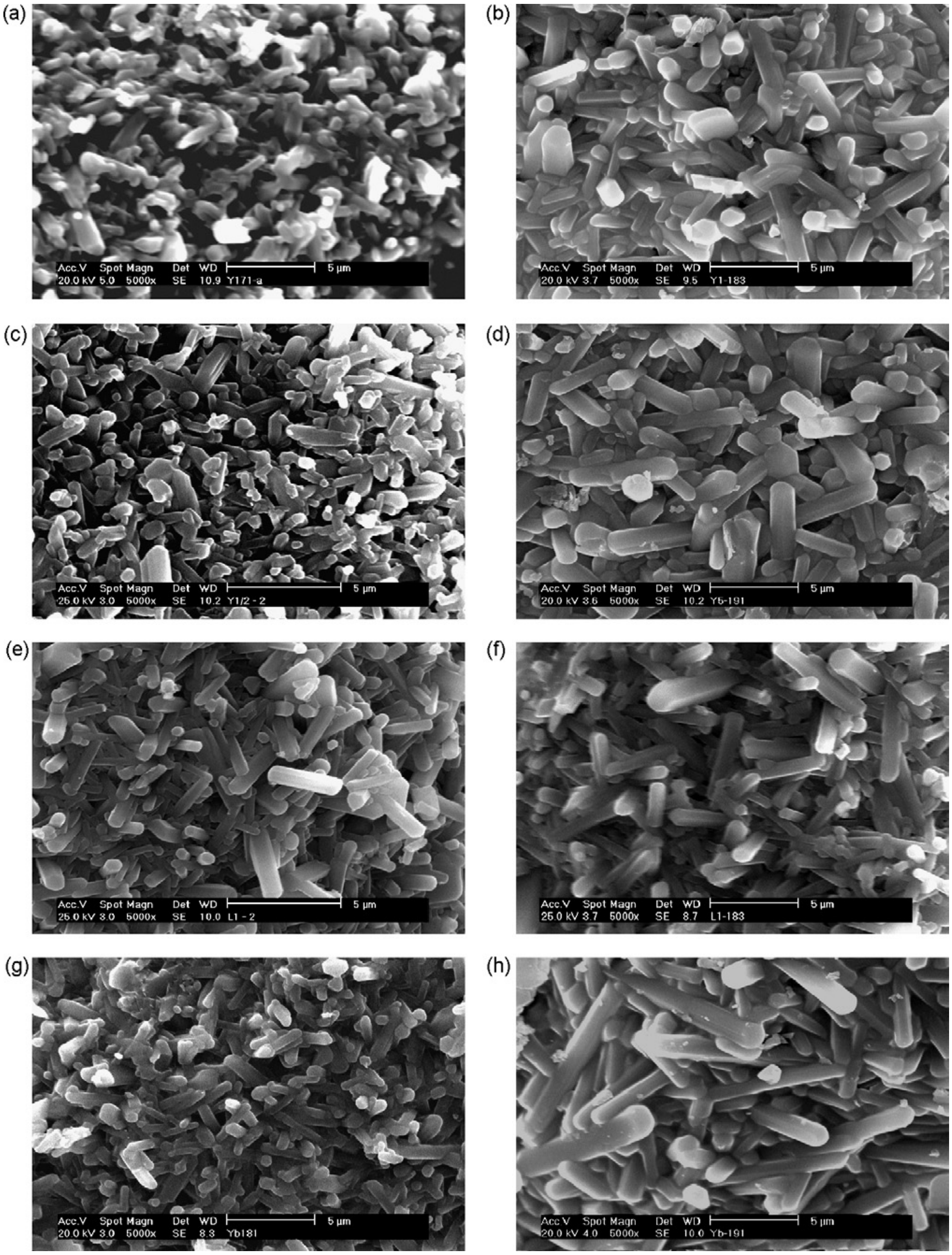

Fig. 3. Aggregates of β-Si_3N_4 particles synthesized with different compositions and with different heat treatments: (a) Y7-172; (b) Y7-183; (c) Y3-181; (d) Y3-192; (e) L7-182; (f) L7-183; (g) Yb7-181; (h) Yb7-192. All pictures with same magnification.

of this alternative approach for two compositions with different amounts of liquid phase forming additives, i.e. Y_2O_3 and Al_2O_3 in the formulation. From the data presented in Fig. 6 for Y3 and Y7, it can be deduced that β-Si_3N_4 particle growth rate (both diameter and length) decreased with increase in liquid phase content. Therefore, on the basis of the model proposed in,[28] particle growth kinetics in this investigation is controlled by lattice diffusion. Several investigations on modeling and simulation of Si_3N_4 grain growth[29–31] support this conclusion, especially if the predicted values of the exponent n is higher than 3. However, it is important to emphasize that the existing data on β-Si_3N_4 grain growth is controversial. Thus Kramer et al.,[32] contrary to the above results and after thorough analysis of the activation energies of nucleation and growth of β-Si_3N_4 crystals reached a conclusion that anisotropic grain growth of β-Si_3N_4 grain length, direction (0 0 1), is controlled by diffusion, while the growth of the grain diameter, direction (2 1 0), is controlled by interface reactions.

The data on dependence of aspect ratio on temperature and time of heat treatment (Fig. 6c) indicate that for the different sample compositions, the growth rate of the β-Si_3N_4 particle diameter is higher than that of the length, resulting in reduction of the aspect ratio with increase in temperature and duration of heat treatment. Similar tendencies were reported in

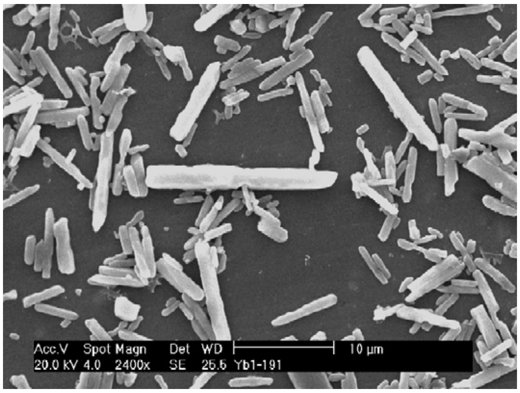

Fig. 4. β-Si_3N_4 particles dispersed after chemical treatment. Sample Yb7-192.

other investigations,[19] and theoretically predicted by modeling studies.[29]

In grain growth studies, it is also possible to consider, from yet another perspective, the data on quantitative analysis of β-Si_3N_4 particle growth. A marked influence of ionic radius of the lanthanide (Ln) used as a sintering aid on β-Si_3N_4 grain growth in the presence of Ln–Si–Al–O–N liquid phase during α → β phase transformation was reported.[33] It is also known that the ionic radius of the liquid-forming Ln strongly influences the viscosity of the liquid phase.[34] That is, Ln with smaller ionic radii increases the viscosity of the liquid phase. Liquid phase viscosity can be related to the diffusion coefficient by the Stokes–Einstein equation[20]:

$$\eta = \frac{\kappa T}{6\pi r D} \tag{2}$$

where η is the liquid viscosity, r the diffusion distance of the species, and D is the diffusion constant.

According to this equation, the diffusion coefficient of the species in the liquid phase is directly proportional to the ionic radius of the RE element in the sintering additive. Moreover, if the diffusion coefficient/diffusion distance ($D/\Delta X$) ratio is much smaller than the interface reaction constant (K), i.e., $D/\Delta X \ll K$, grain growth is controlled by diffusion. On the other hand, if $D/\Delta X \gg K$, grain growth is controlled by the interface reaction. If the values of ($D/\Delta X$) and K are close, both processes influence the grain growth. Thus it can be concluded that by varying the Ln in the sintering additive formulation, it is possible to change the viscosity of the liquid phase and, thereby, the diffusion coefficient as well. This in turn can alter the controlling mechanism of grain growth. On the basis of the above considerations and applying them to the results of this investigation in which the RE element varied in the system Ln–Si–Al–O–N (Ln = Y, La and Yb), it is possible to conclude that in mixtures containing Ln with a larger ionic radius (La), the viscosity of the liquid phase during heat treatment was lower and, consequently, the diffusion coefficient was higher. Higher diffusion coefficients

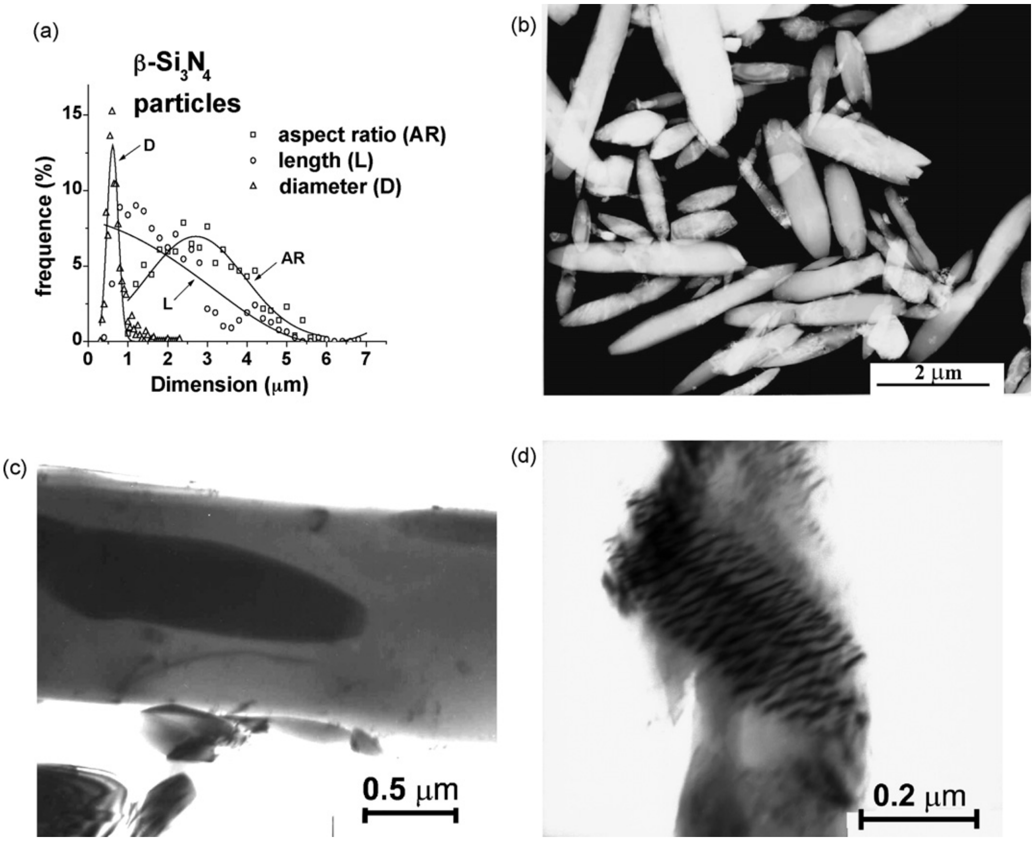

Fig. 5. Transmission electron micrograph of synthesized β-Si_3N_4 particles: (a) dimensional characteristics of the particles; (b) dispersed particles; (c) epitaxial grain growth on the pre-existing β–Si_3N_4 nuclei in the starting Si_3N_4 powder; (d) defect structure with a network of stacking faults.

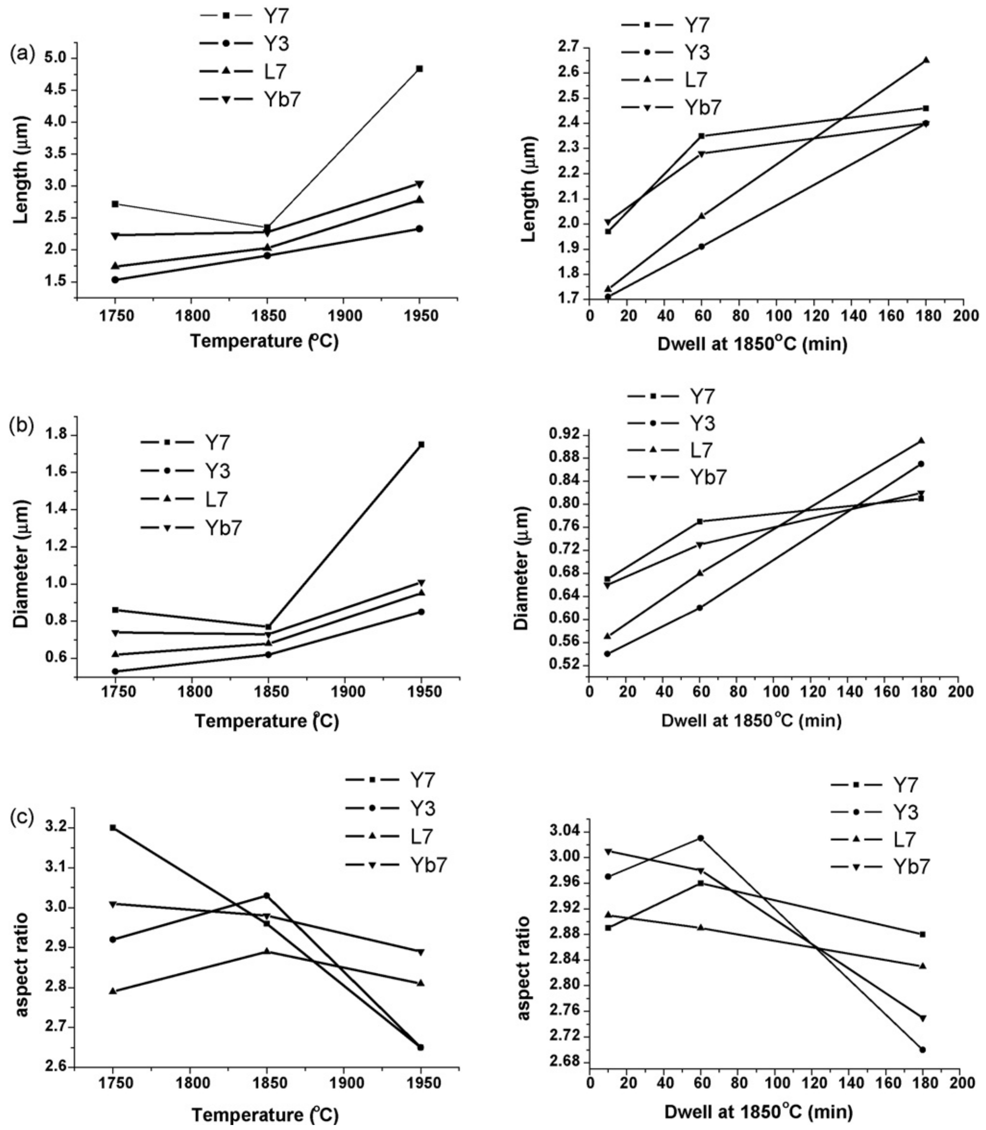

Fig. 6. Effect of temperature (60 min dwell time) and dwell time (at 1850 °C) on morphological features of β–Si_3N_4 particles: (a) particle length; (b) particle diameter; (c) aspect ratio.

are supposed to increase particle growth rate in the direction where diffusion controls the rate.

According to Kramer at al.,[32] this should result in growth rate increase of β-Si_3N_4 grain length only, where as according to our prior analysis of the influence of liquid phase content on grain growth (compositions Y7 and Y3), variation of the LN element in the system should influence β-Si_3N_4 grain growth both in length and diameter. According to the data presented in Fig. 6 for the La containing mixture, a higher grain growth rate was observed both in terms of grain length and grain diameter. This indicates that the conclusions reached in the course of our analysis of the influence of the liquid phase content, and of the type of Ln element introduced into the system Ln–Si–Al–O–N, on grain growth, are in good agreement. Therefore, it is possible to summarize that the β-Si_3N_4 grain growth kinetics, both in the length and the diameter directions are rate controlled by diffusion of the species in the liquid phase.

4. Conclusion

The method used to synthesize β-Si_3N_4 particles in this investigation was both efficient and simple. Moreover, this method allowed β-Si_3N_4 particles to be obtained with desired morphological characteristics by varying processing parameters, in particular the formulation of the sintering aid and the heat treatment (temperature and dwell). Further, this method can be used for fundamental studies of the mechanism of grain growth under conditions of liquid phase sintering where the real dimensions of the synthesized particles can be measured with precision.

The growth behavior of β-Si_3N_4 particles from the different mixtures was similar, both in the length direction as well as in the direction of the diameter, with the increase in heat treating temperature or with dwell time. The growth rate in the direction of the diameter was slightly higher, provoking a reduction in aspect ratio with heat treatment.

Finally, it can be concluded that the β-Si_3N_4 particle growth under the synthesis conditions used in this investigation is rate controlled, both in length and in diameter, by diffusion of species through the liquid phase.

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