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Ca-α SiAlON hollow spheres prepared by carbothermal reduction–nitridation from different SiO_2 powders

Mikinori Hotta [a,*], Junichi Tatami [a], Cheng Zhang [a,1], Katsutoshi Komeya [a], Takeshi Meguro [a], Mark R. Terner [b], Yi-Bing Cheng [b]

[a] Graduate School of Environment and Information Science, Yokohama National University, 79-7, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
[b] Department of Materials Engineering, Monash University, Clayton, Melbourne, Victoria 3800, Australia

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Abstract

The formation process of hollow spheres composed of nanosized Ca-α SiAlON particles was investigated using SiO_2 starting powders with different characteristics in particle size, shape and crystalline state. TEM observations showed Ca-α SiAlON hollow spheres composed of a large number of nanosized particles in the products prepared at 1450 °C for 120 min in nitrogen. In all systems, the Ca-α SiAlON hollow spheres were always produced through an intermediate Si–Al–Ca–O liquid phase in the same mechanism, regardless of the characteristics of SiO_2 starting powders used. Spherical solid particles consisted of amorphous phase containing Si, Al, Ca, O and a small amount of N were generated at the initial stage of carbothermal reduction–nitridation. These spherical solid particles changed into hollow particles with the progression of the reaction from the liquid phase to the crystalline Ca-α SiAlON with increasing temperature.

Keywords: D. Sialon; Powders; Microstructure

1. Introduction

SiAlON, α- and β-SiAlON, have been well known as representative groups in engineering ceramics because of their high hardness, excellent wear and corrosion resistance in severe environment [1–4]. α-SiAlON is a solid solution of the α-Si_3N_4 crystal structure in which metal cations are incorporated as a stabilizer. The general formula for α-SiAlON is $M_{m/\nu}Si_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$, where ν is the valency of the stabilizing cation M. M may be Li, Mg, Ca, Y or most rare-earth elements. Among α-SiAlON, Ca-α SiAlON ceramics have a number of advantages. Calcium compounds such as CaO and $CaCO_3$ are cheaper than rare-earth elements. Calcium also has a higher solubility per unit cell in the α-SiAlON lattice, hence the quantity of residual glass in the grain boundary of Ca-α SiAlON ceramics can be less and the formation range of α-SiAlON single phase would be wider compared to α-SiAlONs containing rare-earth elements [2,5]. Furthermore, thermal stability in Ca-α SiAlON is superior to rare-earth stabilized α-SiAlON [3]. The toughness of α-SiAlON ceramics can be improved due to the development of Ca-α SiAlON ceramics with elongated grains [1].

α-SiAlON ceramics have been generally produced from powder mixture of Si_3N_4–AlN–M_xO_y at high temperatures through a liquid phase sintering process [1–4,6,7]. In order to improve the reliability of α-SiAlON ceramics, it is important to develop homogeneous and fine α-SiAlON powders. α-SiAlON powders have been prepared by carbothermal reduction–nitridation (CRN) from SiO_2–Al_2O_3–(Ca- or Y-) oxides [8,9], clay–metal compounds [10], talc–halloysite clay minerals [11,12] and slag–clay mixtures [13,14] mixing with carbon in flowing N_2 gas.

In our previous study, Ca-α SiAlON powders were synthesized by CRN of mixtures of SiO_2, Al_2O_3 and $CaCO_3$ fine powders [15,16]. The resultant Ca-α SiAlON powders had a spherical hollow morphology composed of large numbers of nanosized particles. Solid spherical particles consisting of Si–

* Corresponding author. Present address: Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan. Tel.: +81 6 6879 4374; fax: +81 6 6879 4374.
E-mail address: hotta@jwri.osaka-u.ac.jp (M. Hotta).
[1] Present address: Department of Materials Engineering, Shanghai Institute of Technology, Shanghai 200233, China.

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Table 1
Particle size and phase present of the starting powders.

Raw powders	Particle size (μm)	Phase present	Supplies
SiO_2	0.005–0.05	Amorphous-SiO_2	Tokuyama, QS-102
	0.6	Amorphous-SiO_2	Admatechs, SO-C2
	>10	Quartz	Fukushima-Yogyo
Al_2O_3	0.2	Corundum	Sumitomo Chemical, AKP-50
$CaCO_3$	1	Calcite	Junsei Chemical
C	0.02	Amorphous-C	Mitsubishi Chemical, #650B

Al–Ca–O liquid phase were formed at the initial stage of CRN, and nanosized particles were subsequently generated on the surface of their solid spherical particles. The solid spherical particles gradually changed into hollow particles with progression of the reaction to Ca-α SiAlON. Moreover, nanosized Ca-α SiAlON powder could be easily obtained by grinding the synthesized hollow spheres, and then the nanosized powder was sintered using spark plasma sintering [17]. As a result, fully dense Ca-α SiAlON ceramics consisting of nanosized grains were successfully fabricated without sintering additive.

The Ca-α SiAlON spherical hollow powder is excellent for fabrication of dense Ca-α SiAlON ceramics. However, the formation process of the Ca-α SiAlON hollow spheres is considered to be complicated because of the involvement of many elements in this reaction. Thus, the characteristics of starting powders may have an influence on the formation of the Ca-α SiAlON hollow spheres. The Ca-α SiAlON hollow spheres were obtained by using nanosized and amorphous SiO_2 starting powder as major components for the synthesis of SiAlON powder in our previous study [15,16]. In the present work, the formation process of the Ca-α SiAlON hollow spheres was investigated using SiO_2 starting powders with different particle sizes, shapes and crystalline states.

2. Experimental procedure

SiO_2, Al_2O_3, $CaCO_3$ and carbon black were used as staring powders. Three kinds of SiO_2 powders having different particle sizes, shapes and crystalline states were used in the present study. Typical characteristics of the starting powders and morphology of the SiO_2 powders are shown in Table 1 and Fig. 1, respectively. $CaCO_3$ in the mixture decomposes above 900 °C to form CaO and CO_2. The amount of SiO_2, Al_2O_3 and CaO (after decomposition of $CaCO_3$) powders in the mixture was calculated to give a nominal composition of $Ca_{1.0}Si_{9.0}Al_{3.0}O_{1.0}N_{15.0}$. This composition is chosen based on our previous understanding that the maximum Ca-α SiAlON compatibility with the hollow sphere microstructure occurred at the composition $Ca_xSi_{12-3x}Al_{3x}O_xN_{16-x}$ ($x = m/\nu = n$) with $x = 1.0$ [16]. The expected overall reaction during the CRN process can be written as follows:

$$1.0CaO + 9.0SiO_2 + 1.5Al_2O_3 + 22.5C + 7.5N_2 \rightarrow Ca_{1.0}Si_{9.0}Al_{3.0}O_{1.0}N_{15.0} + 22.5CO \quad (1)$$

The content of carbon powder was fixed at 1.2 times of the required stoichiometric value depending on Eq. (1) in order to complete the CRN. The starting powders were mixed with a small amount of ethanol in an agate mortar. The mixed powders were dried, and passed through a sieve. They were placed in a graphite crucible and then heated in a horizontal electrical furnace at temperatures of 900 to 1450 °C for 0 to 120 min. A constant high-purity N_2 gas was flowed into the furnace at a rate of 0.5 L/min. The heating rate was 10 °C/min and the cooling

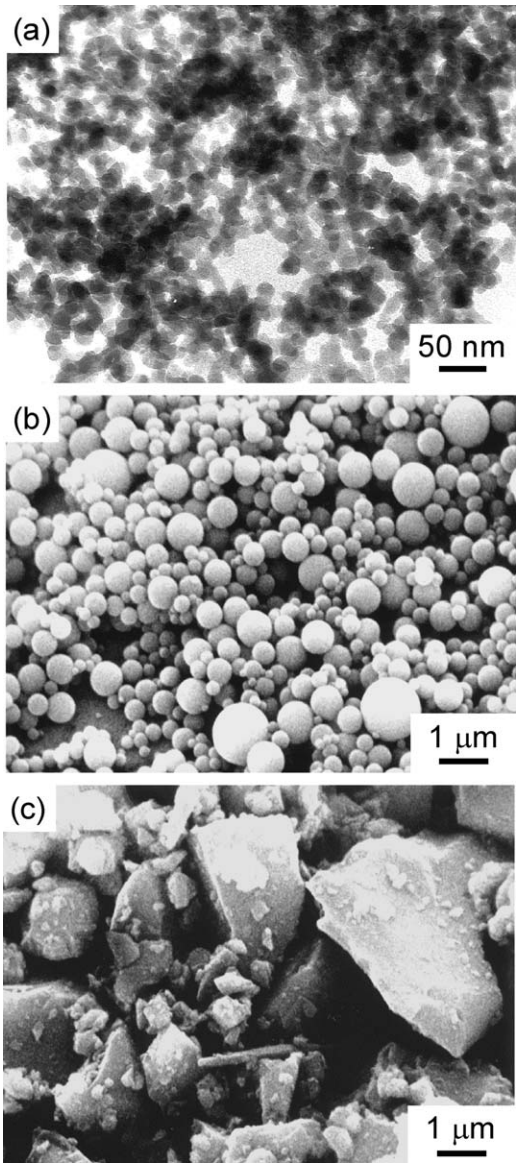

Fig. 1. SEM micrographs of SiO_2 starting powders; (a) nanosized amorphous, (b) submicron-sized amorphous and (c) micron-sized crystalline SiO_2 powders.

Table 2
Phase content in the specimens prepared at 1450 °C for 120 min from different SiO_2 powders.

SiO_2 powders	Phase content (%)		
	Ca-α SiAlON	AlN	β-SiAlON
Submicron-size and amorphous	85 ± 4	15 ± 4	0
Micron-size and crystalline	80 ± 3	15 ± 3	5 ± 2
Nanosize and amorphous[a]	85 ± 5	15 ± 5	0

[a] The data of our previous study [16].

rate was approximately 20 °C/min. The residual carbon was finally eliminated by burning the resultant powders at 700 °C for 120 min in air. The crystalline phases appeared in the samples were identified using X-ray diffractometry (XRD; RINT-2500, Rigaku Co.). The semi-quantitative estimation of α-SiAlON, β-SiAlON and AlN phase contents was based on a calibration curve by using the peak intensity of (1 0 2) α-SiAlON, (1 0 1) β-SiAlON and (1 0 1) AlN. The particle morphology of the samples was characterized by scanning electron microscopy (SEM; JSM-5200, JEOL Ltd.) and transmission electron microscopy (TEM; JEM 2000FXII, JEOL Ltd.). An energy dispersive spectrometer (EDS) installed on the TEM was used to analyze the elemental distribution in the samples.

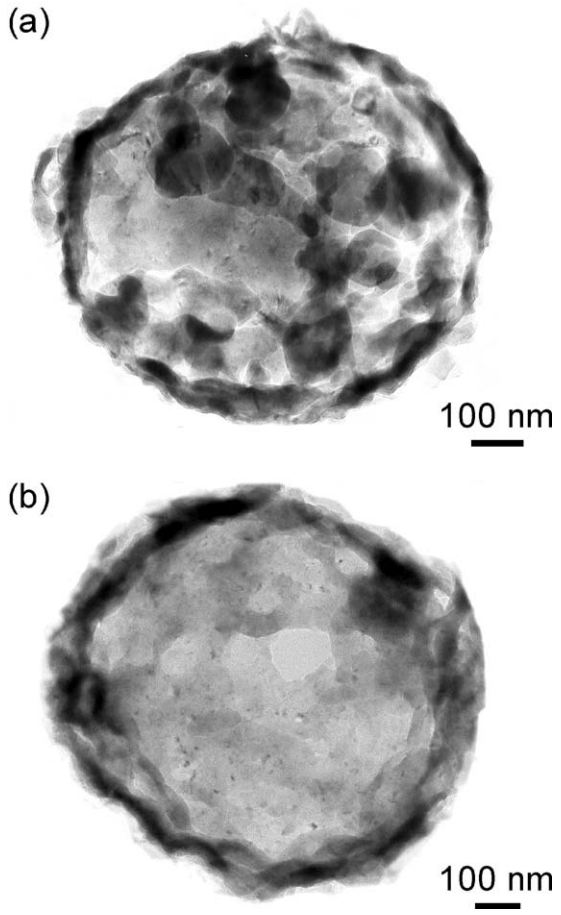

Fig. 2. TEM micrographs of the specimens prepared at 1450 °C for 120 min from different SiO_2 powders; (a) submicron-sized amorphous SiO_2, and (b) micron-sized crystalline SiO_2.

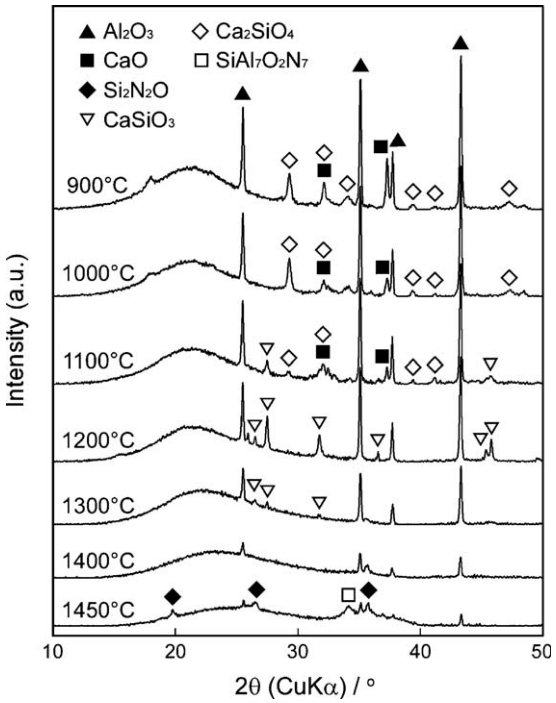

Fig. 3. XRD patterns of the specimens prepared from submicron-sized amorphous SiO_2 powder at different temperatures without a soaking time.

3. Results and discussion

Table 2 shows the phase contents in the specimens prepared at 1450 °C for 120 min from different SiO_2 starting powders. The specimens obtained using both nanosized amorphous SiO_2 and submicron-sized amorphous SiO_2 in the starting powders consisted of 85% Ca-α SiAlON and 15% AlN. In the case of

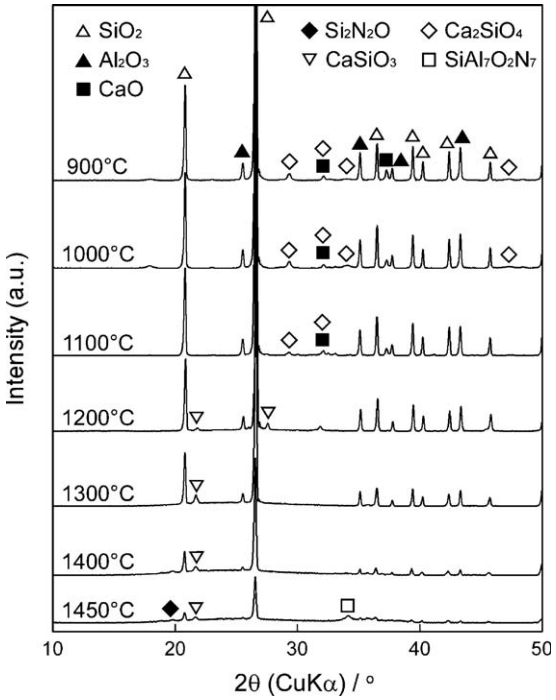

Fig. 4. XRD patterns of the specimens prepared from micron-sized crystalline SiO_2 powder at different temperatures without a soaking time.

micron-sized crystalline SiO_2 starting powder, on the other hand, 5% β-SiAlON formed in the specimen, as well as 80% Ca-α SiAlON and 15% AlN. The statistical error in the phase contents was within ±5%.

Fig. 2 shows TEM micrographs of the samples prepared at 1450 °C for 120 min from (a) submicron-sized amorphous SiO_2 and (b) micron-sized crystalline SiO_2 starting powders. Hollow spheres composed of a large number of fine particles, similar to the sample obtained from nanosized amorphous SiO_2 starting powder [16], were observed in both specimens. The TEM observations revealed that different SiO_2 starting powders had no identifiable influence on the final SiAlON particle morphology.

Fig. 3 shows XRD patterns of the samples prepared using submicron-sized amorphous SiO_2 starting powder at different temperatures without a soaking time. CaO, Ca_2SiO_4 and $CaSiO_3$ phases were identified together with Al_2O_3 in the samples at low temperature. Furthermore, the broad hump detected around $2\theta = 20–25^\circ$ indicated the existence of an amorphous SiO_2 phase corresponding to the starting powder. With increasing temperature, the peak intensities of Al_2O_3 and calcium silicates phases decreased. A very weak Al_2O_3 peak and a broad hump were observed at 1400 °C, suggesting the existence of an amorphous phase consisting of SiO_2, Al_2O_3 and CaO [15]. At 1450 °C, Si_2N_2O and $SiAl_7O_2N_7$ phases formed and the intensity of the broad hump decreased. The changes in phase compositions were identical between the sample made from submicron-sized amorphous SiO_2 and that from nanosized amorphous SiO_2 in the previous study [15].

Fig. 4 shows XRD patterns of the samples prepared using micron-sized crystalline SiO_2 starting powder at different temperatures without a soaking time. The intensities of CaO, SiO_2 and Al_2O_3 peaks decreased with increasing temperature. A small hump was detected around $2\theta = 20–25^\circ$ when the crystalline SiO_2 phase significantly decreased at 1400–1450 °C. This implies that an amorphous phase consisting of

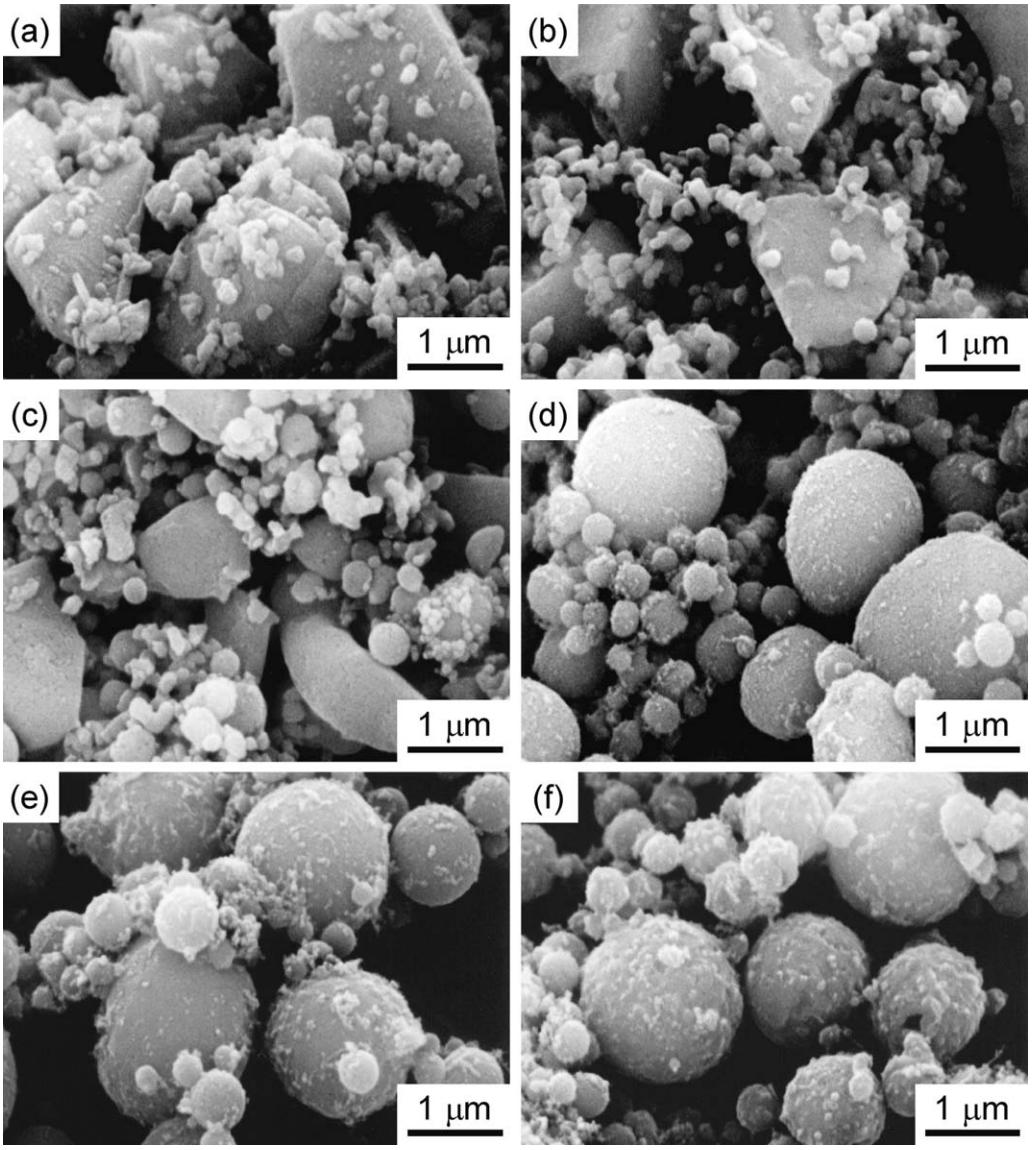

Fig. 5. SEM micrographs of the starting mixture and the specimens prepared from micron-sized crystalline SiO_2 powder at different temperatures without a soaking time; (a) powder mixture, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1400 °C and (f) 1450 °C.

SiO_2, Al_2O_3 and CaO was present in the sample. At 1450 °C, Si_2N_2O and $SiAl_7O_2N_7$ phases formed. The XRD results in Figs. 3 and 4 show the same phase development with the system that used nanosized amorphous SiO_2 starting powder [15]. It revealed that Ca-α SiAlON formed through a Si–Al–Ca–O liquid phase at the initial stage of CRN, regardless of the different characteristics of SiO_2 starting powders.

Fig. 5 demonstrates SEM micrographs of the starting mixture and the samples prepared at various temperatures without a soaking time using micron-sized crystalline SiO_2 starting powder. The morphology of the sample obtained below 1100 °C was similar to that of the starting mixture. With heating at 1200 °C, fine spherical particles <0.5 μm in diameter and coarse angular particles >1 μm were observed. These solid spheres would be a Si–Al–Ca–O liquid phase formed above the eutectic temperature of 1170 °C in the SiO_2–Al_2O_3–CaO system (quote the relevant phase diagram here). In fact, in our previous study, the formation of the spherical particles prepared from nanosized amorphous SiO_2 starting powder also appeared at the same heating temperature of 1200 °C [15]. With increasing temperature, the coarse angular particles started to change into round shape and a large number of spheres <0.5 μm were produced. Some very fine particles were observed at the surface of the spheres when temperature increased to 1300 °C. As temperature increased to 1400 °C, there appeared a wide distribution of spheres of 0.2 to 1.5 μm in diameter. In the case of the submicron-sized amorphous SiO_2 starting powder (Fig. 6), the morphology of the samples prepared at different temperatures was almost identical to that of the micron-sized crystalline SiO_2 starting powders, while very fine particles were produced at the surface of the spheres when temperature increased to 1300 °C. The amount of these very fine particles increased with nitridation temperature and thus may be associated with the nitridation of the Si–Al–Ca–O

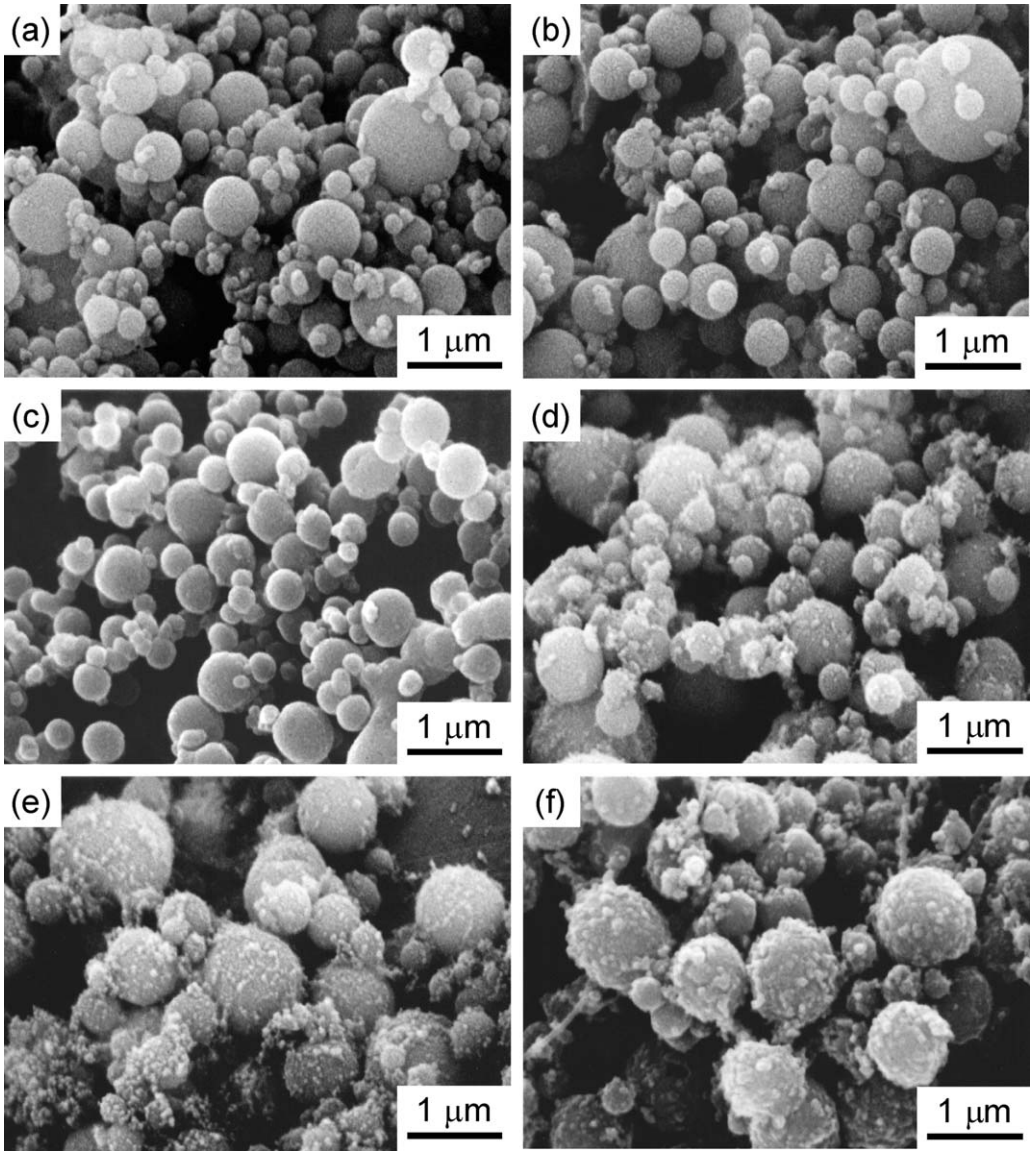

Fig. 6. SEM micrographs of the starting mixture and the specimens prepared from submicron-sized amorphous SiO_2 powder at different temperatures without a soaking time; (a) powder mixture, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1400 °C and (f) 1450 °C.

liquid phase. The size of the solid spheres formed at the initial stage of CRN revealed to be dependent on that of SiO_2 starting powder (Figs. 5 and 6).

Fig. 7 shows TEM micrograph and EDS spectra of the spherical particles prepared at 1450 °C without a soaking time from submicron-sized amorphous SiO_2 starting powder. Spherical solid particles and a small number of hollow particles were clearly observed from the TEM image. The chemical composition for all solid spheres (Fig. 7(a)) was uniform and contained Si, Al, Ca, O and a small amount of N. Additional electron diffraction analysis of the solid particles showed only an amorphous halo. These results were similar to that using nanosized amorphous SiO_2 starting powder in the previous study [15]. On the other hand, the hollow spheres had a chemical composition of Si, Al, Ca, O and N (Fig. 7(b)), but its nitrogen concentration was much higher than that in solid spheres, implying that the morphological change from solid to hollow spheres was accompanied by progression of CRN.

Fig. 8 shows TEM micrograph and EDS spectra of a solid sphere prepared at 1450 °C without a soaking time from micron-sized crystalline SiO_2 starting powder. Grains with angular edges were observed in the sphere by TEM. EDS analysis showed relatively intense peaks for Si and N at the angular grains (Fig. 8(a)) compared to another areas (Fig. 8(b)). Crystalline SiO_2 and Si_2N_2O phases were detected in the specimen by XRD analysis, as shown in Fig. 4. These results suggested that the spherical solid particles in this sample might contain some crystalline SiO_2 and Si_2N_2O grains in a matrix of a Si–Al–Ca–O–N amorphous phase. Because micron-sized crystalline SiO_2 starting powder had large particle size, a Si–Al–Ca–O liquid phase might partially form at the initial stage of CRN, leaving some crystalline SiO_2 grains remained in the solid spheres. Continuous nitridation of the SiO_2 and Si_2N_2O

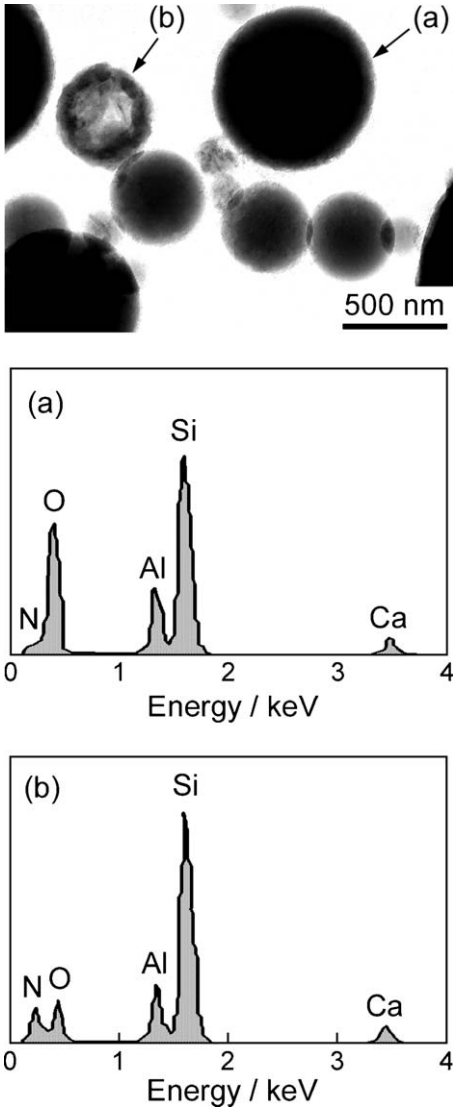

Fig. 7. TEM micrograph shows a solid sphere (a) and a hollow spheres (b), and their respective EDS spectra for the specimen prepared from submicron-sized amorphous SiO_2 powder at 1450 °C without a soaking time.

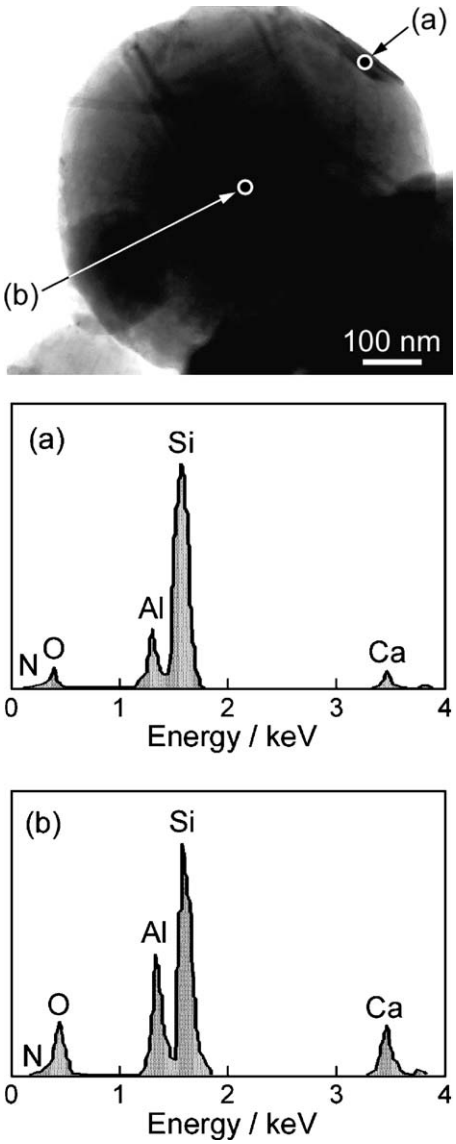

Fig. 8. TEM micrograph and EDS spectra of the specimen prepared at 1450 °C without a soaking time from micron-sized crystalline SiO_2 powder.

phases resulted in the formation of β-SiAlON, in addition to Ca-α SiAlON and AlN, in the final specimen prepared at 1450 °C for 120 min using micron-sized crystalline SiO_2 starting powder, compared to Ca-α SiAlON and AlN two phases in the final specimens when nanosized and submicron-sized amorphous SiO_2 starting powders were used (Table 2).

4. Conclusions

The products prepared using SiO_2 starting powders with different characteristics were analyzed by XRD, SEM, TEM and EDS in order to investigate the formation process of Ca-α SiAlON hollow spheres. Hollow spheres composed of a large number of nanosized Ca-α SiAlON particles formed in the all final products prepared at 1450 °C for 120 min in nitrogen. It is revealed that the Ca-α SiAlON hollow spheres are form through a similar nitridation process of a Si–Al–Ca–O liquid phase, irrespective of particle size, shape and crystalline state of the SiO_2 starting powders. Spherical solid Si–Al–Ca–O–N particles were produced from the liquid phase at the initial stage of the CRN process. With increasing temperature and time in nitridation, the solid spheres changed into hollow spheres containing nanosized Ca-α SiAlON grains.

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