Effects of starting composition and carbon content on the formation of Ca-α SiAlON powders by carbothermal reduction–nitridation

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Ca-α SiAlON powders were prepared at different starting compositions and carbon contents at 1450°C for 2 h in N2 from mixtures of SiO2, Al2O3, CaCO3 and carbon powders by carbothermal reduction–nitridation. Crystalline phases and particle morphology of the products were investigated. With increasing the x value in nominal Ca-α SiAlON compositions Ca4Si12–3xAl3O2N16–x, the number of small hollow spheres decreased and the size of primary grains consisting of the hollow spheres increased. The addition of carbon powder to more than 1.2 times of the necessary stoichiometric value was required to form Ca-α SiAlON hollow spheres composed of ultrafine grains.

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SiAlON ceramics are advanced structural ceramics due to their high hardness and corrosion resistance, excellent high-temperature strength and good thermal shock resistance.1–4 β-SiAlON has been produced from powder mixtures of the Si3N4–AlN–Al2O3 system, and is represented by the general formula Si6–xAl2O3N6–x (0 < x ≤ 4.2). α-SiAlON was found very shortly after β-SiAlON6 with the formula MxSi12–4xAl12–6xO16–7x–2y where x is the valence of the stabilizing cations M, which is one of Li, Mg, Ca, Y and rare earth elements, and has been generally fabricated from mixtures of the Si3N4–AlN–Al2O3–M2O3 system. β- and α-SiAlON powders have been prepared from natural minerals such as kaolinite (Al3Si4O10(OH)8)5,6 and halloysite (Al4Si3O10(OH)3)7,8 SiO2–Al2O3 mixtures9 and SiO2–Al2O3–M2O3 mixtures10–15 with carbon as a reducing agent by carbothermal reduction–nitridation (CRN). We successfully synthesized Ca-α SiAlON hollow spheres composed of nanosized grains of 10 to 30 nm in diameter using a mixture of SiO2, Al2O3, CaCO3 and carbon powders in a starting composition Ca4Si12–3xAl3O2N16–x with x = 1.0 by the CRN technique at 1450°C for 2 h.11 The Ca-α SiAlON hollow spheres were formed through an intermediate liquid phase produced by the reduction of Si–Al–Ca–O elements at the initial stage of CRN.12,13 The purpose of this paper is to study the effects of starting composition and carbon content on the formation of Ca-α SiAlON powders via CRN of SiO2–Al2O3–CaCO3 powder mixtures.

SiO2 (QS-102, Tokuyama Co., particle size: 0.005–0.05 μm), Al2O3 (AKP-50, Sumitomo Chemical Co., Ltd., 0.21 μm), CaCO3 (Junsei Chemical Co., Ltd., 1.0 μm) and carbon (#650B, Mitsubishi Chemical Co., 0.018 μm) powders were used as starting materials. Ca-α SiAlON powders were prepared from the powder mixtures at nominal Ca-α SiAlON compositions of Ca4Si12–3xAl3O2N16–x (x = m/v = n) with different x values of 0.4 to 1.4. The increase in the x value means the increase in the amount of Ca and Al in the starting compositions. Carbon powder was added to SiO2–Al2O3–CaCO3 mixtures in the content of 1.0 to 2.0 times of the required stoichiometric value according to the expected overall reaction Eq. (1).

\[
x\text{CaO} + (12 - 3x)\text{SiO}_2 + (1.5x)\text{Al}_2\text{O}_3 \\
+ (24 - 1.5x)\text{C} + (16 - x)/2\text{N}_2 \\
\rightarrow \text{Ca}_4\text{Si}_{12-3x}\text{Al}_{3}\text{O}_{2}\text{N}_{16-x} + (24 - 1.5x)\text{CO}
\]  

(1)

The powders were weighted according to the designed compositions and mixed with a small amount of ethanol in an agate mortar. The mixed slurry was dried and then passed through a sieve. The resultant mixtures were placed in a graphite crucible and subsequently heated at 1450°C for 2 h in high-purity nitrogen. The heating and cooling rates were fixed at 10 and 20°C/min respectively. The residual carbon was removed by firing the resultant powders at 700°C for 2 h in air. X-ray diffractometry (XRD; RINT-2500, Rigaku Co.) was used to identify the crystalline phases in the products. The content of the Ca-α SiAlON phase was calculated from the intensities of the XRD peaks. Scanning electron microscopy (SEM; JSM-5200, JEOL Ltd.) and field emission scanning electron microscopy (FESEM; JSM-6340F, JEOL Ltd.) were applied for observation of the particle morphology.

Figure 1 shows the FESEM micrographs of the specimens prepared for compositions Ca4Si12–3xAl3O2N16–x with different x values of 0.4 to 1.4 and a carbon content of 1.2 times of the required stoichiometric value at 1450°C for 2 h. At the composition of x = 0.4, rod-like and spherical particles were mostly formed, but hollow spheres composed of nanosize...
primary grains were not observed. The resulting rod-like particles may consist of β-SiAlON, because a large amount of β-SiAlON phase was produced in the composition with x value <0.4 as shown in our previous study.\(^\text{10}\) When the x value increased in the compositions ranging from x = 0.8 to 1.4, the sizes of hollow spheres and primary grains consisting of the spheres increased. This may be due to the formation of a great amount of liquid phase appeared at the initial stage of the CRN process in the compositions with large amounts of Ca and Al. Ca-α SiAlON hollow spheres composed of nanosized particles might have formed through an intermediate Si-Al-Ca-O-N liquid phase.\(^\text{12,13}\)

**Figure 2** demonstrates the XRD patterns of the specimens prepared for carbon content of 1.0 to 2.0 times the required stoichiometric value with x value of 1.0 at 1450°C for 2 h. Si\(_3\)N\(_4\) and Al\(_2\)O\(_3\) phases were detected as well. Si\(_3\)N\(_4\) and Al\(_2\)O\(_3\) phases were formed at the initial stage of the CRN process as intermediate products for the formation of Ca-α SiAlON in our previous work.\(^\text{12,13}\) Therefore, the carbon content of the required stoichiometric value would be insufficient to form Ca-α SiAlON via CRN of the SiO\(_2\)-Al\(_2\)O\(_3\)-CaCO\(_3\) system. In preparation of Si\(_3\)N\(_4\) powder using CRN of SiO\(_2\), the actual carbon content should be higher than the stoichiometric value to achieve full nitridation from SiO\(_2\) to Si\(_3\)N\(_4\).\(^\text{16}\) In a previous work on the synthesis of Mg-α SiAlON powder via CRN of talc and halloysite mixture, spinel (Mg\(_2\)Al\(_2\)O\(_4\)) was produced due to a shortage of carbon.\(^\text{7}\) It was found in this work that Ca-α SiAlON and AlN phases, 85% and 15% respectively, were formed in the specimen prepared at carbon content of 1.2 times the required stoichiometric value.\(^\text{11}\) Consequently, it revealed that a higher carbon content than the stoichiometric value was necessary for the full conversion to Ca-α SiAlON by the CRN process. The crystalline phases appeared in specimens containing carbon content of 1.2 to 2.0 times the required stoichiometric value were Ca-α SiAlON and AlN, and the content of Ca-α SiAlON was 85 to 90% in all the specimens. Sharp XRD peaks were observed with increasing the carbon content from 1.2 to 2.0 times of the required stoichiometric value, indicating improved crystallinity for Ca-α SiAlON and AlN phases. In the preparation of β-SiAlON powder from the SiO\(_2\)-Al\(_2\)O\(_3\) mixture, more AlN and 15R-AlN polytypoid phases were formed when the carbon content increased.\(^\text{5,10,17}\) In the present work on preparing Ca-α SiAlON powders from the SiO\(_2\)-Al\(_2\)O\(_3\)-CaCO\(_3\) mixture, however, the increase of AlN and the formation of 15R were not observed.

**Figure 3** shows the SEM micrographs of the specimens prepared for carbon content of 1.0 to 2.0 times the required stoichiometric value with x value of 1.0 at 1450°C for 2 h. Hollow spheres composed of nanosized grains were formed in the product prepared at the carbon content of 1.2 times the
required stoichiometric value.\textsuperscript{11) At carbon content of the required stoichiometric value, many particles were found to have irregular shapes and a very little of hollow spheres composed of ultrafine grains were observed. This may be a result of insufficient CRN reaction due to an inadequate amount of carbon concentration in the composition. The size of the primary grains that formed hollow spheres was also increased with increasing carbon content.

In conclusion, the effects of starting composition and carbon content on the formation of Ca-\(\alpha\) SiAlON powders by CRN were investigated for the SiO\(_2\)-Al\(_2\)O\(_3\)-CaCO\(_3\)-carbon mixture. At \(x = 0.4\) in nominal Ca-\(\alpha\) SiAlON compositions Ca\(_x\)Si\(_{2-x}\)Al\(_2\)O\(_3\)N\(_{16-x}\), a large amount of \(\beta\)-SiAlON were produced and rod-like particles were observed. The number of small hollow spheres decreased and the size of the primary grain that formed the hollow spheres increased with increasing \(x\) value from 0.8 to 1.4. At the required stoichiometric carbon content, Si\(_3\)N\(_2\)O and SiAlO\(_2\)N\(_7\) phases, which were intermediate products for the formation of Ca-\(\alpha\) SiAlON, were detected. The significant amount of particles with irregular shapes was observed in addition to a very small amount of hollow spheres in the product prepared with the required stoichiometric carbon content. As carbon content increased to more than 1.2 times, Ca-\(\alpha\) SiAlON became a dominant phase, about 85--90\% in the product. The increased carbon content also resulted in an increase in the size of the primary grains consisting of the hollow spheres.

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\textbf{References}


