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Reaction characteristics of combustion synthesis of β -SiAlON using different additives

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Abstract

Reaction characteristics of combustion synthesis (CS¹) of β -SiAlON powders in a horizontal CS chamber were compared by including two types of additives (β -SiAlON and NaCl) in Si, SiO₂, and Al powder raw materials. The results showed that the reaction characteristics were influenced by the additives, which exerted a strong effect on the reaction rate and the morphology of the products. At the respective maximum combustion temperatures, a relatively slow conversion rate, with a reacted fraction (η) of 58.7%, was achieved with the addition of 12 mass% NaCl to the raw materials, whereas the addition of 45 mass% β -SiAlON powders afforded $\eta = 88\%$. The NaCl additive yielded rod-like crystals, which were well developed by a long after-burn time. However, self-sintering occurred in the presence of β -SiAlON powders. The results indicate that some degree of control over the conversion rate of the reaction and the microstructures of the product can be achieved by varying the type of additives.

Keywords: Combustion synthesis; β -SiAlON; Reaction characteristics; Temperature profile; Microstructure

¹ Abbreviations: Al/ β -SiAlON, Al and β -SiAlON; CS, combustion synthesis; D45, 45 mass% β -SiAlON; η , reacted fraction; LED, light-emitting diode; N12, 12 mass% NaCl; Q , endothermic value; SEM, scanning electron microscopy; VLS, vapor-liquid-solid; XRD, X-ray diffraction.

1. Introduction

β -SiAlONs, derived from the β -Si₃N₄ structure by the equivalent substitution of Si–N with Al–O, have the general formula Si_{6-z}Al_zO_zN_{8-z} ($0 < z \leq 4.2$). They are attractive materials for application in high-temperature engineering systems because of their high strength and hardness, good thermal and chemical stability, and superior wear and thermal shock resistance [1-3]. Recently, rare-earth-doped β -SiAlONs have been recognized as potential phosphors for application to white light-emitting diodes (LEDs) because of their intense photoluminescence and high thermal stability [4-6].

Low-cost production of β -SiAlON is crucial for achieving widespread applications. Their synthesis generally involves sintering of high-purity Si₃N₄, AlN, and Al₂O₃ at temperatures of 1700–2000 °C for many hours under nitrogen pressure [7,8]. Si₃N₄ and AlN must be synthesized prior to the sintering process as an additional step. Consequently, the process is limited by many disadvantages such as the need for multistep processes that are energy- and time-consuming. The carbothermal reduction and nitridation (CRN) [9,10] method using kaolin and a carbon mixture as raw materials is regarded as an economically attractive process for producing β -SiAlON. However, the practical application of this method has been limited thus far by the low purity of the products, as they usually contain a number of undesirable by-products, such as SiC and AlN.

Combustion synthesis (CS) is a recognized alternative to conventional methods of powders synthesis for producing various industrial materials [11-14], particularly ceramics [15-18]. This process exploits a self-sustaining regime that utilizes the heat generated during a strongly exothermic reaction. No external energy is required, except for the ignition energy. This method has many advantages, including low energy input, a short reaction time, simple equipment, and high-purity products. Most reported syntheses of β -SiAlON via CS required high N₂ pressure (2–150 MPa) to drive the reaction to completion [19]. However, β -SiAlONs have been successfully synthesized under a low nitrogen pressure of 1 MPa as well [20-22]. Additionally, inexpensive Si, Al, and SiO₂ powders have been used as raw materials. Nevertheless,

the combustion temperatures are extremely high and Si particles melt in the combustion front and coalesce during reaction, which inhibits complete nitridation. To decrease reaction heat as well as to slow down the combustion temperature, a large amount of the β -SiAlON product (50 mass%) must be added to the starting materials as a diluent [23-25], which, however, decreases the product yield. Moreover, using final product as diluents does not usually provide a product with submicron particles although the CS temperature decreases. Thus, to obtain a product with a fine grain size, the post-synthesis treatment is necessary.

Recently, NaCl has been used as a diluent in CS for the synthesis of some ceramics, such as TiC, ZrB₂, and TiB₂ powders [26-28]. It was reported that the addition of NaCl lowers the CS temperature and results in a decrease in the particle size of the final products. In our previous work, single-phase β -SiAlON powders with submicron dimensions were successfully synthesized by addition of a small amount of NaCl [29]. NaCl acted as an efficient diluent that absorbed the reaction heat by converting it to the latent heat of phase transformation. However, execution of this new CS process under industrial conditions using a large sample size is still a challenge.

Herein, this novel synthesis process is extended to industrial conditions, in which the sample was positioned horizontally. In order to compare, the same experiment was carried out using the β -SiAlON product as a diluent. This is the first execution of this method using a horizontal-type chamber and employing low-cost Si, Al, and SiO₂ as raw materials, along with the comparison of the characteristics of the reaction process and kinetic of the reaction on propagation using Boddington's model.

2. Experimental procedure

Our previous work has merely been examined under laboratory conditions using a small amount of raw materials. Furthermore, the sample was longitudinally positioned and the top of the sample was ignited according to the classical CS process, which is not suitable for commercial processing. Therefore, in this work, to execute this new CS process under industrial conditions, the sample was positioned horizontally. Besides, amount of β -SiAlON powders were used to surround the sample, which can reduce the heat exchanges with the surroundings.

The starting materials used in this work were commercially available powders of Si (6 μ m, purity >98%, Kinseimatec Co., Ltd., Japan), Al (14 μ m, purity >99.7%, Minalco Co., Ltd., Japan), SiO₂ (12 μ m, purity >99%, Takeori. Co., Ltd., Japan), β -SiAlON (0.5 μ m, ISMAN J Corporation, Kawasaki, Japan), and NaCl (purity 99.9%, Kojundo Chemical Laboratory Co., Ltd., Japan). The reaction characteristics of the combustion synthesis process were compared for the addition of either 45 mass% β -SiAlON (denoted D45) or 12 mass% NaCl (denoted N12) to the starting materials. The reactions for the combustion synthesis of β -Si₅AlON₇ (β -Si_{6-z}Al_zO_zN_{8-z}, $z = 1$) using β -SiAlON and NaCl as the diluent can be described by the following equations:

All reactants were weighed according to the stoichiometric ratio. The reactant powders were mechanically activated by planetary ball-milling at a ball-to-sample mass ratio of 10:1 for 15 min. Then, 120 g of the activated mixture was loosely packed into a graphite crucible with dimensions 80 × 130 × 45 mm. The experimental setup is shown in Fig. 1. Two W-Re type thermocouples protected by alumina sheaths were inserted into the center of the sample to record the combustion temperature profiles. The propagation velocity of the combustion front was determined by measuring the time that lapsed between the two thermocouples, which were embedded at a distance of 40 mm. Nitrogen (purity: 99.999%) was charged into the

chamber up to a pressure of 1 MPa. To minimize the oxygen concentration in the chamber, the vacuuming/pressurizing with nitrogen was repeated twice. Combustion was triggered by igniting the Al and β -SiAlON (Al/ β -SiAlON = 50/50 mass%) powders by passing an electric current through the carbon foil placed on one end of the sample.

The experimental procedures employing both types of additives are compared in Fig. 2. As shown in this figure, when using 45 mass% β -SiAlON product as diluents, the as-synthesized β -SiAlON product generated by addition of commercial β -SiAlON powder (ISMAN J, 0.5 μm) as the diluent was crushed in a mortar and then sieved through a 220-mesh sieve and milled to approximately 5 μm to be used as the diluent for the second combustion reaction under the same conditions. This process was repeated for several times. It is obvious that this approach has a drawback of having multistep pathways and a low product yield. Furthermore, the products were extremely hard and difficult to mill into powders. However, using 12 mass% NaCl as the diluent has the merit of high-efficiency and energy-saving process. In addition, the product obtained by addition of NaCl was readily pulverized by crushing.

The phase compositions of the combustion-synthesized products were analyzed via X-ray diffraction (XRD, Cu K α , Rigaku, Japan), the accelerating voltage and current are 30 kV and 15 mA, respectively, and the scanning angle of the detector was varied within the range 10–60° (2 θ) with a step of 0.02° and fixed counting time of 0.5 s. The lattice parameters of the hexagonal β -SiAlON were calculated from the XRD peaks (100), (110), (200), (101), (210), (201), (301), (320), (321), and (411) using pure Si as an internal standard. The microstructures were observed via scanning electron microscopy (FE-SEM, JSM-7400F, JEOL, Japan). The data for calculating the heat change caused by NaCl was taken from the database of the HSC Chemistry software Ver. 5.11.

3. Results and discussion

3.1. Characterization of the raw materials

The morphology of the raw materials before CS of β -SiAlON is presented in Fig. 3. When using 45 mass% β -SiAlON powders as diluents, Si grains are covered by some small ones, which are agglomerated together. In contrast, the raw materials exhibit well-distributed particles when using 12 mass% NaCl as diluents. The result indicates NaCl prevented the agglomeration of the raw materials during the milling. To obtain a precise estimation of the particle-size distribution for the two kinds of raw materials, particle-size distribution measurement was performed by laser particle-size analyzer. The results are given in Fig. 4. D45 was composed of particles with a median diameter of $\sim 4.2 \mu\text{m}$, which are smaller than that of N12 with a median diameter of $\sim 6 \mu\text{m}$. The differences are attributed to the addition of amount of small sized β -SiAlON diluents in D45.

3.2. Change in enthalpy of the raw materials

Fig. 5 shows the heat contents of β -SiAlON and NaCl during the CS processes, which were calculated using the data acquired from a laser-flash method and taken from the database of HSC Chemistry software Ver.5.11, respectively. The endothermic value (Q , kJ/kg) of β -SiAlON was estimated using the following equation:

$$Q_{\beta\text{-SiAlON}} = \int_{T_0}^T Cp(T)dT \quad (1)$$

where $Cp(T)$ is the specific heat capacity of β -SiAlON ($z = 1$) in kJ/(kg·K), and Q in kJ/kg, $Cp = 0.731$ kJ/(kg·K) was the measured value from the laser-flash method. The endothermic value of NaCl was calculated using the specific heat and latent heat of its melting and evaporation, which could be determined from the following formula:

$$Q_{\text{NaCl}} = \int_{T_0}^{T_m} Cp(T)dT + Q_{sl} + \int_{T_m}^{T_b} Cp(T)dt + Q_{lg} + \int_{T_b}^T Cp(T)dt \quad (2)$$

and Cp was 0.861 kJ/(kg·K), the data used in this calculation were taken from

software HSC chemistry Ver.5.11. The values of specific heat capacity and heat capacity formula of β -SiAlON and NaCl can be found in Table 1. It is evident that the endothermic value of NaCl (1403 kJ/kg at 1073K) was larger than that of β -SiAlON (938 kJ/kg at 1073K) at temperatures of equal and higher than the NaCl melting point because of the high latent heat of phase transformation of NaCl.

Based on our previous studies [29,30], two endothermic processes can be defined with the addition of these additives, corresponding to a two-stage exothermic process for the CS of β -SiAlON. The first stage exothermic process involving the reaction of Al and N_2 to form AlN and Al and SiO_2 to form Al_2O_3 and Si around 1473 K: $2Al + N_2(g) \rightarrow 2AlN$, $2Al + 1.5SiO_2 \rightarrow Al_2O_3 + 1.5Si$; and second exothermic occurs at 1473–1900 K, with the exothermic nitridation of Si and simultaneous formation of β -SiAlON: $3Si + 2N_2(g) \rightarrow Si_3N_4$, $Si_3N_4 + AlN + Al_2O_3 \rightarrow \beta$ -SiAlON. Therefore, we define the first and second endothermic processes as at temperatures of 298–1473 K and 1473–1900 K, respectively. In fact, during the entire process for synthesis of β -SiAlON, there are several endothermic reactions, such as Al-Si eutectic (eutectic melting point 570 °C), the melting of Al (melting point 660 °C) and Si (melting point 1414 °C), however, these endothermic reactions can be ignored due to small endothermic peaks observed from the temperature curves [30].

Fig. 6 shows the changes in the enthalpy of the raw materials (ΔH in kJ/kg), estimated using $\Delta H1$ and $\Delta H2$ that correspond to the two major exothermic processes. It is notable that the value of the total enthalpy change ($\Delta H1 + \Delta H2$) of sample D45 is higher than that of N12, and the $\Delta H1$ value is significantly higher than $\Delta H2$, mainly because the endothermic region in the former located at temperatures of 298–1473 K, which is longer than the latter that at temperatures of 1473–1900 K .

3.3. Temperature profiles

All the temperature profiles analyses were made from the thermocouple T. C. 1 data (see Fig. 1). In fact, the thermocouples are located at the level of the middle of the sample. The typical time-temperature profiles obtained during the CS of

β -SiAlON for the D45 and N12 samples by using raw reactants Si, Al, and SiO₂ under 1 MPa nitrogen pressure are shown in Fig. 7. The temperatures rapidly reached the maximum values after ignition, which then decreased at a slow rate for both samples; however, for N12, this process is followed by a longer period of after-burn, in which the temperature decreases, than with D45. This difference arises because of different reaction rates, as discussed in a subsequent section. The maximum measured temperature for D45 and N12 are 1681 °C and 1505 °C, respectively. The calculated wave propagation velocities by measuring the time that lapsed between the two thermocouples are presented in Table 2. Several times of the repeated experiments show the identical results although there was slightly variance in the maximum measured temperature.

3.4. Conversion rate

Fig. 8 shows the first and second derivatives of the temperature profiles acquired during the CS of β -SiAlON. The first derivatives ((a) and (c)) of the temperature profiles for the two samples show similar trends, although the variation tendency and maximum value are remarkably different. The two peaks in the heating rate (dT/dt) curves indicate a two-stage exothermic process, consistent with the aforementioned reaction mechanism. For sample D45, the first peak in the dT/dt curves is observed at a maximum value of 11 °C/s, which is lower than that of N12 with a maximum value of 13 °C/s, as indicated by peaks of 1 and 1' in (a) and (c), respectively; the second dT/dt peak of D45 rises sharply to reach a value as high as 18 °C /s (peak 2 of (a)). However, the second dT/dt peak for N12 (peak 2' of (c)) approaches a stationary value of 10 °C/s and persists for a long period. The significant change in the profile of these curves is attributed to the change in the enthalpies (ΔH) of the raw materials. Compared with Fig. 6, it is clear that a high value of ΔH results in a slow heating rate, and a low value contributes to a rapid heating rate.

The reaction rate, $\partial\eta/\partial t$, can generally be calculated from the temperature

profile using the following equation [31]:

$$\partial \eta / \partial t = [(T - T_0) t_x^{-1} + (\partial T / \partial t) - t^* (\partial^2 T / \partial t^2)] / \tau_{ad} \quad (6)$$

where $t^* = \alpha / v^2$; α is the effective thermal diffusivity, v is the wave velocity, and τ_{ad} denotes the temperature rise under adiabatic conditions. In general, the values of the parameters t^* , t_x , and τ_{ad} are determined from the profile as follows [32,33]:

$$1/t^* = 1/t_r - 1/t_d \quad (7)$$

$$t_x = t_d - t_r \quad (8)$$

$$\tau_{ad} = \frac{t_r}{t_d - t_r} \tau(t_1) + \frac{t_d}{t_d - t_r} \tau(t_2) + \frac{1}{t_d - t_r} \int_{t_1}^{t_2} \tau dt \quad (9)$$

where t_r and t_d are the rise and decay times in the remote inert zones of the temperature profile, respectively, and can be determined from the linear slopes of the plot of $\ln (T - T_0)$ vs. t in these two regions, as shown in Fig. 9. The parameter t_x is the thermal relaxation time of the system. The calculated parameters t_r , t_d , t_x , and t^* are listed in Table 3. The values of t_1 and t_2 are arbitrarily chosen times located in the remote rise and decay zones, respectively. $\partial T / \partial t$ and $\partial^2 T / \partial t^2$ are the first and second derivatives of the temperature profiles, as shown in Fig. 8. Therefore, the reaction rate is readily computed from the temperature profiles.

Fig. 10 shows the calculated reaction rate ($d\eta/dt$) and the reacted fraction (η) for the CS of β -SiAlON using the two types of additives. For sample D45, the maximum value of the reaction rate corresponds to a reacted fraction (η) of 70% at ~ 1587 °C; whereas η was only 46% for sample N12 for the maximum value of $d\eta/dt$ at ~ 1370 °C. The results indicate that the maximum reaction rate is not achieved at the maximum temperature for both samples. At the maximum measured temperature, for sample D45, $\eta = 88\%$, which indicates that essentially complete conversion is achieved. In contrast, the reaction is only partially completed for sample N12 with $\eta = 59\%$. The lower reaction rate was considered to result from significant heat reduction because of the evaporation of NaCl during the second exothermic process. As a result, η continued to increase as the reaction continued, well past the passage of the combustion wave, and a long after-burn time was required to reach completion of the reaction.

3.5. Phase composition of the products

Fig. 11 shows the XRD patterns of the combustion-synthesized β -SiAlON powders. No impurity peaks were observed for either of the two samples, and all the observed peaks could be indexed to the pure β -SiAlON phase. The results indicate that complete nitridation of the Si was achieved with the respective quantities of β -SiAlON and NaCl additives. NaCl peaks were not detected in the product of N12, which indicates that their complete evaporation was achieved under the high reaction temperature and separated out of the reaction system [29]. The lattice parameters of the β -SiAlON phase calculated from these XRD peaks are well matched with those documented in JCPDS 48-1615 ($a = 7.635 \text{ \AA}$, $c = 2.934 \text{ \AA}$). Furthermore, the z value of the synthesized β -SiAlON was calculated using the lattice constants a and c according to the reference method [2]. The calculated parameters are summarized in Table 2.

3.6. Morphology of products

Fig. 12 shows the SEM images of the combustion-synthesized β -SiAlON powders obtained using the two types of additives. The sample D45 that was prepared by adding 45 mass% of β -SiAlON powder consisted of ball-like particles and columnar crystals of various sizes, most of which exhibited extensive agglomeration to form large blocks. Compared with sample D45, the rod-like crystals of sample N12, prepared by addition of 12 mass% NaCl, had larger sizes with lengths $\sim 3 \text{ }\mu\text{m}$ and diameters $\sim 2 \text{ }\mu\text{m}$. The formation of large crystals was induced by rapid mass diffusion, precipitation, and crystal growth of β -SiAlON nuclei caused by the long period of after-burning, as shown in the temperature profile presented in Fig. 7. The crystals of both samples had rounded tips, typical of crystals formed by the vapor-liquid-solid (VLS) process. In this process, a liquid droplet is initially formed, and then reactant molecules in the vapor phase are transported by diffusion to the liquid–solid interface.

With precipitation and crystal growth, the droplet is detached from the substrate [34,35]. When the β -SiAlON powder was used as the additive, the vapor phase precipitated and grew on the surface of the powders. Solid-state diffusion between the newly formed β -SiAlON crystals and the added ones provides a source of atoms to fill up the concave areas to diminish the outer surface of the particle, resulting in self-sintering [36]. However, when NaCl is used as an additive, the melted NaCl creates a potential diffusion barrier between the β -SiAlON crystals; hence, sintering of the β -SiAlON particles could be prevented. The melted NaCl may then be vaporized because of the high combustion temperature, followed by outward diffusion leaving space between the particles, thus generating well-isolated crystallized particles.

4. Conclusions

The reaction characteristics of the CS of β -SiAlON in a horizontal-type chamber were compared using two types of additives (β -SiAlON and NaCl). The results revealed that the various additives produced different changes in the enthalpies of the raw materials, which affected the reaction rate and morphology of the products. With addition of the β -SiAlON powder to the starting materials, the reaction was largely completed within the combustion front at the maximum temperature; in contrast, a relatively slow conversion rate was achieved (with $\eta = 58.7\%$) when 12 mass% NaCl was used as the additive. This difference is attributed to the high latent heat of evaporation of NaCl, with consequent occurrence of a long after-burn effect that is beneficial for the formation of well-developed rod-like crystals.

The originality of this work is to analyze kinetic of the reaction on propagation based on a model established by Boddington, which shows that different additives give rise to different reaction rate and degree of conversion. These conclusions are very important, since they permit a better approach to the complexity of CS processes. We are now able to better control any reaction system, and thus the application of CS.

Additionally, the comparative analysis indicates that NaCl is a potential additive for industrial-scale production of β -SiAlON powders, which is a more economic and energy-efficient synthesis process. This new process has several notable advantages: the production efficiency should be greatly improved because of the small amount of additive, a product with a fine grain size is obtained, and the high cost of postsynthesis treatments such as crushing and milling is avoided. Therefore, the overall production cost of β -SiAlON can be significantly reduced, and the lower price of these β -SiAlON powders may open up new applications for these materials.

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Figure captions

Fig. 1 Schematic diagram of horizontal-type combustion synthesis (CS) apparatus.

Fig. 2 Experimental procedure for CS of β -SiAlON using (a) 45 mass% β -SiAlON product as diluent, which was first CSed with addition of commercial SiAlON, and (b) 12 mass% NaCl.

Fig. 3 SEM images of raw materials for CS of β -SiAlON: (a) D45, (b) N12.

Fig. 4 Particle size distribution of the raw materials for CS of β -SiAlON: (a) D45, (b) N12.

Fig. 5 Heat content of β -SiAlON and NaCl during CS. Zones I and II were determined based on previous studies (Ref. 29 and 30).

Fig. 6 Changes in enthalpy of raw materials ΔH (kJ/kg) for CS of β -SiAlON powders with addition of β -SiAlON and NaCl, calculated from Fig. 3; “1” and “2” indicate first and second endothermic stages.

Fig. 7 Temperature profiles (T. C. 1) recorded during CS of β -SiAlON: (a) D45, (b) N12.

Fig. 8 First derivative dT/dt (a and c) and second derivative d^2T/dt^2 (b and d) of temperature profiles during CS of β -SiAlON, D45 (a and b) and N12 (c and d).

Fig. 9 Plots of $\ln(T-T_0)$ vs. t for inert zone of temperature profiles, rise zone (a and c) and decay zone (b and d).

Fig. 10 Time dependence of reaction rate ($d\eta/dt$) and fraction reacted (η) for CS of β -SiAlON: (a) D45 and (b) N12.

Fig. 11 XRD patterns of CSed β -SiAlON powders, (a) D45 and (b) N12.

Fig. 12 SEM images of CSed β -SiAlON powders: (a) D45 and (b) N12.

Table 1

Specific heat capacity and heat capacity formula of β -SiAlON and NaCl

Materials	Cp (kJ/kg·K)	Heat capacity formula				
	(T=298K)	(kJ/kg·K)				
β -SiAlON	0.731	$-0.17304+3.99*10^{-3}T-3.51967*10^{-6}T^2+1.05768*10^{-9}T^3$				
		(298≤T≤1900K)				
NaCl	0.861	$A+B*10^{-3}T+C*10^5T^{-2}+D*10^{-6}T^2$				
		A	B	C	D	T
		0.96328	-0.2227	-0.05857	0.374074	(298≤T≤900K)
		1.003319	-0.30512	-0.08372	0.42005	900≤T≤1073.
		-0.43311	1.303886	6.810277	-0.30219	1073≤T≤1500
		1.145458	0	0	0	1500≤T≤2500

Table 2

Characteristic parameters calculated from samples

Sample	Wave velocity (mm/s)	Lattice constant (Å)		Calculated z value
		a	c	
D45	0.168	7.6350	2.9331	1.05
N12	0.185	7.6310	2.9309	0.94

Table 3

Parameters calculated from temperature profiles

Sample	t_r (s)	t_d (s)	t_x (s)	t^* (s)	τ_{ad} (K)
D45	19.75	363.64	343.89	20.89	2040
N12	11.19	483.09	471.90	11.46	2271

t_r : inert rise time

t_d : inert decay time

t_x : thermal relaxation time of system

$1/t^* = 1/t_r - 1/t_d$

τ_{ad} : temperature rise under adiabatic conditions

Fig. 1

(a) Conventional method

(b) Proposed Method

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

(a) D45

(b) N12

Fig. 10

Fig. 11

Fig. 12