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# Carbon-thermal reduction and nitridation of mixtures of $SiO_2$ and $Al_2O_3 \cdot 2H_2O$

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Sialon powders have been prepared by heating mixtures of $SiO_2$, $Al_2O_3 \cdot 2H_2O$ and carbon in flowing nitrogen at 1470° C. The nitrogen content in the product powder increased with increasing added carbon, and was independent of both the flow rate of nitrogen gas and the surface area of pellet. The amount of SiO lost increased with an increase in the flow rate of nitrogen gas and surface area of the pellet and with a decrease in the amount of added carbon. A major part of the SiO evolved by the carbon reduction was trapped by carbon then consumed by carbon reduction and nitridation to form the sialon powder. The rest of the SiO was carried out of the system by the nitrogen gas. The amount of SiO lost and the nitrogen content can be estimated using the residual carbon content.

## 1. Introduction

$\beta$-sialon of a general formula $Si_{6-z}Al_zO_zN_{8-z}$ ($0 < z \leqslant 4.2$) [1] has been obtained not only by heating mixtures of $Si_3N_4$, AlN and $Al_2O_3$ [2, 3] but also by reduction and nitridation of powders in the system $SiO_2$–$Al_2O_3$ [4–8]. However, the evolution and loss of SiO during the preparation of the sialon powder have not been examined. In a previous study [9], we prepared sialon powders by heating a mixture of $SiO_2$, $Al_2O_3 \cdot 2H_2O$ and carbon in a flowing nitrogen atmosphere, and discussed the effect of the heating temperature on the formation and morphology of the sialon powder. It has been indicated [9] that some of the silicon atoms are lost in the form of SiO during carbon reduction and the nitridation reaction at 1470° C, whereas no silicon atoms are lost during the reaction at 1350° C. However, conditions for the nitridation reaction have not been correlated with the evolution and loss of SiO.

In the preparation of $Si_3N_4$ from $SiO_2$ by carbon reduction and nitridation, the SiO produced due to the carbon reduction of $SiO_2$ is involved in the reaction process [10]. Therefore, it seems that the process of preparing sialon should involve the formation of SiO. On this basis, the participation of SiO in the carbon reduction and nitridation reaction is one of the major concerns of this paper. The chemical composition of the resulting sialon powder is dependent on the amount of SiO lost, which may depend on experimental factors such as the amount of carbon, size of pellets, nitrogen flow rate or treatment time. Thus chemical analysis of the sialon is necessary. It is convenient to elucidate the relationship between the loss of SiO and the residual carbon for evaluating the chemical composition of the sialon powders because the amount of residual carbon can be determined more easily than the silicon or nitrogen content. The amount of SiO lost will be correlated with the residual carbon, and the composition of the sialon powder will be estimated for comparison with the analysed one.

## 2. Experimental details

Amorphous silica, 1 to 10 μm particle size (Denki Kagaku Kogyo Co. Ltd, Tokyo), and carbon black with 10 wt % ignition loss (MA600, Mitsubishi Chemical Industries, Ltd, Tokyo) were employed as the source of $SiO_2$ and C [9], respectively. $Al_2O_3 \cdot 2H_2O$ was supplied by Iwatani Kagaku Co. Ltd, Tokyo (commercial name: RH40) [9]. Equation 1 shows the carbon reduction and nitridation reaction for a mixture of $SiO_2$ and $Al_2O_3 \cdot 2H_2O$ (molar ratio $Si/Al = 1$)

$$3SiO_2 + 1.5(Al_2O_3 \cdot 2H_2O) + xC + (x/3)N_2 \rightarrow Si_3Al_3O_{(10.5-x)}N_{2x/3} + xCO + 3H_2O \qquad (1)$$

The product powder is not necessarily composed of a single phase but is usually a mixture of a few phases like $\beta$-sialon, $\alpha$-$Al_2O_3$ or AlN-polytype sialons. The product with $x = 7.5$ has the same composition as $\beta$-sialon with $z = 3$ ($Si_3Al_3O_3N_5$). SiO is evolved by the carbon reduction of $SiO_2$ above 1400° C and is lost by evaporation into the atmosphere [9]

$$SiO_2 + C \rightarrow SiO + CO \qquad (2)$$

From Equations 1 and 2, the over-all reaction of the carbon and nitridation of the system $SiO_2$–

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$Al_2O_3 \cdot 2H_2O$ is

$$3SiO_2 + 1.5(Al_2O_3 \cdot 2H_2O) + xC + (x - y)/3N_2 \rightarrow ySiO + Si_{(3-y)}Al_3O_{(10.5-x-y)}N_{2(x-y)/3} + xCO + 3H_2O \quad (3)$$

where $x$ and $y$ represent the amount (mol) of consumed carbon and lost SiO, respectively. Aluminium is not lost during the reaction. The value of $x$ is obtained from the amount of added $(=x_a)$ and residual $(=x_r)$ carbon

$$x = x_a - x_r \quad (4)$$

$C_a$ represents the ratio of excess carbon defined as the ratio $x_a/7.5$ where the stoichiometric reaction proceeds with $x = 7.5$ mol in Equation 1 and produces $Si_3Al_3O_3N_5$. With $l$, $m$ and $n$ denoting the amount (mol) of silicon, oxygen and nitrogen in the product, respectively, the composition of the product powder can be represent as $Si_lAl_3O_mN_n$, where

$$\begin{aligned} l &= 3 - y \\ m &= 10.5 - x - y \\ n &= 2(x - y)/3 \end{aligned} \quad (5)$$

The batches of $SiO_2$, $Al_2O_3 \cdot 2H_2O$ and carbon were mixed in an agate ball mill for 2 h in the presence of $n$-hexane. The molar ratio of silicon and aluminium was held at Si/Al = 1 in accordance with Equation 3. $C_a$ was varied between 0.8 and 1.4. After drying, the batches were moulded under a pressure of 30 MPa into pellets of 25 mm diameter. The height of the pellet ranged from 2.6 to 5.2 mm, depending on the charged amount of the batches from 2 to 4 g. The relative density of the pellets was about 60%. From the radius, $r$, height, $h$, and weight, $w$, of the pellet, the apparent specific surface area, $S_p$ ($cm^2\ g^{-1}$), is

$$S_p = 2\pi r(r + h)/w \text{ or } 2(1/r + 1/h)/d \quad (6)$$

where $d$ represents the bulk density ($g\,cm^{-3}$) of the pellet.

The pellets were placed in a mullite tube furnace heated by an SiC element. The temperature was raised at a rate of 10° C $min^{-1}$ and was held at 1470° C for 0 to 5 h. During the heat treatment, nitrogen flowed at a linear rate, $R_N$, of 0 to 70 cm $min^{-1}$ (0 to 490 $cm^3\ min^{-1}$ in volume flow rate).

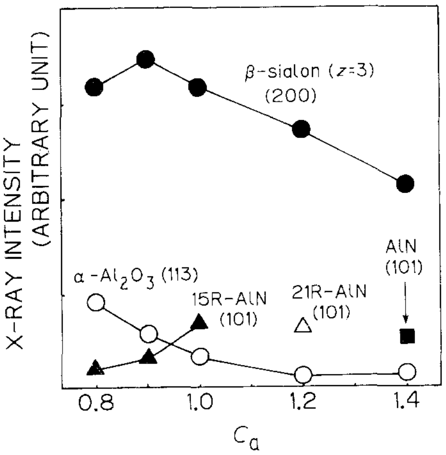

*Figure 1* Change in the XRD intensities for each crystalline phase in the sialon powder from the batches of various amounts of the added carbon, $C_a$, after the treatment at 1470° C for 5 h; $R_N$ = 40 cm $min^{-1}$, $S_p$ = 4.3 $cm^2\ g^{-1}$. The indices of the planes are indicated in parentheses.

The crystalline phases in the product powder were identified by the X-ray diffraction (XRD) technique using Cu$K\alpha$ radiation. The product powder was chemically analysed as in the previous study [8]. Silicon and aluminium were determined by the dehydration method (Japan Industrial Standard, M8854) and by titration with CyDTA and zinc standard solution, respectively [11]. The residual carbon content was analysed by measuring the volume of $CO_2$ which was evolved on firing the product. The nitrogen content was calculated from the volume of $NH_3$ which was evolved by the reaction of the product with NaOH. The oxygen content was obtained by subtraction.

## 3. Results and discussion

### 3.1. Compositions of the product powder

The XRD traces indicated the presence of α-$Al_2O_3$, AlN-polytype sialon (15R–AlN, 21R–AlN) [1] and AlN as well as β-sialon in the product powders. For the powder due to the treatment at 1470° C for 5 h under $R_N$ = 40 cm $min^{-1}$ (280 $cm^3\ min^{-1}$ volume flow rate), the measured lattice constant shows that the β-sialon is the stoichiometric phase with $z = 3$. Fig. 1 shows the XRD intensity of the (2 0 0) plane for β-sialon ($z = 3$), the (1 1 3) plane for α-$Al_2O_3$, and the (1 0 1) plane for the 15R–AlN, 21R–AlN and AlN. The β-sialon had the strongest XRD intensity amongst the crystalline phases in each powder. The intensity of the (2 0 0) reflection for the β-sialon reached a maximum for $C_a = 0.9$ and decreased in the range $C_a > 0.9$. 15R–AlN appeared in the range $0.8 \leqslant C_a \leqslant 1.0$. 21R–AlN and AlN were detected for $C_a$ = 1.2 and 1.4, respectively. The nitrogen content in the β-sialon ($z = 3$), 15R–AlN, 21R–AlN and AlN is 25, 25, 28 and 37 wt %, respectively. Thus, the phase having the higher nitrogen content was produced in the batches with larger $C_a$.

Table I lists the content (wt %) of silicon, aluminium, carbon, nitrogen and oxygen for the same product powders which have been indicated in Fig. 1. The nitrogen content increased and the oxygen content decreased with increasing $C_a$. It should be noted that some of the added carbon was left unreacted in the product as residual carbon. According to Table I, 78 to 96 mol % carbon in the batches had been consumed

TABLE I Analysed compositions of a series of sialon powders prepared by the treatment of $SiO_2$–$Al_2O_3 \cdot 2H_2O$–C batch pellets at 1470° C for 5 h. Linear nitrogen flow rate, $R_N$ = 40 cm $min^{-1}$; apparent specific surface area of pellets, $S_p$ = 4.3 $cm^2\ g^{-1}$; $C_a$ denotes the ratio of excess carbon, $x_a/7.5$ (see text)

| $C_a$ | Analysed content (wt %) | | | | |
|---|---|---|---|---|---|
| | Si | Al | C | N | O |
| 0.8 | 23.8 | 32.8 | 1.3 | 18.7 | 23.4 |
| 0.9 | 25.1 | 31.6 | 1.9 | 20.6 | 20.8 |
| 1.0 | 25.6 | 31.4 | 3.0 | 22.2 | 17.8 |
| 1.2 | 26.8 | 30.4 | 4.6 | 25.5 | 12.7 |
| 1.4 | 26.7 | 28.2 | 9.6 | 26.1 | 9.4 |

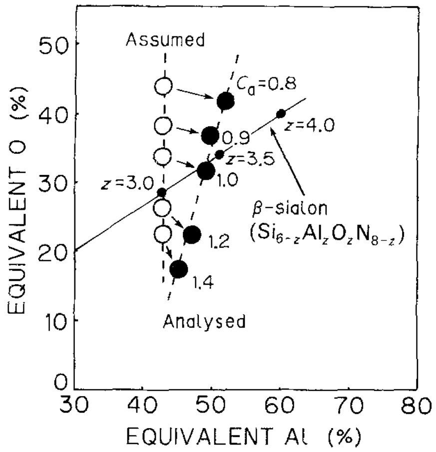

*Figure 2* Compositions of sialon powders prepared at 1470° C for 5 h are plotted in the sialon constitutional diagram for each $C_a$ (●). The vertical broken line represents the trace of the composition $Si_3Al_3O_{(10.5-x)}N_{2x/3}$ (○), where $x$ is the amount of consumed carbon (see Equation 1). The solid line represents the composition of β-sialon, $Si_{6-z}Al_zO_zN_{8-z}$. $R_N$ = 40 cm min$^{-1}$, $S_p$ = 4.3 cm$^2$ g$^{-1}$.

during the treatment. Fig. 2 is the sialon constitutional diagram in which the composition of the product powders is plotted. Equivalent aluminium and oxygen are represented as [1]

$$\text{equivalent Al} = 3[\text{Al}]/(3[\text{Al}] + 4[\text{Si}]) \times 100\ (\%)$$

$$\text{equivalent O} = 2[\text{O}]/(2[\text{O}] + 3[\text{N}]) \times 100\ (\%)$$

where [Al], [Si], [O] and [N] are the molar fractions of the elements in the product powder. Equivalent nitrogen and silicon are complementary quantities of equivalent oxygen and aluminium, respectively. The larger solid circles in Fig. 2 represent the analysed compositions indicated in Table I. The open circles represent the compositions calculated by assuming that the reaction proceeds as shown by Equation 1 without the loss of silicon. The assumed compositions, $Si_3Al_3O_{(10.5-x)}N_{2x/3}$, depends only on the values of equivalent oxygen and nitrogen. Thus they fall on the vertical broken line. The solid line indicates a trace of the composition of β-sialon ($Si_{6-z}Al_zO_zN_{8-z}$) for various values of $z$, and the plots for $z$ = 3, 3.5 and 4 are indicated by the smaller solid circles. Fig. 2 illustrates that the difference between the analysed composition and the assumed composition, i.e. the length of the arrows, decreases as $C_a$ increases, and that the analysed composition is richer in aluminium and nitrogen than the assumed composition. This result indicates that silicon has been lost during the treatment in the form of SiO which is produced by carbon-reduction of $SiO_2$ (Equation 2). According to Equation 1, the batch with $C_a$ = 1.0 can be expected to result in the product of the same composition as the stoichiometric β-sialon ($z$ = 3). However, the analysed composition of the product for $C_a$ = 1.0 is almost the same as that of β-sialon with $z$ = 3.4. The larger values of $C_a (> 1)$ results in the higher equivalent nitrogen in the product than in β-sialon, suggesting that the larger $C_a$ causes the greater extent of the carbon-reduction and nitridation. Similar results have been obtained for other series of powders prepared under different conditions.

## 3.2. Factors controlling the carbon reduction and nitridation reactions

The change in the content of each component atom during the treatment has to be calculated and properly represented. The subtraction of the content (wt %) in the product powder from that in the batch gives no proper change (gain or loss) in the amount of the component because the total amount of the reacting powder always varies: for example, carbon is lost as CO as the reaction proceeds. On this basis, the nitrogen content and the amount of lost SiO have been represented by $n$ and $y$ (mol) appearing in Equations 3 and 5.

### *3.2.1. The linear flow rate of nitrogen, $R_N$*

Fig. 3a illustrates the plot of $n$ and $y$ as a function of the linear flow rate of nitrogen gas ($R_N$) for the pellets with $C_a$ = 0.9 and $S_p$ = 4.3 cm$^2$ g$^{-1}$ (3.9 mm high), treated at 1470° C for 3 h. $n$ is almost zero in the absence of flowing nitrogen, and is approximately 3.5 mol with $R_N \geqslant$ 10 cm min$^{-1}$. Not only is nitrogen the reactant, but it also plays the role of carrying gas for SiO and CO. Van Dijen *et al.* [7] reported that for very low values of $R_N$ the nitridation reaction rate is determined by the mass transfer, i.e. the removal of CO from the reactor. According to Equation 1, CO has to be removed for the nitridation reaction to proceed. Because CO is difficult to remove from the reactor at $R_N$ = 0, the nitridation reaction hardly takes place. On the other hand, for sufficiently larger values of $R_N$, the chemical reaction is the rate-controlling-step [7]. This is the reason why $n$ appears independent of $R_N$ at $R_N \geqslant$ 10 cm min$^{-1}$. The amount of lost SiO, $y$, increased with increasing $R_N$. The value of $y$ at $R_N$ = 70 cm min$^{-1}$ is about twice as large as that at $R_N$ = 10 cm min$^{-1}$, and is about 20% of the total amount of silicon. Such a relationship between

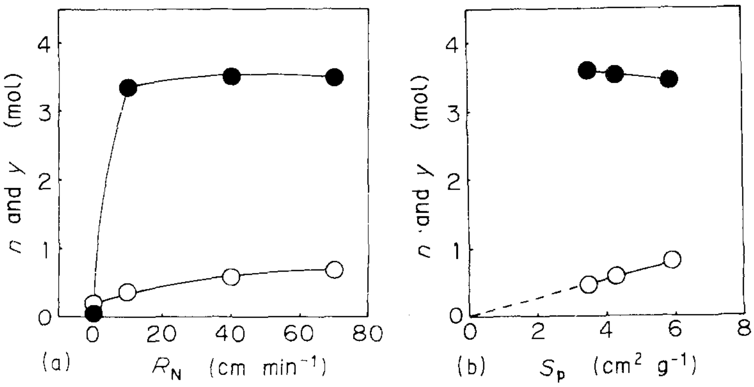

*Figure 3* (a) The nitrogen content, (●) $n$, and the amount of lost SiO, (○) $y$ (mol), as a function of nitrogen flow rate, $R_N$, after the treatment at 1470° C for 3 h. $S_p$ = 4.3 cm$^2$ g$^{-1}$, $C_a$ = 0.9. (b) (●) $n$ and (○) $y$ (mol) as a function of apparent specific surface area of pellet, $S_p$, after the treatment at 1470° C for 3 h. $R_N$ = 40 cm min$^{-1}$, $C_a$ = 0.9.

the loss of SiO and $R_N$ should be emphasized because the formation reaction of SiO (Equation 2) does not explicitly involve nitrogen. If all of the evolved SiO is lost and does not contribute to the sialon formation, the mass transfer seems to be the rate-controlling step for the evolution of SiO. However, if any portion of the evolved SiO is involved in the sialon formation, the increase in $y$ (lost SiO) with $R_N$ can be attributed to some process other than the mass transfer.

### 3.2.2. *Apparent specific surface area, $S_p$*

Fig. 3b illustrates the variation of $n$ and $y$ as a function of the apparent specific surface area, $S_p$, of the pellets which have been treated at 1470° C for 3 h under $R_N = 40\,\mathrm{cm\,min^{-1}}$. $n$ is almost independent of $S_p$ around 3.5 mol, while $y$ is proportional to $S_p$ and increases up to 0.8 mol. In other words, the nitrogen content is independent of the size of the pellet, and the amount of lost SiO increases with decreasing size of the pellet because $S_p$ decreases with increasing radius or height of the pellet as shown by Equation 6. If the rate of evolution of SiO determined by the mass transfer, i.e. the amount of evolved SiO is equal to that of lost SiO, the amount of lost SiO has to be independent of $S_p$ under the constant value of $R_N$. However, Fig. 3b indicates the dependence of lost SiO on $S_p$. Therefore, it is suggested that the amount of evolved SiO is not equal to that of lost SiO, i.e. a portion of evolved SiO is lost with the carrying gas and the rest of the SiO participates in the nitridation reaction. The SiO evolved near the surface of the pellet will be most easily lost. This is why the amount of lost SiO is dependent on the flow rate of the carrying gas and the specific surface area of the pellet as seen in Figs 3a and b.

### 3.2.3. *The amount of carbon, $C_a$*

$n$ and $y$ are plotted as a function of soaking time up to 5 h in Figs 4a and b, respectively. The pellets have been treated at 1470° C under $R_N = 40\,\mathrm{cm\,min^{-1}}$. It is shown that the nitridation reaction rigorously occurs within 2 h then proceeds slowly. It is reasonable that $n$ should increase with increasing $C_a$, because greater amounts of added carbon will enhance the carbon reduction and subsequent nitridation. In Fig. 4b, $y$ decreases with increasing $C_a$, showing that carbon depresses the loss of SiO. $y$ increased rapidly between 2 and 3 h for $C_a = 0.8$, between 3 and 4 h for $C_a = 0.9$ and between 4 and 5 h for $C_a = 1.0$. The broken line corresponds to $y = 0.54$ mol above which $y$ increases rapidly again. The region for $y < 0.54$ mol is termed Region I and that for $y > 0.54$ mol is termed Region II.

## 3.3. Reactions in the pellet

The values of $y$ in Fig. 4b have been plotted in Fig. 5 as a function of the residual carbon content, $x_r$, in the product powders for various values of $C_a$ ranging from 0.8 to 1.4: the treatment is conducted at 1470° C for 0 to 5 h. The variation of $y$, irrespective of the soaking time and $C_a$, can be represented by the two fragments of line, except the plot for $C_a = 1.4$ shown by the open squares. A bending is seen at $x_r = 0.8$ mol. The slope of the line in the range $x_r < 0.8$ mol is much greater than that in the range $x_r > 0.8$ mol. It is noted here that the ranges $x_r < 0.8$ and $x_r > 0.8$ mol correspond to Regions II and I in Fig. 4b. The results indicate that the residual carbon controls the loss of SiO: in Region I, with much carbon in the reacting system, the evolved SiO can be easily trapped by carbon and nitrided, while in Region II the SiO has less chance to be trapped for the nitridation because of the lower residual carbon content.

Fig. 6 proposes a model of the carbon reduction and nitridation. As nitrogen is supplied to the pellet by the gas flow, the carbon reduction and nitridation take place at the inner part of the pellet and the flowing nitrogen carries away the evolved CO. Most of the SiO which is evolved inside the pellet is trapped by the carbon. The rest of the SiO cannot be trapped by the carbon and is evaporated into the carrying nitrogen gas. The SiO gas evolved near the surface of the pellet is difficult to trap by the carbon because of a shorter transfer pass and time, and is probably lost. The trapped SiO is used for the carbon reduction and nitridation (Equation 7) because silicon and SiC cannot be detected in the product by analysis.

$$\mathrm{SiO} + \mathrm{N}^- + \mathrm{C} \rightarrow \mathrm{Si{-}N} + \mathrm{CO} \qquad (7)$$

The sialon powder is formed by the reaction of Si–N and Al–O. This process is similar to the formation of $\mathrm{Si_3N_4}$ by the carbon reduction and nitridation of $\mathrm{SiO_2}$ [10]. With $C_a = 1.4$, the carbon reduction and nitridation of $\mathrm{Al_2O_3}$ ($\mathrm{Al{-}O} + \mathrm{N}^- + \mathrm{C} \rightarrow \mathrm{Al{-}N} + \mathrm{CO}$)

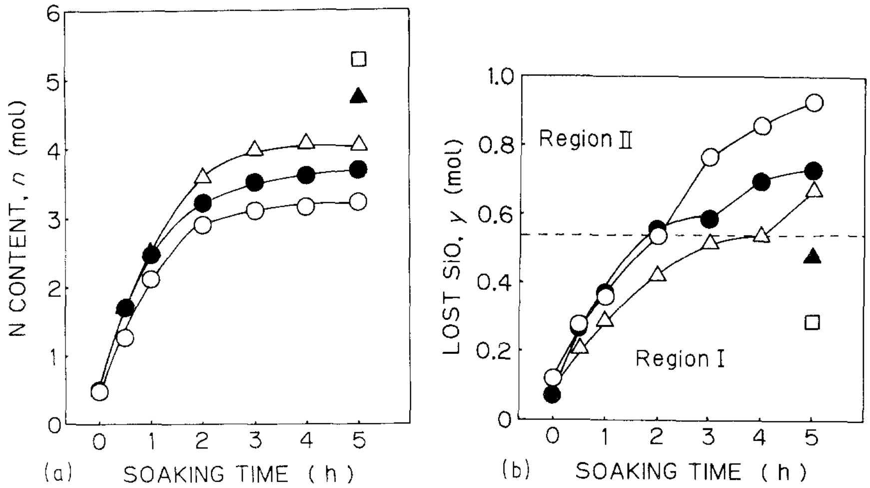

*Figure 4* Change in (a) the nitrogen content, $n$ (mol), and (b) the amount of lost SiO, $y$ (mol), with soaking time; $R_N = 40\,\mathrm{cm\,min^{-1}}$, $S_p = 4.3\,\mathrm{cm^2\,g^{-1}}$, treating temperature = 1470° C. $C_a$ = (○) 0.8, (●) 0.9, (△) 1.0, (▲) 1.2, (□) 1.4.

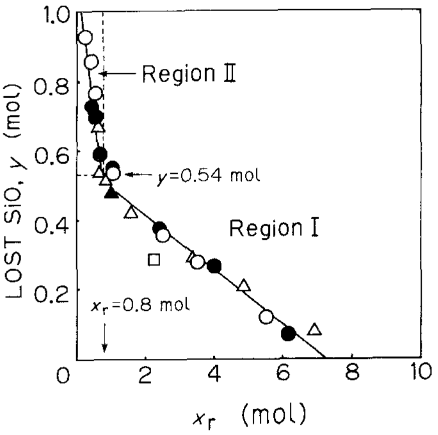

*Figure 5* Plots of the loss of SiO, $y$ (mol), as a function of the residual carbon content, $x_r$ (mol). The data are cited from Fig. 4b. $C_a$ = (○) 0.8, (●) 0.9, (△) 1.0, (▲) 1.2, (□) 1.4.

also takes place because AlN is detected in the XRD traces as shown in Fig. 1. This is the reason for the deviation of the plot for $C_a = 1.4$ from the $y$ against $x_r$ curve in Fig. 5.

## 3.4. Evaluation of the composition

For the chemical analysis of the product, the determination of silicon and nitrogen contents requires complicated procedures, whereas the residual carbon content is determined in a much easier way. Fig. 5 indicates that the amount of lost SiO and the nitrogen content can be correlated to the amount of residual carbon as long as the experimental conditions of the heat treatment (temperature, nitrogen gas flow rate, size of pellet and etc.) are known. Equation 8 is the empirical relation between $y$ and $x_r$ obtained from the least squares fit for the curves in Fig. 5

$$\begin{aligned} y &= -0.08x_r + 0.58 \qquad (0.8 < x_r)\ (\text{mol}) \\ &= -0.8x_r + 1.13 \qquad (0 \leqslant x_r \leqslant 0.8)\ (\text{mol}) \end{aligned} \tag{8}$$

The nitrogen content, $n$ (mol), in the product is $2(x - y)/3$ according to Equation 5. Therefore, it can be expressed in the terms of $x_a$ and $x_r$

$$\begin{aligned} n &= (x_a - 0.92x_r - 0.58)2/3 \qquad (0.8 < x_r)\ (\text{mol}) \\ &= (x_a - 0.2x_r - 1.13)2/3 \\ &\qquad (0 \leqslant x_r \leqslant 0.8)\ (\text{mol}) \end{aligned} \tag{9}$$

Fig. 7 illustrates the correlation between the nitrogen content from the chemical analysis and that from the estimation due in Equation 9. The maximum and average deviation of the estimated value of the nitrogen content from the analysed one is 0.3 and 0.1 mol, respectively. It is concluded that the estimated nitrogen content of the product in this study agrees well with the analysed nitrogen content.

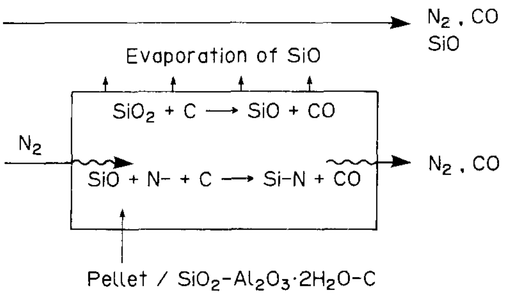

*Figure 6* A proposed model for the carbon reduction, nitridation and loss of SiO in the pellet during the heat treatment.

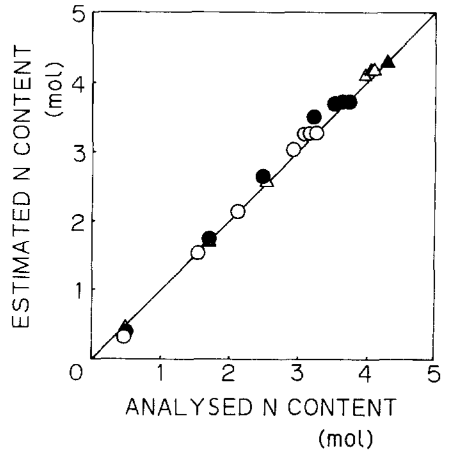

*Figure 7* A comparison between the estimated nitrogen content (from Equation 9) and the analysed nitrogen content. $C_a$ = (○) 0.8, (●) 0.9, (△) 1.0, (▲) 1.2.

## 4. Conclusion

The carbon reduction and nitridation of the mixture of $SiO_2$ and $Al_2O_3 \cdot 2H_2O$ was carried out in a flowing nitrogen atmosphere at 1470° C and sialon powders were prepared chiefly composed $\beta$-sialon ($z = 3$). A major part of the evolved SiO was consumed by the carbon reduction and nitridation to constitute the sialon powder. The rest of the SiO was evaporated into the flowing nitrogen gas. The amount of the SiO lost increased with increasing flow rate of nitrogen gas and the surface area of the pellets. The nitrogen content and amount of the SiO lost have been correlated with the amount of residual carbon in the product from which the composition of the product powder can be estimated.

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