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The carbothermal reduction process of a montmorillonite–polyacrylonitrile intercalation compound

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To develop a carbothermal reduction process for the conversion of oxides to nitrides, a montmorillonite–polyacrylonitrile (PAN) intercalation compound was applied as a precursor. Montmorillonite–carbon mixtures were heated as well as the intercalation compound in N_2 at 1100 to 1500° C for comparison. From the intercalation compound, β-sialon, AlN and SiC were mainly formed. Oxides were reduced without their crystallization. On the other hand, in the reactions of the mixtures, some oxides and other kinds of nitride were obtained as principal products in addition to these phases. Furthermore, the intercalation compound was more favourable than the mixtures having a larger amount of carbon in terms of the reduction of oxides and the formation of nitrides. These observations suggest that the layered structure of the intercalation compound led to an effective and specific carbothermal reduction process.

1. Introduction

Sialons are compounds in the Si_3N_4–AlN–Al_2O_3–SiO_2 system [1]. Among them, β-sialon ($Si_{6-z}Al_zO_zN_{8-z}$, $z \doteqdot 0$ to 4.2) has a β-Si_3N_4 structure, and has been regarded as a candidate for structural materials as well as silicon nitride and silicon carbide. β-sialon can be obtained directly by the carbothermal reduction of aluminosilicates; kaolinite [2–8], pyrophyllite [5], illite [7] and volcanic ash [9] have been converted to β-sialon.

It is well known that some oxides having layered structures can take up a variety of organic materials to form intercalation compounds [10]. When carbonizable polymer is intercalated, carbonaceous layers form in the interlayer space by heat treatment in an inert atmosphere. The resulting compound is an extremely intimate mixture of oxides and carbonaceous materials, since both kinds of layer show a thickness of nanometre order.

In terms of the mixing condition of the starting materials for carbothermal reduction. Zhang and Cannon [11] observed little difference between the mixture of fine particles and that obtained by using a sol-gel process during the conversion of SiO_2 to Si_3N_4. Nevertheless, the intercalation compounds are more specific due to their ordered two-dimensional structures. Hence, they can be more advantageous as precursors for the carbothermal reduction process.

Montmorillonite is one of the common clay minerals having an SiO_2–Al_2O_3-based composition, and it forms a variety of intercalation compounds [12]. The present authors have already reported preliminary results on the conversion of a montmorillonite–polyacrylonitrile (PAN) intercalation compound to β-sialon [13] and SiC [14]. In the present study, the carbothermal reduction process of the montmorillonite-PAN intercalation compound in an N_2 atmosphere was characterized by infrared (IR) spectroscopy, inductively coupled-plasma emission spectroscopy (ICP), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA) as well as X-ray powder diffraction (XRD). Also, the process in montmorillonite–carbon mixtures was investigated to clarify the advantages arising from the formation of the intercalation compound.

2. Experimental procedure

2.1. Preparation of the intercalation compound

The preparation of the montmorillonite–PAN intercalation compound and its heat treatment for the cyclization of PAN were the same as described before [13]. In the present work, n-butylammonium-montmorillonite was used instead of n-hexylammonium-montmorillonite. The intercalation of PAN and its cyclization were confirmed by XRD (Rigaku RAD II-A, Fe*Kα* radiation with manganese filter), IR (Shimadzu IR-400, KBr method) and thermogravimetry (TG) (Shimadzu TGA-20) in the same manner as reported previously [13]. After heat treatment at 220° C in air, the basal spacing of the complex was 1.83 nm, which was larger than that of n-butylammonium-montmorillonite (1.33 nm). The carbon content of the heat-treated complex was 44.7 wt %. After the amount of the residue from the ammonium ion was subtracted, the amount of carbon involved in the reaction was calculated on the basis of the assumption that the carbon yield from PAN was 50% [15].

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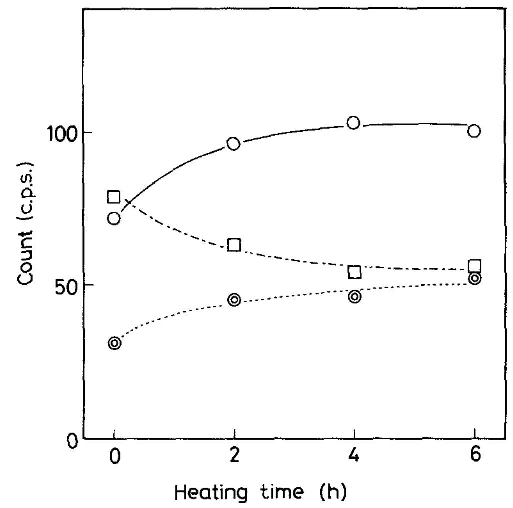

Figure 1 The variation in the composition of the products from the montmorillonite–PAN intercalation compound with heating time. (○) β-sialon, (□) SiC, (◎) AlN.

When it was expressed as a molar ratio of carbon to the SiO_2 component of montmorillonite (C/SiO_2), the ratio was found to be about 2.7.

2.2. Preparation of the mixtures

The montmorillonite–carbon mixtures were prepared as follows. Montmorillonite (– 100 mesh) and carbon black (Koso Chemical Co., Tokyo, $< 22\,\mu m$) were mixed with an excess of n-hexane. The mixing ratios (expressed as the C/SiO_2 ratio) were 2 and 5 in the present work. The mixtures were dried and crushed to pass a 100 mesh sieve.

2.3. Heat treatment in N_2

About 0.7 g of these samples was placed in an Al_2O_3 boat ($\leqslant 1400°$ C) or a BN boat (at 1500° C) in a tube furnace and heated in an N_2 flow. The reaction temperature varied from 1100 to 1500° C for the 2 h treatment. For variation in heating time, the reaction temperature was fixed at 1400° C. The heating and cooling rates were $5°\,C\,min^{-1}$ above 700° C. The flow rate of N_2 gas was $500\,ml\,min^{-1}$ in all the experiments.

2.4. Analyses

The products were analysed by XRD to identify crystalline phases. For quasi-quantitative analysis, the peak height of each phase was measured after decarbonization at 650° C for 3 h in air. The peaks used were as follows; β-sialon: (1 1 0), $d = 0.380$ nm for Fig. 1 (below) and (1 0 0), $d = 0.663$ nm for Fig. 2 (d values are for β-Si_3N_4); AlN: (1 1 0), $d = 0.156$ nm; the O′ phase: (2 0 0), $d = 0.444$ nm (d value is for Si_2N_2O); SiC: (2 2 0), $d = 0.154$ nm (Miller index is for the β form); and mullite: (1 1 0), $d = 0.539$ nm. No peaks were available for spinel in Fig. 2 due to the overlapping. In addition, approximate compositions of β-sialon were determined from the positions of its XRD peaks. Because most of its intense peaks were overlapped with those of other phases, only the (2 0 0) line was available*. The compositions were then calculated from the obtained lattice parameter a [1]. IR spectra (Shimadzu IR-435, KBr method) of the products were recorded in the range from 1300 to $400\,cm^{-1}$. Also, the morphology of the products and their EPMA analysis were studied (Hitachi HXM-2B).

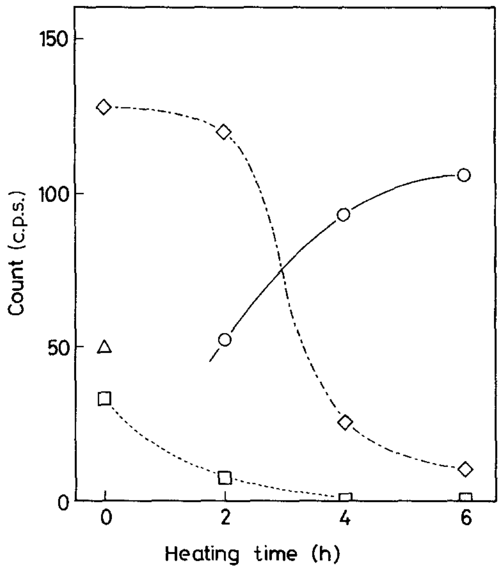

Figure 2 The variation in the composition of the products from the montmorillonite–carbon mixture ($C/SiO_2 = 2$) with heating time. (○) β-sialon, (□) SiC, (◇) O′ phase, (△) mullite.

Furthermore, the products were dissolved to determine the ratios of metals. About 30 to 50 mg of the products was heated in a platinum crucible with ca. 2 g of Na_2CO_3 at ca. 1000° C for 1 h. After the dissolution of SiO_2 in water, 200 ml of 0.5 M HNO_3 was added. Then the solutions were diluted to a total volume of 250 ml with water. They were analysed by ICP (Nippon Jarrell-Ash ICAP-575 II) to obtain Si/Al and Mg/Al ratio.

3. Results and discussion

3.1. Thermal transformation of montmorillonite

Initially, the thermal transformation of the montmorillonite used in the present study was investigated, because the high-temperature phases depended on its occurrence [16]. The raw montmorillonite was heated under the same conditions without the presence of any carbonaceous materials. Table I shows the crystalline phases. Cristobalite, mullite ($3SiO_2{\cdot}2Al_2O_3$), spinel ($MgAl_2O_4$) and cordierite ($Mg_2Al_4Si_5O_{18}$) were formed by the treatments at 1100 to 1400° C. Their formation is in line with the thermal transformation of the montmorillonites which were classified as the mixture of Cheto and Wyoming types by Grim and Kulbicki [16].

3.2. The variation in the compositions of the crystalline phases

3.2.1. Preparation from the montmorillonite–PAN intercalation compound

Table I lists the crystalline phases obtained from the montmorillonite–PAN intercalation compound. As main products, β-sialon, AlN and SiC were detected. A trace of the X phase was formed by the treatment

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*The (2 0 0) diffraction line of silicon with Fe$K\beta$ was used as an internal standard.

TABLE I Principal crystalline phases of the products

Reaction temperature (°C)	Heating time (h)	Phases*			
		Montmorillonite	n-$CH_3(CH_2)_3NH_3^+$–Montmorillonite–PAN complex	Montmorillonite–carbon mixtures	
				$C/SiO_2 = 2$	$C/SiO_2 = 5$
1100	2	Cri $\gg$ Mu, Sp	β	Mu $\gg$ sp	Mu $\gg$ Cri, Sp
1200	2	Mu > Sp	$\beta \gg$ SiC, X	SiC, Mu > Cor, Sp	α, SiC, Mu, Cor > Sp
1300	2	Mu > Cor	β, SiC $\gg$ AlN	O′, SiC, Mu > β, Sp	α, SiC, Mu, Sp > β, Cor > O′
1400	0	–	SiC > β > AlN	O′, SiC, Mu > Sp	SiC $\gg \beta$, Sp > α
1400	2	Mu	β, SiC > AlN	β, O′, SiC > Sp	SiC > β > α > AlN, Sp
1400	4	–	β, SiC > AlN	β, SiC, Sp > O′	SiC > β > α > AlN > Sp
1400	6	–	β, SiC > AlN	β, SiC > Sp > O′	SiC > β > α > AlN
1500	2	–	SiC > β, AlN	β > 15R-AlN, AlON	SiC $\gg \alpha$, β, AlN

*α = α-Si_3N_4, β = β-Sialon, X = X phase, O′ = O′ phase, AlON = $Al_{(8/3)+(x/3)}O_{4-x}N_x$, Cri = cristobalite, Mu = Mullite, Sp = spinel, Cor = cordierite.

at 1200° C. In addition, an unidentified peak was observed at $d = 0.269$ nm with various heating conditions. The same peak was also detected in the reactions of the montmorillonite–carbon mixtures. It is worth noting that no crystalline oxides were formed of the kind observed in the thermal transformation of the raw montmorillonite. Since PAN was transformed to carbon with a high yield of ca. 50% [15], the layers of carbonaceous material from PAN still divided the oxide layers at high temperatures. Hence the crystallization of the oxides before their reduction was prevented. Similar observations have been reported for another montmorillonite–polymer intercalation compound [17] and a magadiite–PAN intercalation compound [18, 19].

On heating at 1100° C, a trace of β-sialon was detected. Its formation was remarkable in the reactions above 1200° C. AlN was obtained on heating the complex above 1300° C. In the reactions at 1500° C a large amount of SiC was obtained, whereas β-sialon formation was suppressed. Lee and Cutler [2] reported the presence of a boundary temperature above which SiC and AlN formed instead of β-sialon in the carbothermal reduction process of kaolinite. The present results showed a similar tendency, although the change in the compositions was not complete.

It is difficult to confirm the presence of α-SiC from the XRD patterns of the products due to the overlapping of its characteristic peaks. When the n-hexylammonium-montmorillonite–PAN complex was heated in argon, both α- and β-SiC were obtained by the treatments above 1300° C [14]. Hence, one can assume that α-SiC was also formed in the reactions above 1300° C in the present system.

TABLE II The approximate composition of β-sialon

Starting material	z*		
	Reaction temperature (°C)		
	1300	1400	1500
n-$CH_3(CH_2)_3NH_3^+$–Montmorillonite–PAN complex	2.3	2.0	2.0
Montmorillonite–carbon mixture ($C/SiO_2 = 2$)	–	2.5	3.6
Montmorillonite–carbon mixture ($C/SiO_2 = 5$)	–	1.7	1.8

*z for $Si_{6-z}Al_zN_zO_{8-z}$, obtained from the position of the (200) line.

Table II summarizes the approximate z values of β-sialon for various reaction temperatures. The values obtained were ca. 2 to 2.3, and no remarkable tendency was observed. When the SiO_2/Al_2O_3 ratio in the raw montmorillonite is assumed to be maintained during the conversion, the z value becomes 1.85. Thus the obtained β-sialon had slightly aluminium-rich compositions.

Fig. 1 shows the variation in the compositions of the products with heating time at 1400° C. In the treatment for 0 h only β-sialon, AlN and SiC formed; no oxides crystallized. It is also suggested that the reactions proceeded to a great extent during the heating and cooling schedules. As the heating time increased, the peak heights of β-sialon and AlN increased. On the other hand, that of SiC obviously decreased. This suggests that SiC was converted to β-sialon during the reactions at 1400° C. This can be ascribed to the reaction between SiO_2 and SiC [20] or the equilibrium between SiC and Si_3N_4 [21].

3.2.2. Preparation from the montmorillonite–carbon mixtures

Table I demonstrates the crystalline products from montmorillonite–carbon mixtures. In comparison with the reactions of the complex, those of the mixtures were complicated. In addition to the peaks due to the following phases, several unidentified peaks were detected.

When the C/SiO_2 ratio was 2, nitridation occurred above 1300° C. β-sialon was formed on heating above 1300° C, while the O′ phase was obtained by the treatments at 1300 and 1400° C. In the product heated at 1500° C, aluminium oxynitride (AlON) and the 15R-AlN phase were also detected. On the other hand, SiC formation was observed in the reactions at 1200 to 1400° C.

With $C/SiO_2 = 5$, nitridation occurred even at 1200° C. The crystalline compositions greatly differed from those with $C/SiO_2 = 2$. α-Si_3N_4 was formed by the treatments above 1200° C, whereas β-sialon was detected in the products heated above 1300° C. AlN formation was observed on heating the mixture above 1400° C. Also, a trace of the O′ phase was obtained by the treatment at 1300° C. SiC formed in the reactions above 1200° C. Its formation was more remarkable than that in the reactions of the mixture with $C/SiO_2 = 2$. In terms of β-sialon and AlN formation, their threshold temperatures in the reactions of the mixture were higher than those in the reactions of the complex in spite of the larger carbon content.

With both the C/SiO_2 ratios, the oxides which were obtained by the thermal transformation of raw montmorillonite were present in the products heated below 1400° C; mullite, cristobalite, spinel and cordierite were formed. Hence, the reactions of the mixtures involved the crystallization of the oxides.

The z values of β-sialon were different between the products with two C/SiO_2 ratios (Table II). Apparently, large values were obtained from the mixture with $C/SiO_2 = 2$. This observation is hard to interpret, since the products consisted of several phases.

Fig. 2 shows the effect of heating time on the compositions of the products at 1400° C. When the mixture with $C/SiO_2 = 2$ was heated for 0 h, mullite and spinel formed as well as the O′ phase and β-sialon. Mullite was reduced by the 2 h treatment, whereas spinel was still present after the treatment for 6 h. With an increase in heating time, the peak height of the O′ phase decreased while that of β-sialon increased (Fig. 2). Therefore, the O′ phase was an intermediate for β-sialon formation. SiC behaved in the same manner as the reactions of the complex. In the reactions of the mixture with $C/SiO_2 = 5$, a similar tendency was observed: initial crystallization of spinel and its reduction and nitride formation during the reactions.

3.3. IR spectra of the products

Fig. 3 shows the IR spectra of the products from the montmorillonite–PAN intercalation compound. From the IR spectra, the behaviour of the oxides was monitored, since no oxides crystallized during the reactions of the complex. The IR spectra of the products from the mixtures revealed no additional information.

The spectrum of the product heated at 1100° C (Fig. 3a) was interpreted as that of the amorphous oxides, because the amount of β-sialon in the product was only a trace. Bands at ca. 1050 and about 460 cm^{-1} were assigned to an Si–O stretching and an Si-O-Si bending mode, respectively [22]. A 560 cm^{-1} band can be ascribed to an Al–O stretching mode [23]. On heating at 1200° C (Fig. 3b), an obvious shoulder appeared at ca. 900 cm^{-1}, which was assigned to an Si–N stretching mode. Also, new bands were detected at 571 and 433 cm^{-1}, which were due to the vibrational modes of Si–N–Si and N–Si–N groups [24]. Although β-sialon shows a band at about 1030 cm^{-1} [24], the profile of the spectrum greatly differed from that of β-sialon; the intensity of the 1050 cm^{-1} band was strong for that of β-sialon. Therefore, the band in Fig. 3b was partly ascribed to the Si–O stretching mode, indicating the presence of a certain amount of amorphous SiO_2 in the products.

For treatments above 1300° C, the profiles of the spectra became similar to that of β-sialon (Figs 3c and e). Hence, most of the amorphous SiO_2 was reduced by the treatments. However, the behaviour of the Al_2O_3 component cannot be clarified from the present results. Fig. 3d shows the spectrum of the product heated at 1400° C for 0 h. It suggests that most of the amorphous SiO_2 was reduced during the heating and cooling schedules. In comparison with the behaviour of the oxides in the reactions of the mixtures with $C/SiO_2 = 5$, these observations indicate the advantage arising from forming the intercalation compound in the reduction of the SiO_2 component.

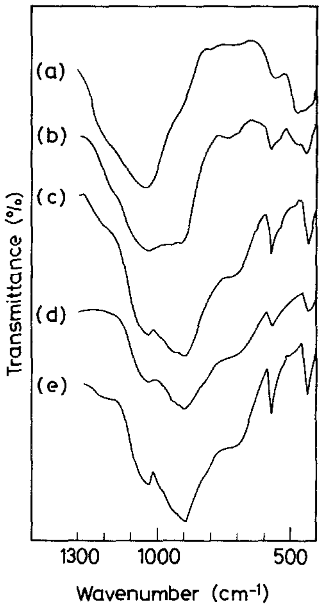

Figure 3 The IR spectra of the products from the montmorillonite–PAN intercalation compound: (a) heated at 1100° C for 2 h, (b) at 1200° C for 2 h, (c) at 1300° C for 2 h, (d) at 1400° C for 0 h, (e) at 1400° C for 2 h.

3.4. SEM and EPMA observations

The morphology of the products is shown in Fig. 4. Fig. 4a reveals the morphology of the montmorillonite–PAN intercalation compound heated at 1500° C for 2 h. The particles still showed the characteristic shape of the layered structure. However, they actually consisted of fine products. Small amounts of whiskers were detected in the products from the complex. The EPMA observation indicated that they contained aluminium.

When the mixture with $C/SiO_2 = 2$ was heated similarly, products formed on the surface of the particles (Fig. 4b). Whiskers were also observed, and some of them also contained aluminium. Therefore, a gaseous aluminium-containing species participated in the reactions in both systems.

3.5. ICP observations

Fig. 5 shows the Si/Al and Mg/Al atomic ratios as a function of reaction temperature. Dotted lines represent those of the raw montmorillonite. The Si/Al ratio must deviate when either is selectively lost. In the reactions of the montmorillonite–PAN intercalation compound, the Si/Al ratios were similar to that of the raw montmorillonite. On the other hand, those of the products from the mixtures were smaller

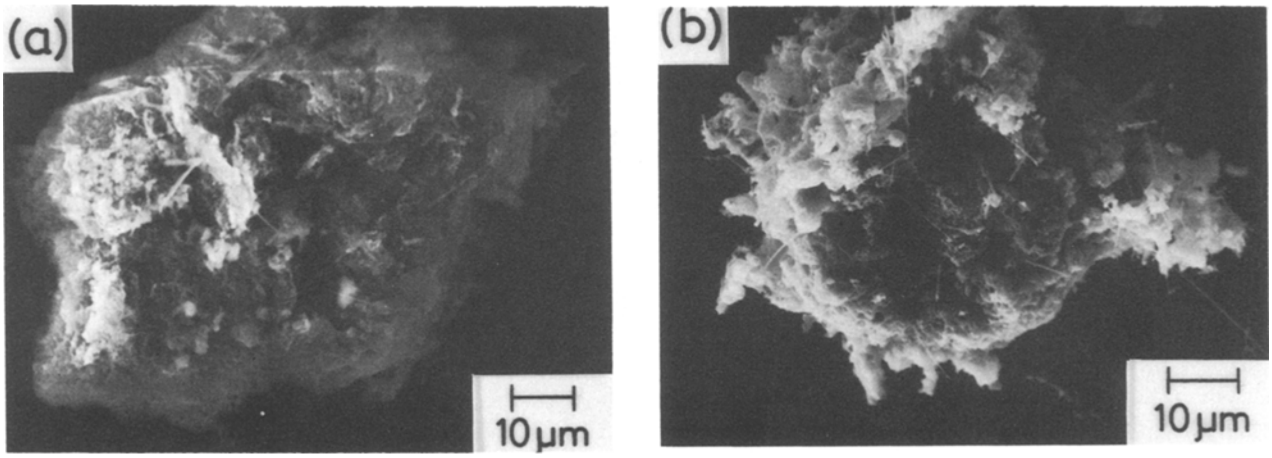

Figure 4 Scanning electron micrographs of the products heated at 1500° C for 2 h: (a) from the montmorillonite–PAN intercalation compound, (b) from the montmorillonite–carbon mixture with $C/SiO_2 = 2$.

than that of the raw montmorillonite. With $C/SiO_2 = 5$, the ratios were constant. On the other hand, the ratio drastically decreased with an increase in reaction temperature, when the C/SiO_2 ratio was 2.

The previous investigations on the reduction of SiO_2 generally agreed on the participation of gaseous SiO as an intermediate [25]. Hence, silicon was lost as SiO. The mechanism of the reduction of Al_2O_3 was uncertain. However, the EPMA observation suggested the presence of the gaseous aluminium-containing species in the present systems. Although the degree of the loss of aluminium was obscure, the present results apparently indicated that the loss of SiO was remarkable in the reactions of the mixture, especially with $C/SiO_2 = 2$.

From the Mg/Al ratio, the reduction of the MgO component was monitored, since magnesium was lost essentially due to the following reaction [26];

$$MgO + C \rightarrow Mg + CO$$

By the treatment even at 1300° C, a part of the MgO component in the complex was reduced. On heating at 1500° C, most of the component was reduced. On the other hand, the mixtures showed larger values than that of the complex heated similarly. Therefore, the reduction rate of the MgO component in the complex was obviously greater than that of the component in the mixture with $C/SiO_2 = 5$, though the carbon content of the complex corresponded to $C/SiO_2 = 2.7$.

4. Conclusions

The montmorillonite–polyacrylonitrile intercalation compound was a highly ordered precursor because of its layered structure. Hence, its carbothermal reduction process in N_2 became a novel one. In comparison with the reactions of the montmorillonite–carbon mixtures, the following observations have been pointed out:

1. No oxides were formed during the reactions of the intercalation compound, whereas those of the mixtures involved the formation of the oxides.
2. The reactions of the intercalation compound were simplified; β-sialon, AlN and SiC were mainly

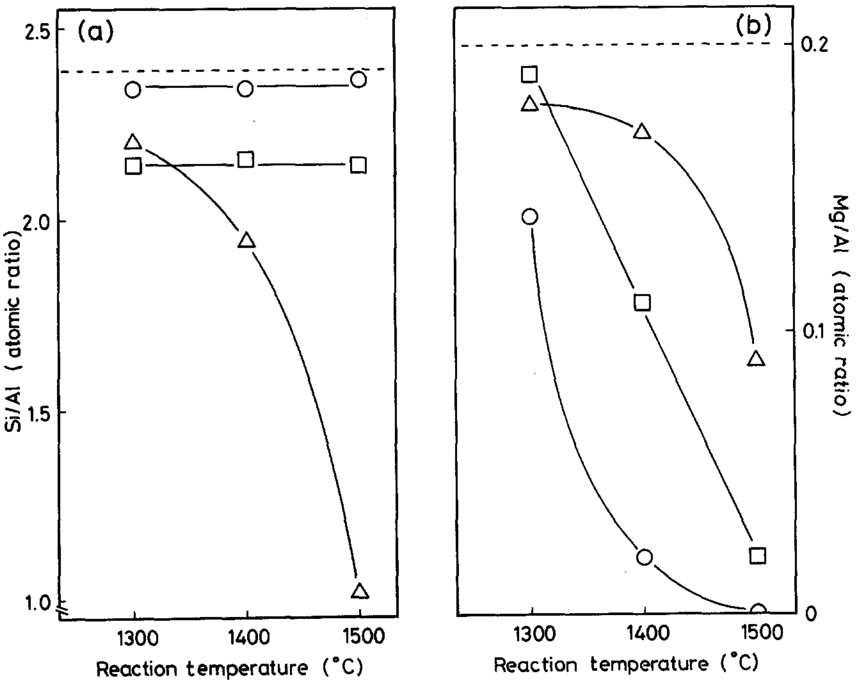

Figure 5 The metal ratios of the products: (a) Si/Al, (b) Mg/Al. Dotted lines are for the raw montmorillonite (○: montmorillonite–PAN complex, △: montmorillonite–carbon mixture ($C/SiO_2 = 2$), □: montmorillonite–carbon mixture ($C/SiO_2 = 5$).

formed. On the other hand, various nitrides were obtained from the mixtures.

3. The rates of reduction and nitridation for the intercalation compound were greater than those of the mixture with $C/SiO_2 = 5$ in spite of the smaller carbon content of the intercalation compound.

4. A smaller amount of SiO was lost during the reactions of the intercalation compound.

These observations suggest that the application of the intercalation compound was advantageous for nitride production by carbothermal reduction.

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