Carbide Formation from a Montmorillonite-Polyacrylonitrile Intercalation Compound by Carbothermal Reduction

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The montmorillonite-polyacrylonitrile (PAN) intercalation compound was heated in Ar flow for the application of clay-organic complexes to the preparation of carbide through the carbothermal reduction. β -SiC was formed at 1200°C and both α -SiC and β -SiC were detected above 1300°C. SiO_2 component was reduced without forming any crystalline compounds, while Al_2O_3 component formed Mg-Al-O compound. Compared with the reactions of a montmorillonite-carbon mixture, it was clarified that the presence of PAN in the interlayer space led to the formation of α -SiC and suppressed the crystallization of oxides.

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モンモリロナイト-ポリアクリロニトリル層間化合物からの 熱炭素還元による炭化物生成

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粘土-有機複合物を熱炭素還元による炭化物合成に応用することを目的として、モンモリロナイト-ポリアクリロニトリル (PAN) 層間化合物を Ar 雰囲気にて焼成した。1200°C では β -SiC が生成し、1300°C 以上では α -及び β -SiC が生成した。酸化物では SiO_2 成分が全く結晶化しなかったのに対し、 Al_2O_3 成分は Mg-Al-O 系の化合物として結晶化した。モンモリロナイト-炭素混合物からの反応との比較により、層間の PAN の存在が α -SiC の生成をもたらし、酸化物の結晶化を抑制したことが明らかとなった。

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Key-words: Intercalation compound, Montmorillonite, Polyacrylonitrile, Silicon carbide, Carbothermal reduction

1. Introduction

Silicon carbide is expected as a candidate for structural materials. Among the preparation methods, the carbothermal reduction of SiO_2 is one of the main procedures, and is utilized for the industrial fabrication as "Acheson process"¹⁾. In spite of its industrial importance, the process has not been investigated sufficiently. Recently, the syntheses from various SiO_2 sources have been studied. Wei et al.²⁾ prepared SiC powder from gel-derived precursors, which gave more intimate mixture of SiO_2 and carbon. Lee et al.³⁾ first reported the formation of SiC from rice hull by

thermal decomposition and subsequent reduction. Sharma et al.⁴⁾ also reported the formation of SiC whisker from it. Moreover, the synthesis from SiO_2 - Al_2O_3 compositions was investigated, since a large part of compounds containing SiO_2 exists as aluminosilicates. The first preparation was reported by Bechtold et al.⁵⁾. They used a typical clay mineral of kaolinite, and obtained SiC with the successful separation of Al_2O_3 . The synthesis from Shirasu glass was also studied. Shimada et al.⁶⁾ reported the formation of SiC with the formation of Al-rich glass. They also studied the result of sintering⁷⁾.

Montmorillonite, which is one of common clay minerals, has a specific property of "intercalation", and can form intercalation compounds with a wide variety of organic molecules⁸⁾. Among complexes, the montmorillonite-polyacrylonitrile (PAN) intercalation compound was used as a starting material for the synthesis of nitrides through carbothermal reduction⁹⁾. In the complex, the layers of montmorillonite and PAN, whose thickness is about 1 nm, are stratified alternatively. Thus the intimate mixture of oxide and carbon could be obtained by their thermal transformation in an inert atmosphere. In this study, the behavior on the carbide formation from the montmorillonite-PAN complex was investigated, comparing with that of a montmorillonite-carbon mixture. This investigation could clarify the advantage arisen from the formation of the intercalation compounds, and the possibility of being a starting material for the synthesis of SiC.

2. Experimental

2.1 Sample preparation

The preparation of the *n*-hexylammonium-montmorillonite-PAN intercalation compound and its heat treatment for cyclization of PAN were described elsewhere⁹⁾. It is assumed that a certain amount of PAN was adsorbed on the external surface of the particles as well as in the interlayer spaces. Nevertheless, it is reasonable to consider that the presence of the carbon on the external surface scarcely influenced to the whole reaction process in an inert atmosphere due to the reactions previously reported³⁾. Thus its effect could be excluded. In this study, the amount of organic materials determined by TG was about 61 wt% after the heat treatment. According to the report on the synthesis of carbon fiber¹⁰⁾, 42-56 wt% of PAN was transformed to carbon. Thus, the actual amount of carbon which was involved in the reactions was considered to be about a half of that

of organic materials contained in the sample before firing in Ar.

The preparation of the montmorillonite-carbon mixture was as follows. Montmorillonite (−100 mesh) and carbon black (Koso Chemical Co., reagent grade) were mixed using *n*-hexane. The mixing rate of carbon was 26.9 wt%, which was stoichiometric for the formation of SiC from SiO₂ component.

2.2 Heat treatment in Ar

About 0.7 g of sample (−100 mesh) was heated in Ar flow for 1 h. Reaction temperature varied from 1100°C to 1400°C. After decarbonization at 650°C for 3 h, products were analyzed by X-ray Diffraction (XRD) (Rigaku Denki, RAD II-A, Fe *K*α) to identify crystalline phases. IR spectra were measured using Hitachi Infrared Spectrophotometer 260-50. The sample was mixed with dried KBr (1 : 50) and pressed into a pellet, and its spectrum was recorded in the region from 1500 to 250 cm^{−1}. The morphology of the products was studied by Hitachi HXM-2B, and its electron probe microanalysis was also conducted using the same instrument.

3. Results and discussion

3.1 Thermal transformation of montmorillonite

At beginning, the thermal transformation of montmorillonite under the same condition was investigated to identify the oxides formed at high temperatures. Results are summarized in Table 1.

Table 1. High temperature crystalline phases of montmorillonite*.

Reaction Temperature (°C)	Heating Time (h)	Phases
1100	1	Cristobalite, Mullite, Spinel
1200	1	Mullite > Cordierite, Spinel
1300	1	Mullite > Cordierite
1400	1	Mullite > Cordierite

* Samples were heated in Ar flow.

Table 2. Heating condition and crystalline composition.

Reaction temp. (°C)	Heating time (h)	Phases
		complex mixture
1100	1	spinel, Mullite
1200	1	β-SiC, β-SiC, spinel, Mullite, Cordierite
1300	1	β-SiC, α-SiC, Mg-Al-O** β-SiC, spinel, Mullite, Cordierite
1400	1	β-SiC, α-SiC, Mg-Al-O β-SiC, spinel, Mullite, Cordierite

** Al rich composition with spinel structure

Table 1 shows the formation of cristobalite, mullite, cordierite as SiO_2 related oxides, and spinel as a SiO_2 -free oxide. The results agreed with the previous report¹¹⁾.

3.2 Variation of crystalline phases with reaction temperature

Table 2 lists the crystalline phases obtained from both the montmorillonite-PAN complex and the montmorillonite-carbon mixture. Figure 1 shows the XRD patterns of products from the montmorillonite-PAN complex, and Fig. 2 reveals the XRD patterns from the montmorillonite-carbon mixture.

In the reactions of the montmorillonite-PAN complex, the pattern at 1100°C revealed no crystalline phases, indicative the presence of oxides as an amorphous form. At 1200°C, the formation of β -SiC was observed, while both α - and β -SiC were formed above 1300°C. The behavior on the formation of oxides was quite different from that of montmorillonite (Table 2). The only formation of oxide as an Al-Mg-O

Fig. 1. XRD patterns of products from montmorillonite-PAN complex;

(a) 1100°C, (b) 1200°C, (c) 1300°C, (d) 1400°C
(□ : α -SiC, ○ : β -SiC, ▼ : Mg-Al-O).

Fig. 2. XRD patterns of products from montmorillonite-carbon mixture;

(a) 1100°C, (b) 1200°C, (c) 1300°C, (d) 1400°C
(○ : β -SiC, ■ : Mullite, ● : Cordierite, ▲ : Spinel).

compound with spinel structure¹²⁾ was observed above 1300°C. The compound contained much more Al_2O_3 than spinel, and the formation of the compound instead of spinel was indicated by the shift of each peak to higher angle than that of spinel. And no oxides containing SiO_2 were detected.

In Fig. 2, on the other hand, the formation of oxides was almost the same as Table 1 except the formation of no crystalline SiO_2 . Mullite was formed above 1100°C, and cordierite was detected above 1200°C. Furthermore, spinel formed above 1100°C with the same composition as that formed by the thermal transformation of montmorillonite. SiC was formed above 1200°C only in the β modification, and the corresponding intensity decrease of peaks due to cordierite was observed at 1400°C.

The most notable fact indicated from Fig. 1 and Fig. 2 was that the formation of α -SiC was observed only in the reactions of the montmorillonite-PAN complex. This suggests that the reaction process of the montmorillonite-PAN complex differs from that of the montmorillonite-carbon mixture. However, the mechanisms of the formation of α - and β -SiC through carbothermal reduction have not been clarified yet, thus this difference could not be interpreted.

In the investigation of the preparation from Shirasu glass, Shimada et al.⁶⁾ reported 2H type of α -SiC above 1600°C in Ar flow. And Hase et al.¹³⁾ reported the formation of 2H from colloidal silica and carbon in the presence of Al at 1440°C in ca. 10^{-1} mmHg. These results suggest that the presence of Al leads to the formation of 2H among α -SiC polytypes at relatively lower temperatures through carbothermal reduction process.

However, the XRD patterns revealed the possibility of the formation of both 2H and 4H, because of the lacking of the characteristic peaks of 2H and 4H and the overlapping of the peaks with those of β -SiC. Although the thermal stability also indicated that the formation of 2H was more probable than that of 4H^{14), 15)}, the possibility of the formation of 4H could not be excluded due to the stabilization of 4H by Al at higher temperatures^{16), 17)}.

The behavior of the formation of oxides was also quite different between two processes. The suppression of the formation of oxides was arisen from the presence of PAN in the interlayer spaces; PAN divided the particle into each sili-

cate layer, thus the crystallization was inhibited, and the amorphous state was stabilized. The same observation was reported by Oya et al¹⁸⁾.

While no oxides concerning SiO_2 were observed, Al_2O_3 component crystallized as the Mg-Al-O compound in the case of the montmorillonite-PAN complex. This finding was explained with the difference of reactivity over carbon between SiO_2 and Al_2O_3 ¹⁹⁾. The comparison with the reactions of the montmorillonite-carbon mixture indicates that the presence of PAN also influence the composition of the oxide formed.

3.3 IR spectra of products

Figure 3 shows the IR spectra of the products from the montmorillonite-PAN complex, and IR spectra from the montmorillonite-carbon mixture are shown in Fig. 4.

In the case of the montmorillonite-PAN complex, a band due to the Si-O stretching was clearly observed from 1100°C to 1300°C, indica-

tive the presence of amorphous SiO_2 component. Above 1300°C, a strong absorption band at ca. 820 cm^{-1} was observed. In the previous reports, the spectra of β -SiC showed the band at 820-870 cm^{-1} ²⁰⁾, and the band at 820-830 cm^{-1} was observed with the shoulder bands at 790 cm^{-1} and 940 cm^{-1} ²¹⁾ in the case of α -SiC (6H). Thus the band observed was assigned to α - and β -SiC.

On the other hand, the well-defined band at ca. 820 cm^{-1} appeared only at 1400°C in Fig. 4. This finding implied the advantage of the montmorillonite-PAN complex over the montmorillonite-carbon mixture, though no considerable difference was observed in their XRD peaks due to SiC at 1300°C (Figs. 1 and 2).

3.4 SEM observation and electron probe microanalysis

The SEM observation of the products from the montmorillonite-PAN complex (Figs. 5 a and b) showed the characteristic shape similar to the original montmorillonite particles. In addition, fine products were also observed on their surfaces, especially the edge or defect of the particle. Using electron probe microanalysis, the product was assumed to be SiC. This assignment was based on the fact that a lesser amount of Al was detected in this area than in other area. It is well

Fig. 3. IR spectra of products from montmorillonite-PAN complex;

(a) 1100°C, (b) 1200°C, (c) 1300°C, (d) 1400°C.

Fig. 4. IR spectra of products from montmorillonite-carbon mixture;

(a) 1100°C, (b) 1200°C, (c) 1300°C, (d) 1400°C.

Fig. 5. Scanning electron micrographs of products
 (a), (b) from montmorillonite-PAN complex;
 (a) 1400°C, (b) 1300°C
 (c)-(e) from montmorillonite-carbon mixture;
 (c) 1400°C, (d)-(e) 1300°C
 (f) X-ray image of (e); Fe $K\alpha$.

known that the formation of SiC proceeded via the formation of SiO as an intermediate³¹. Thus this was explained on the the assumption that SiO formed in the interior of the particles reacted on the surface to form the fine SiC.

On the contrary, the surface of the montmorillonite-carbon mixture (Figs. 5 c-e) was quite different from that of the montmorillonite-PAN complex. At 1400°C, the particles were not spherical, whereas most of the particles obtained at 1300°C showed spherical shapes. In addition, the hollow particles was also detected at 1300°C (Fig. 5 d). The surface of the product at 1400°C was covered by fibrous products completely. And on the top of the products, spherical products were occasionally observed. The micrograph of the products at 1300°C (Fig. 5 e) revealed that the fibrous products grew from the surface of the spherical particle. Electron probe microanalysis of the surface of the spherical particle suggests the fact that fine products are SiC and spherical products contain a certain amount of Fe (Figs. 5 e and f). During the carbothermal reduction of a SiO₂-Fe₂O₃ mixture, the formation of FeSi was reported²². Thus, this observation was probably due to the progress of such reaction on the surface, although no evidence was obtained from their XRD patterns. These observation indicated that the surface reactions were completely different. However, the reason of the difference

has not be clarified.

4. Conclusion

The montmorillonite-PAN intercalation compound was heated in Ar flow from 1100°C to 1400°C, and its behavior was compared with that of the montmorillonite-carbon mixture.

From the montmorillonite-PAN complex, both α - and β -SiC were formed, while only the formation of β -SiC was observed in the case of the montmorillonite-carbon mixture. And mullite and cordierite were not detected in the reactions of the montmorillonite-PAN complex, though these oxides crystallized in the case of the montmorillonite-carbon mixture. In contrast, Mg-Al-O compounds crystallized in both reactions, but their compositions were different; the compound from the montmorillonite-PAN complex contained much more Al₂O₃ than that from the montmorillonite-carbon mixture.

Moreover, IR spectra implied that the montmorillonite-PAN complex was more reactive than that of the montmorillonite-carbon mixture. And the analyses by SEM and EPMA also indicated that the surface reaction was different.

These findings suggest that the reaction process becomes completely different. All of these results were due to the existence of PAN in the interlayer space.

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