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The preparation and characterization of SiC–AlN–Fe_2Si composites with high porosity from allophane

Y. MORIYOSHI
College of Engineering, Hosei University, Kajinocho 3-7-2, Koganeishi, Tokyo 184, Japan
N. EKINAGA
Tokai Carbon Co. Ltd, Subashiri, Koyamacho, Suntougun, Shizuoka 410-10, Japan
S. KOMATSU, T. ISHIGAKI
NIRIM, Namiki 1-1, Tsukubashi, Ibaraki 305, Japan

The reaction products of an allophane heated with carbon at 850–1600 °C in the stream of nitrogen for a given time were characterized by X-ray diffractometry. As a result, it was found that cristobalite and mullite were stable phases at 850–1300 °C, β-Si_3N_4 and α-Al_2O_3 at 1300–1500 °C, and SiC–AlN–Fe_2Si at temperatures higher than 1500 °C. SiC–AlN–Fe_2Si composites with high porosity of about 50% were easily prepared by a heat treatment at a temperature higher than 1500 °C with carbon in a stream of nitrogen. The formation mechanism of the composites is kinetically discussed from a viewpoint of small-pore shrinkage and large-pore expansion by volume diffusion during heating. The resultant microstructure of the composites obtained is also discussed.

1. Introduction

Porous ceramics are widely applicable as sensors, catalysts, heat-insulating materials, filters, etc. In particular, porous ceramics used at high temperatures are important in the field of automobile, space science, and high-temperature technologies.

From the viewpoint of a raw material for the preparation of porous ceramics, an allophane is very interesting, because it is fairly pure alumino-silicate with high reactivity and easily reacts with carbon and nitrogen. We have found that mixed ceramics of SiC-AlN-Fe_2Si can be prepared by just a heat treatment of an allophane, which has been produced in Japan and which originally contains many pores, with carbon in a stream of nitrogen at a given temperature.

In this paper we describe first the various ceramic powders obtained by heat treatment of an allophane with carbon in a stream of nitrogen at high temperature, secondly, the formation mechanism of porous ceramics by the heat treatment, and finally the microstructure of the ceramics obtained. In connection with the structure of an allophane, several models have been reported [1–7].

2. Experimental procedure

An allophane produced in Tochigi Prefecture in Japan, about 70 km north of Tokyo, was used in this experiment. It was slightly crushed in an agate mortar for 5 min in air. The average size of the slightly crushed powder was determined by SEM to be less than 100 μm. Fig. 1 shows a scanning electron micrograph of the allophane with large amount of spherical pores, that is, many pores are still present in allophane grains which have been crushed slightly. Their size distribution is from 1–8 μm. The average pore size is about 4 μm. X-ray diffraction patterns of the grains indicated that they were amorphous. The chemical analytical data are listed in Table I.

A given weight of the slightly crushed powder was mixed with 30 wt % carbon black (Tokai Carbon Co.

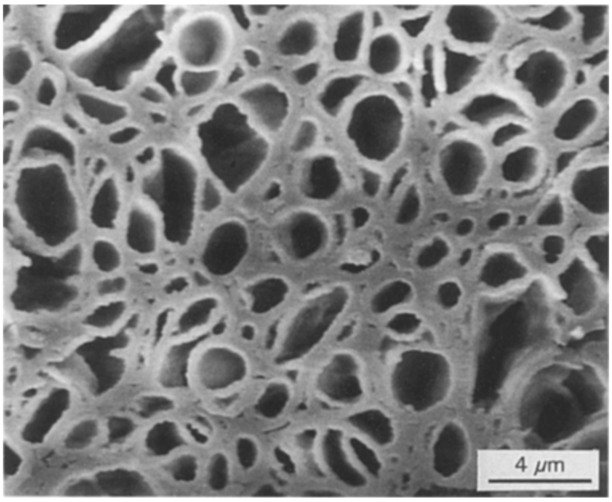


Figure 1 A scanning electron micrograph of allophane particles containing many pores.

TABLE I Chemical composition (wt %) of allophane

SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO
49.5	45.3	3.42	0.59	0.30	0.65	0.21

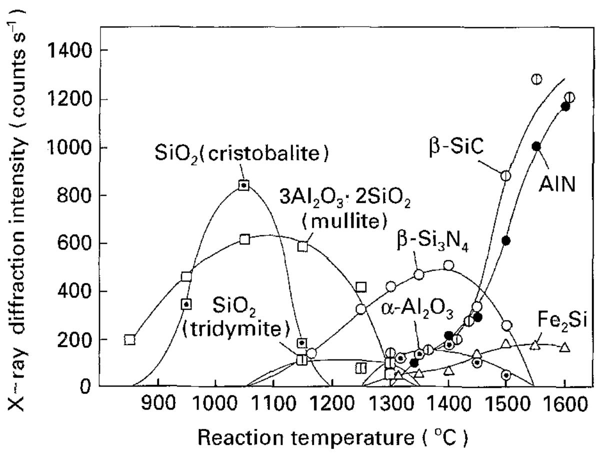


Figure 2 The effect of reaction temperature on the reaction products of allophane.

Ltd) in a plastic crucible for 10 min in air. The average particle size of the carbon black used for the mixing was 50 nm. The resultant mixed powders were placed in an alumina crucible. They were heated to a given temperature at a constant rate of 4 °C min^{-1}. The reaction temperature was 850–1600 °C for 0.5–10 h. During heat treatment, 3 l min^{-1} nitrogen gas was introduced in the reaction zone from the upper part of a reaction tube as shown in Fig. 2. After the reaction, the powders were heated at 650 °C for 4 h in air in order to change unreactive carbon to CO_2. The powder obtained by heat treatment was compacted into a disc at 10 kg cm^{-2} for sintering. The sintered bodies obtained at various temperatures were characterized from scanning electron micrographs, X-ray diffractometry, etc.

3. Results and discussion

Reaction products detected by X-ray diffraction in the powder heated at 850–1600 °C for 5 h are shown in Fig. 2. Clearly from the figure, the powders heated at 850–1300 °C were cristobalite (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$). Cristobalite was generated at 900–1200 °C. Mullite was detected in the powder heated at 850–1300 °C. Chemically analytical data indicated that the composition of the allophane used here was $1.86SiO_2Al_2O_3$. Therefore, the cristobalite and mullite are considered to have been generated from the allophane as follows

$$3(1.86SiO_2Al_2O_3) \rightarrow 3Al_2O_32SiO_2 + 3.58SiO_2 \quad (1)$$

The intensities of both crystobalite and mullite reached maximum values at about 1050 °C. At temperatures higher than 1050 °C the intensities gradually decreased. At the same time, the X-ray diffraction intensities of both tridymite and β-Si_3N_4 began to appear. This indicates that the tridymite resulted from the phase transformation of cristobalite and that β-Si_3N_4 originated from the nitridation of cristobalite or SiO_2 generated from the decomposition of mullite.

The X-ray diffraction pattern of β-Si_3N_4 began to appear at about 1100 °C which is a fairly low temperature, and the intensity reached a maximum value at about 1400 °C. On the other hand, α-Al_2O_3 began to appear at about 1250 °C, with a maximum intensity at about 1400 °C. Their formation is closely related to the decomposition of mullite at high temperature. Fe_2Si began to appear at about 1250 °C, after the mullite had almost disappeared. Fe_2Si gradually increased with increasing temperature and the X-ray diffraction intensity became constant at 1500 °C. β-SiC began to be generated at about 1300 °C and it increased rapidly with increasing temperature. On the other hand, the X-ray diffraction intensity of β-Si_3N_4 decreased with increasing temperature. β-Si_3N_4 changes to β-SiC at higher temperature. AlN also began to appear at 1300 °C and its X-ray diffraction intensity showed the same tendency as that of β-SiC. α-Al_2O_3 was detected between 1250 and 1550 °C. The intensity of α-Al_2O_3 began to decrease gradually at 1300 °C. At temperatures higher than 1550 °C, three phases of β-SiC, AlN and Fe_2Si were present, indicating that they are stable phases in that temperature region.

The relationship between heating time and the X-ray diffraction intensity of reaction products at 1350 °C is shown in Fig. 3. During the initial stages of heating at that temperature, β-Si_3N_4, β-SiC, Fe_2Si, AlN, and α-Al_2O_3 were generated. The β-SiC showed

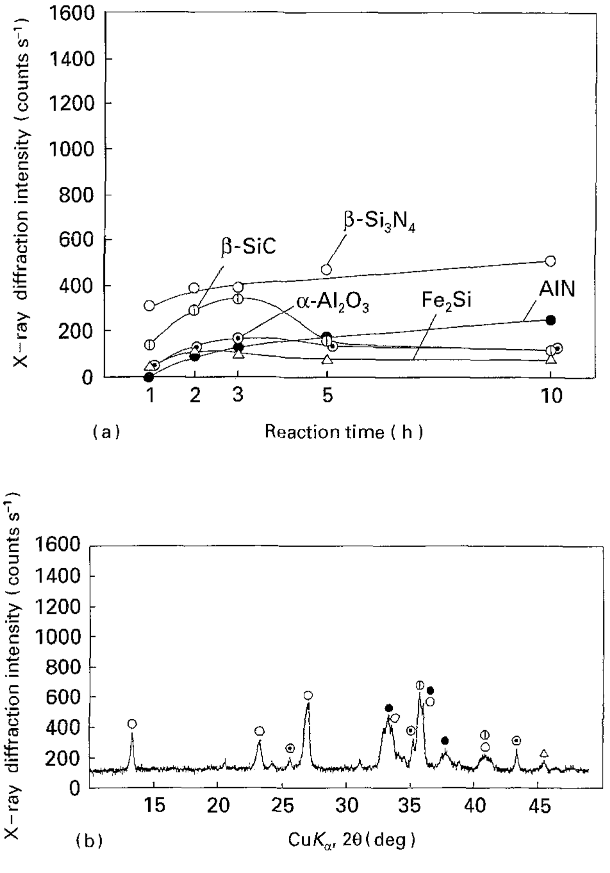


Figure 3(a) The effect of reaction time on the reaction products of allophane heated at 1350 °C for 5 h. (b) The corresponding X-ray diffraction pattern: (○) β-Si_3N_4, (⊙) α-Al_2O_3, (●) AlN, (⦶) β-SiC, (△) Fe_2Si.

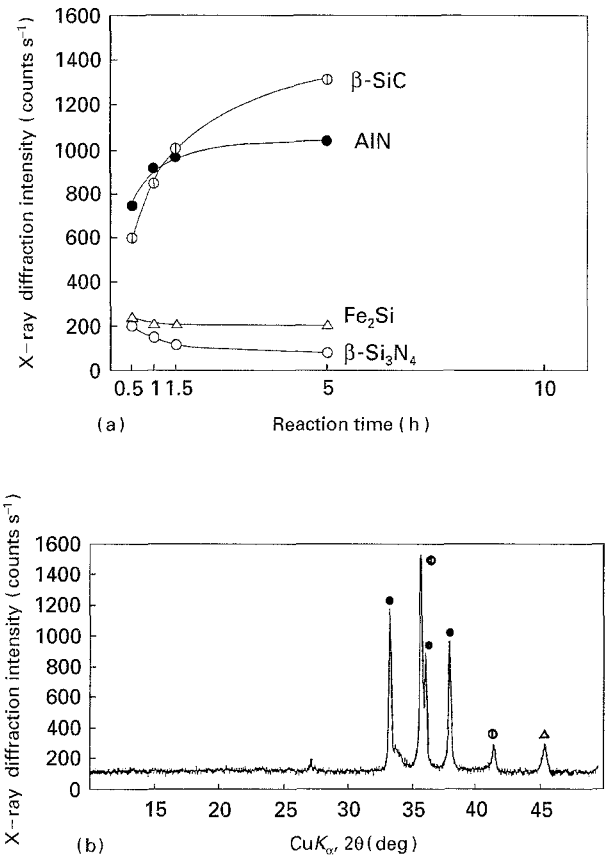


Figure 4(a) The effect of reaction time on the reaction products of allophane heated at 1600 °C for 5 h. (b) The corresponding X-ray diffraction pattern: (●) AlN, (⦶) β-SiC, (△) Fe_2Si, (○) β-Si_3N_4.

a maximum intensity at 3 h and thereafter decreased to a small value with increasing heating time. The intensity of α-Al_2O_3, also decreased gradually to a small value after 3 h. On the other hand, the intensities of Si_3N_4 and AlN gradually increased. This may suggest that these are stable phases at 1350 °C. The X-ray diffraction intensity of Fe_2Si was almost constant, irrespective of heating time. Thus Fe_2Si is also considered to be a stable phase at high temperature.

The relationship between heating time and the X-ray diffraction intensity at 1600 °C is shown in Fig. 4. During the initial stage of heating at that temperature, β-SiC, AlN, Fe_2Si and β-Si_3N_4 were detected. During heating, β-SiC and AlN increased with time, and the X-ray diffraction intensity of Fe_2Si was almost constant. On the other hand, the intensity of β-Si_3N_4 decreased gradually with time. These data suggest that β-SiC, AlN, and Fe_2Si were stable phases; however, β-Si_3N_4 was an unstable phase at the same temperature.

The formation process of a porous body occurs in such a way that some small pores in the starting material of allophane shrink and other large pores expand, resulting in angular pores being generated in the sintered body. This is shown schematically in Fig. 5. If we take a to be the radius of curvature of a small pore and b as the distance between the small pore surface and the large pore surface, the concentration of vacancies at the small pore surface per unit volume, n_s, is higher than that at a plane surface, because of tensile stress. This is expressed as follows [8]

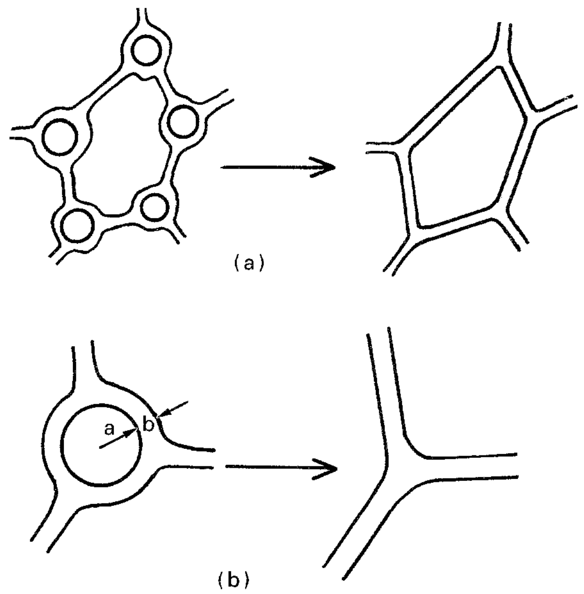


Figure 5 Schematic models of the formation of a porous body by volume diffusion, in which small pores shrink and large pores expand during heating. (a) A model in which five small pores shrink and disappear, resulting in the generation of large pores during heating. (b) A model of small-pore shrinkage.

$$n_s = n + \gamma\Omega n/akT \qquad (2)$$

where n is the concentration of vacancies at a plane surface. On the other hand, the concentration of vacancies at the large pore surface per unit volume, n_L, is lower than that at a plane surface, because of compression stress, and it is expressed as

$$n_L = n - \gamma\Omega n/(a+b)kT \qquad (3)$$

So, the excess concentration of vacancies per unit volume, Δn, is given by

$$\Delta n = n_s - n_L = \gamma\Omega n/kT[1/a + 1/(a+b)] \qquad (4)$$

where k is the Boltzmann constant, γ is the surface energy, n is the concentration of vacancies at a plane surface per unit volume, T is the absolute temperature, and Ω is the atomic volume. As a result, it may be concluded that the surface at the large pore acts as vacancy sink and the surface at the small pore acts as vacancy source, that is, vacancies diffuse away from the surface at the large pore to the surface at the small pore by volume diffusion.

If b is approximately equal to a, Equation 3 is given by

$$\Delta n = (\gamma\Omega n/kT)(3/2a) \qquad (5)$$

As the concentration gradient of vacancies is approximately equal to $\Delta n/a$, Fick's equation for this case can be written

$$\mathrm{d}V/\mathrm{d}t = -A\Omega D^*(\Delta n/a) \qquad (6)$$

where A is the area of the small pore per h length, $A \cong 2\pi ah$, $\mathrm{d}V/\mathrm{d}t$ is the volume change per unit time, $\mathrm{d}V/\mathrm{d}t \cong 2\pi ah\,\mathrm{d}a/\mathrm{d}t$, D^* is the diffusion coefficient for vacancies. Introducing all these values and $nD^* = ND$ (N, the atoms per unit volume, is equal to

$1/\Omega$ if D is the self-diffusion coefficient for atoms) into Equation 6 and integrating at initial t (time) $= 0$ and $a = a_0$ (the initial radius of small pores), we obtain

$$a^3 - a_0^3 = [(-9\gamma\Omega D/(2kT)]t \qquad (7)$$

where a_0 is the initial radius of a small pore and a is the radius of a small pore at time t. Equation 7 indicates that the initial radius of pores decreases with increasing heating time. It is fundamentally similar to an equation of grain growth with impurities, for instance grain growth for MgO-doped Al_2O_3 [9–11].

During the shrinkage processes of small pores, various reactions, such as carbonization, nitration, and silicidation, take place; the processes are assumed to be much more complicated than the pore-shrinkage model mentioned above. However, it is considered important that small pores shrink and disappear, and the large pores expand or remain during heating. As a result we can obtain SiC–AlN–Fe_2Si composites with a high porosity of about 50%. The formation mechanism of the composites is being clarified at the present time.

Fig. 6 shows a scanning electron micrograph of a porous body sintered at 1500 °C for 2 h in a stream of nitrogen. Among the grains, angular pores of various sizes are present. Their size distribution is from 1–7 μm and the average pore size is about 4 μm. The size obtained here corresponds to that of pores in the allophane shown in Fig. 1. Therefore, the pores in the sintered body would have a somewhat similar size to the pores in the raw material of the allophane. The difference in the pore shape between the two may correspond to the discrepancy in their thermal history. During the sintering at 1500 °C, no shrinkage was observed for 2 h. The relative density of the sintered bodies was about 49%, that is, almost half the volume of the sintered compact was pores. As can be seen in the figure, the grain size varied from 2–10 μm. Their shape is plate-like. It has an irregularly piled-up structure of plate-like grains. Such grains may be generated by sintering of allophane during heating, as discussed below. The X-ray diffraction data suggest that these grains consist of mainly β-SiC, β-Si_3N_4, and AlN with a small amount of Fe_2Si.

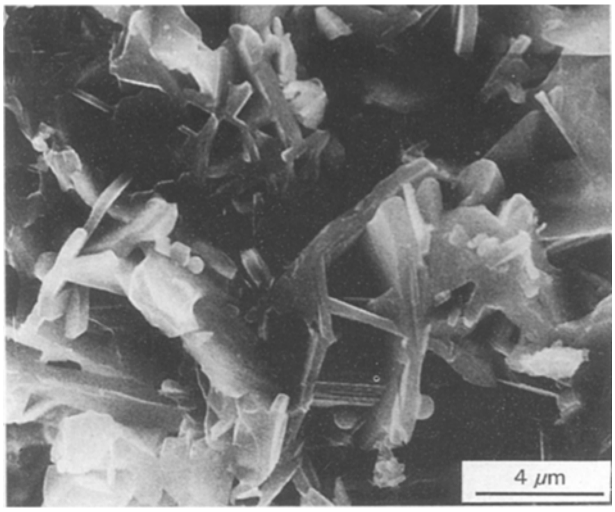


Figure 6 A scanning electron micrograph of a porous body sintered at 1500 °C for 2 h in a stream of nitrogen.

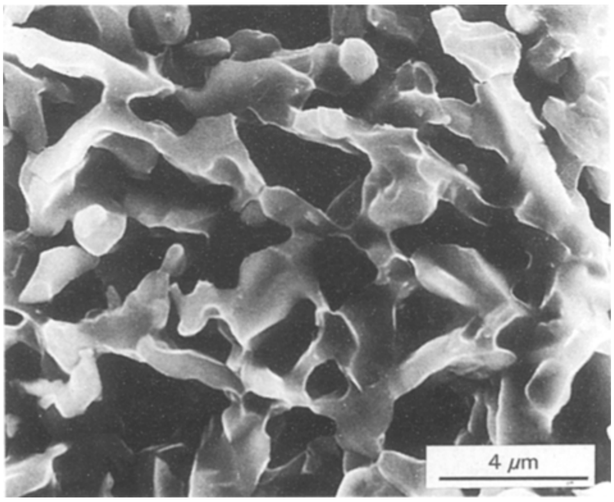
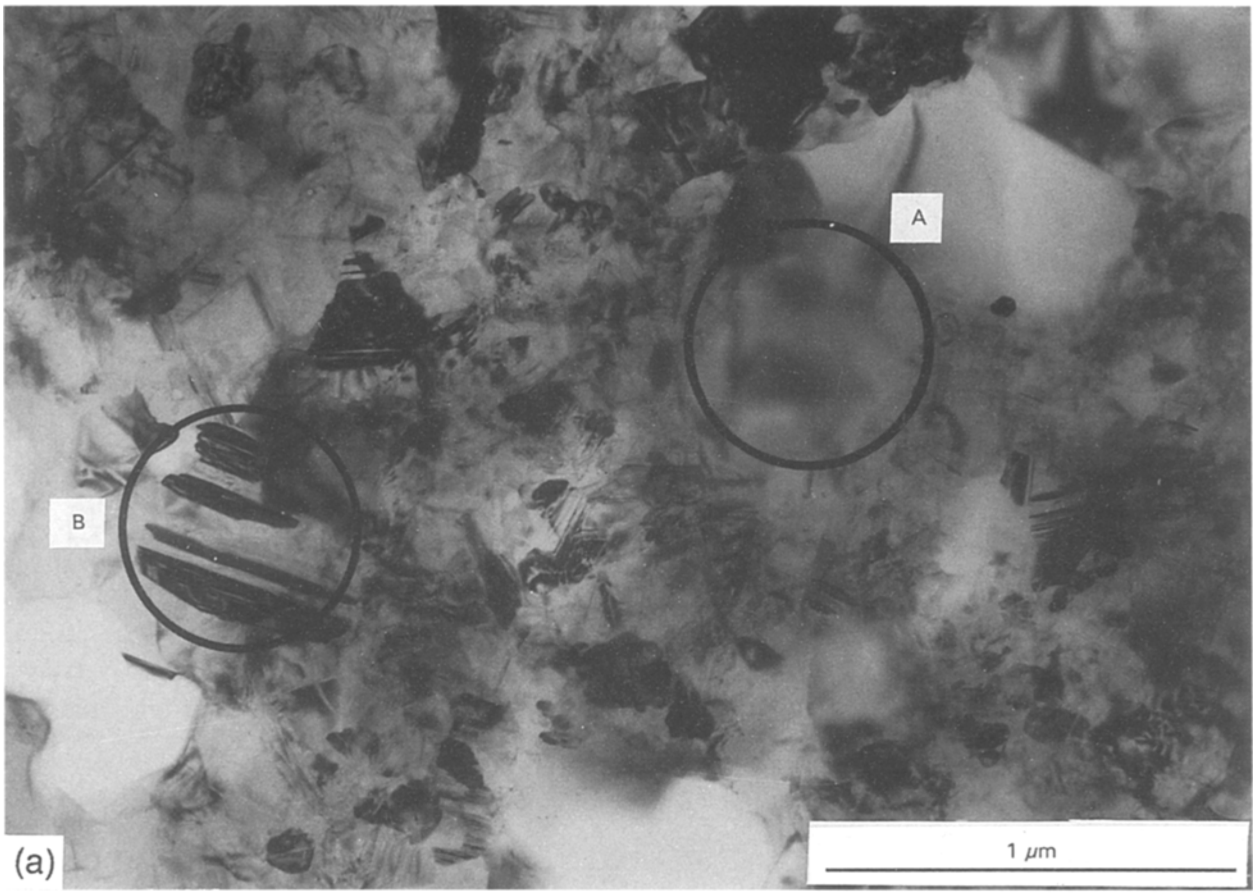


Figure 7 A scanning electron micrograph of a porous body sintered at 1700 °C for 2 h in a stream of nitrogen.

Fig. 7 shows a scanning electron micrograph of a body sintered at 1700 °C for 2 h in a stream of nitrogen. The size of the grains varies from 4–12 μm. The relative density of the sintered bodies is about 50% theoretical, that is, their porosity is about 50%. The shape of the grains is plate-like with wavy surfaces, clearly different from those in the body sintered at 1500 °C as shown in Fig. 5. The different microstructures of the two sintered bodies may be related to two factors; the effect of temperature on sintering, and the different sintering mechanisms, for instance there is a possibility of a liquid-phase sintering occurring. Although it is not clear which factor plays an important role in sintering, there is a fairly high possibility of liquid-phase sintering taking place at 1700 °C. Because there are small amounts of impurities in the raw material of allophane, calcium, magnesium, sodium and potassium have a high possibility of producing a glassy phase with silicon [12]. However, no shrinkage in a compact during sintering could be observed. This may suggest that the glassy phase is too small in quantity to sinter the compact to high density. Another possibility which may be considered is that the sintering temperature of 1700 °C is too low for densification in this system; therefore, we attempted to sinter it at 1900 °C. However, again no densification was observed. The X-ray diffraction data of the sintered body indicated the presence of β-SiC, AlN and Fe_2Si, which agreed with those obtained in Fig. 2.

One method for obtaining SiC–AlN–Fe_2Si composites with high density is by hot-pressing. The transmission electron micrographs of a hot-pressed body at 1800 °C indicated that very small SiC particles were dispersed in the body. They were very easily identified from the structural features of the micrograph, because stacking faults with straight contrast were always present in them, as shown in Fig. 8. EPMA analysis also indicated the presence of a high concentration of silicon. On the other hand, a high concentration of aluminium was detected in grains without stacking faults. That is, some parts in the hot-pressed



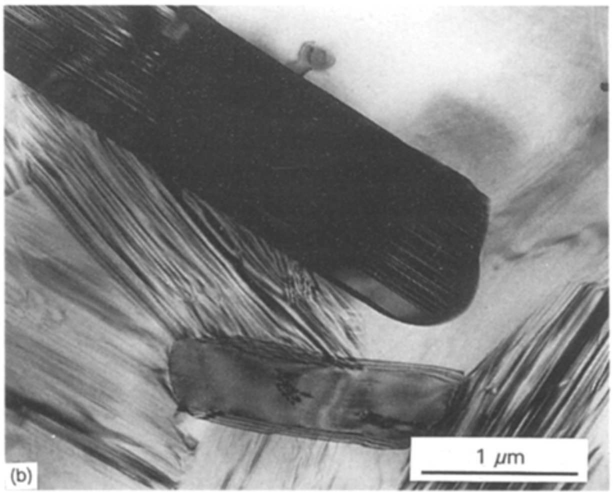


Figure 8(a, b) Transmission electron micrographs of a hot-pressed body (1800 °C for 1 h). EDXS analysis indicates that in (a) the region marked A is rich in AlN and the region marked B is rich in SiC and Fe_2Si. In (b), SiC particles are seen always to have straight contrast, indicating the presence of stacking faults.

body are rich in SiC particles and the other parts are mainly rich in AlN. This may suggest that a phase separation takes place during sintering. The EPMA data for the hot-pressed body indicate that Fe_2Si is always present with SiC rather than with AlN.

In summary, allophane mixed with carbon black was heated at 850–1600 °C in a stream of nitrogen. Its reaction products were characterized mainly by X-ray diffractometry. As a result, it was found that SiC, AlN and Fe_2Si were stable phases at temperatures above 1500 °C. SiC–AlN–Fe_2Si composites with a high porosity (about 50%) were easily prepared by heat treatment at temperatures above 1500 °C with carbon black in a stream of nitrogen. The formation mechanism of the composites was discussed kinetically.

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