

Electron microscopy of hexagonal boron nitride powder

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The morphology and crystalline state of h-BN powder after one-stage or two-stage baking process were investigated extensively. The particles are scale-shaped and the flat surfaces have a (001) habit plane of hexagonal close-packed structure. The side shape of particles after one-stage baking is round, while that after two-stage baking is dodecan, a twelve-faced prism, with the side habit of (100), (110) or their variants. Lattice image observation shows that the side surface of a one-stage baked particle is wavy and thin, while that of a two-stage baked particle is straight and thick. Many particles after one-stage baking are composed of overlapped grains contacting with each other at (001) flat surfaces forming a twist boundary. These grains have relative rotation angles ranging from 5° to 26° around the common [001] axis and have a coincidence lattice relation with respect to (001) flat planes. X-ray photoelectron spectroscopy analysis shows that both C and O segregate onto the surface of one-stage baked particles, while only C segregates onto the surface of two-stage baked particles. Formation of coincidence lattice grain boundary and impurity segregation both restrict the growth of diameter and thickness in scale-shaped particles. It is concluded that two-stage baked particles, having side surface habits, are stable against various environments.

1. Introduction

Boron nitride of hexagonal close-packed structure (h-BN) shows excellent properties in insulation, thermoconductivity and lubrication [1]. It is used in the form of sintered bodies as insulating materials, structural materials or melting pots [1–3] and in powder form as a lubricant or a mould-release agent. Although ceramics are believed to be stable in various environments compared with metals, non-oxide ceramics are chemically attacked by H_2O or other oxidative environments [4–8]. The chemical stability of non-oxide ceramics largely depends on the chemical composition or the atomic structure. In the case of aspirin, for example, the elution in H_2O is affected by the shape or habit plane of the particle and the shape determines the medical effect by means of the solution rate in the digestive organs [9–10]. It is suggested that the chemical stability of BN powder also depends on its shape. The microstructures of hot-press sintered bodies [11–13] and pressureless sintered bodies [8] of h-BN have been widely reported. However, there have been few reports on the microstructure of h-BN powder so far. For these reasons the morphology and

crystallographic property of h-BN powder have been investigated in this report.

2. Experimental procedure

The production process of h-BN powder is shown in Fig. 1; (1) crude BN powder synthesized by nitrification from B-contained materials was purified by baking at 2073 K or 2273 K, (2) the powder was ground and rinsed, (3) after that some powder baked at 2073 K was subjected to a second baking at 2273 K. As shown in Fig. 1 each process is denoted P1, P2, and P3 (P1, one-stage baking at ordinary temperature; P2, one-stage baking at high temperature; and P3, two-stage baking).

The shape of powder was observed by a scanning electron microscope (SEM) after surface coating by C. The internal structure, crystal direction and surface structure were analysed by 400 kV (JEM4000F type) and 100 kV (H600 type) transmission electron microscopes (TEMs) through the observation of electron diffraction (ED), bright field image or lattice image. For the TEM observation the powder was sprinkled

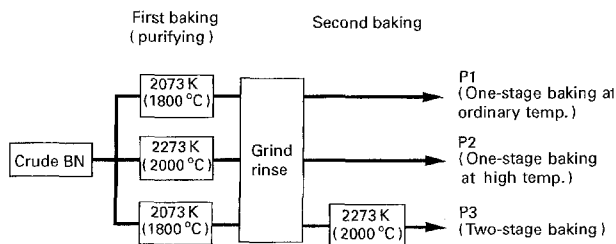


Figure 1 Three production processes of h-BN powders (P1, P2 and P3).

on the C supporting film. The surface element was analysed by XSAM-800 type X-ray photoelectron spectrometer (XPS) using Al-K α X-ray.

3. Experimental results

3.1. Observation by SEM

Typical morphology of BN powder is shown in Figs 2 and 3. Fig. 2 shows that all particles are scale-shaped, and also that each particle, P1, P2 and P3, has the following features. The thickness of the P1 particle is 0.2 ~ 0.4 μm and the diameter is 1 ~ 6 μm (in this paper, each "grain", which will be shown later, constitutes a "particle", which collectively constitutes "powder"). Their side surfaces are round and partly hollowed. Top and bottom surfaces, which will be expressed as "flat surfaces" hereafter, are comparatively smooth. Some of the particles are composed of a single grain, while others are composed of multi-grains which are in contact with each other at flat surfaces as indicated by the arrow in Fig. 2 (a). However, as will be mentioned in section 3.2, in many P1 particles the grains with nearly the same size overlap and they form a multi-grain particle. Therefore the thickness of grains of P1 particle is substantially small.

P2 particles have nearly the same shape as P1 particles. Some of them have a round side surface. Most have no side surface habit, similar to the P1 particle, but some of them, however, do have a side surface habit. The thickness is 0.3 ~ 0.8 μm . The dia-

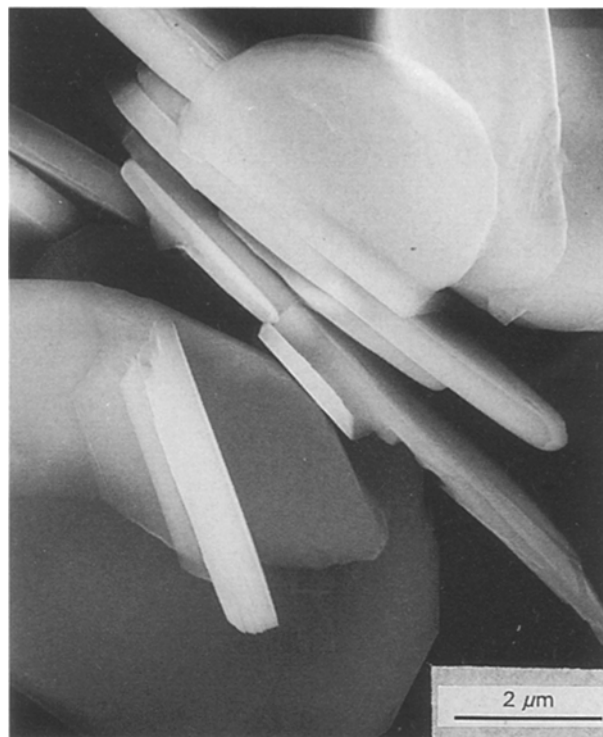


Figure 3 Side view of a P2 particle observed by SEM.

meter is 4 ~ 16 μm , which is significantly larger than that of P1 particles. Many particles have a neck.

P3 particles have different shape from P1 or P2 particles. They are 0.2 ~ 0.5 μm in thickness and 2 ~ 8 μm in diameter. Flat surfaces are smooth, similar to P1 or P2 particles. However, the side surfaces of all particles have a habit. Their shape is dodecan, or twelve-faced, and the relative angle between the neighbouring side planes is 30°.

Fig. 3 shows the side view of P2 particles. Some particles are composed of two or more grains overlapping with each other in contact with the flat surface. The side surface has a round cross-section. Another observation showed that P1 and P2 particles have a round side surface cross-section, while P3 particles have a flat side surface cross-section and the

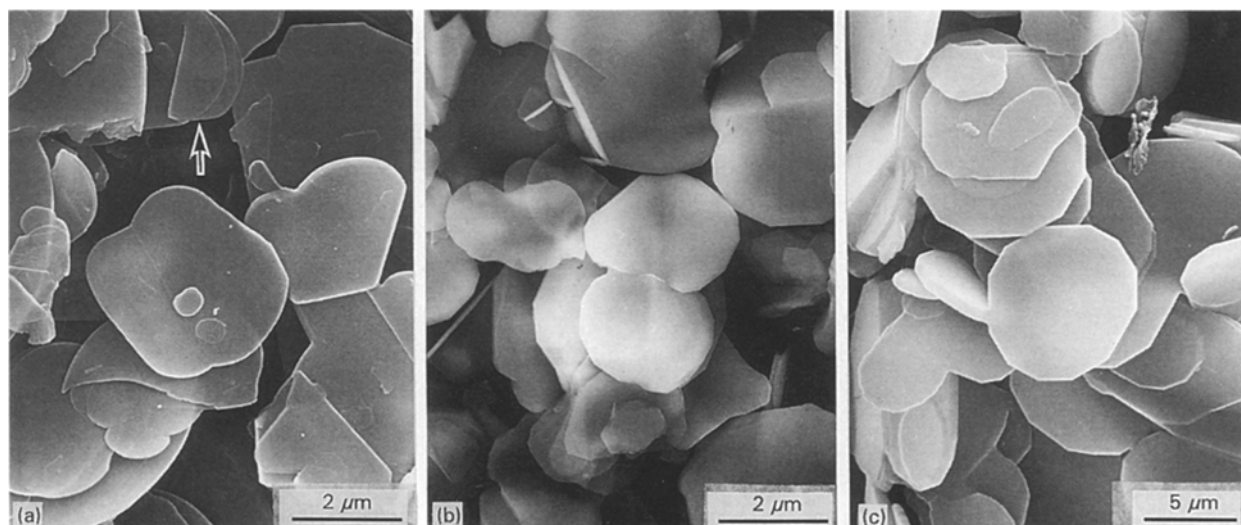


Figure 2 SEM images of (a) P1, (b) P2 and (c) P3 particles.

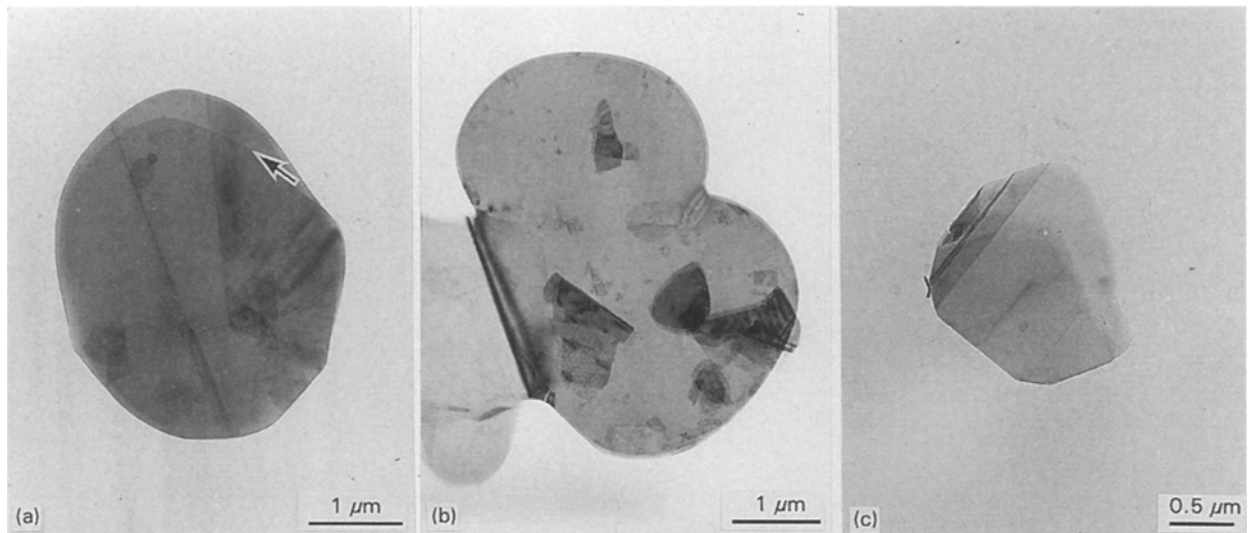


Figure 4 TEM images of (a) P1 and (b), (c) P2 particles.

angle between the flat and side surface normals is a right angle.

3.2. Observation by TEM

Bright field images of P1 and P2 particles were observed using 100 kV TEM, some of which are shown in Fig. 4. The side shape of P1 particles is round. The brightness of the particle changes discontinuously at a boundary line as indicated by the arrow in Fig. 4(a). It indicates that these grains overlap with each other in contact with flat surfaces, forming a multi-grain particle. The diffraction spots in ED pattern were indexed as the lattice planes belonging to $[001]$ zone axis of hexagonal close-packed structure (HCP) structure with the lattice constant of $a = 0.250$ nm and $c = 0.665$ nm. Therefore the habit plane of the flat surface is (001) . No lattice faults such as dislocation, stacking fault, twin or pore was observed, which differs from sintered bodies, in which pores and lattice faults usually exist [14]. According to X-ray diffraction analysis all diffraction peaks were indexed to HCP and no other peak was recognized. To examine the surface structure, the reflection ED was also performed. However, no diffraction spot except h-BN structure was observed.

In the shape of the particles there was no large difference between P1 and P2 particles. However, a partly prism-like particle as shown in Fig. 4(c) was characteristic of P2 powder. The prism-like part is comparatively thick, while the other part is round and thin. It should be noted that an area having the large thickness is observed in the prism-like part. The boundary which separates the thick prism-like part and the thin round part is parallel with one of side habit planes in the prism-like part.

In contrast to P1 or P2 powder, many particles in P3 powder are composed of single grains. Fig. 5 shows a typical example of TEM image and ED pattern from a single-grain particle using 400 kV TEM. The shape of the P3 particle is dodecan whose side surfaces have habits with a relative angle of 30° . Though a speci-

men-tilting operation was attempted, the microstructure was not observed clearly. This indicates that the transparency of the P3 particle was insufficient for the 400 keV electron beam, that is, the P3 particle was much thicker than P1 and P2 particles. The ED pattern in Fig. 5 shows the $[001]$ zone axis and it indicates that the habit plane of the flat surface is (001) and those of the side surface are (100) , (110) and their variants. No difference in shape is recognized between (100) habit plane group and (110) habit plane group.

An example of the ED pattern and its key diagram from a grain-overlapped particle in P1 powder is shown in Fig. 6. Strong spots, indicated by large black circles, are indexed to lattice planes belonging to $[001]$ zone axis of one grain, A. Assuming that the other grain, B, is rotated 21° from grain A around the common $[001]$ axis forming a twist boundary, the structural relationship of the other spots are fairly well explained. That is, the weak spots denoted by small black circles come from the grain B and the weak spots denoted by small white circles are double diffraction ones. The overlapped spots, (in which the spot from A overlaps the spot from B) are denoted by large white circles. In the quadrilateral formed by four large white circles in the key diagram six large black circles from grain A and also six small black circles from grain B exist. According to the coincidence lattice theory, the coincidence lattice relation between two grains, A and B, is presented with Σ value = 7. This is in contrast with sintered bodies, in which no particular crystallographic relation between neighbouring grains exists [14]. Similar analyses showed that many overlapped grains have mutual rotating angles around a common $[001]$ axis of 13° and 22° having coincidence lattice relations with Σ values of 19 and 7, respectively, in P1 particles.

In some P3 particles, several grains were combined with each other at the side surface, as shown in Fig. 7: grain (b) contacts with grain (e) at the side surface and grains (c) and (d) overlap on grain (e). It should be noted that grain (d) contacts with grains (b) and (e) at the boundary. The relative angle between neighbour-

this atomic scale presentation with the period of 40 ~ 60 nm. Gradual increase in contrast from the uppermost side surface to the interior in Fig. 8(a) indicates that the thickness gradually increases also in that direction. On the other hand, the side surface of P3 particle is straight and the contrast is high, as shown in Fig. 8(b), indicating that the side surface of P3 particle is comparatively thick.

P1 particle had clearly the same lattice image with P2 (not shown here). Neither lattice distortion nor surface crystalline phase was recognized in the vicinity of the side surface of these particles. Reflection ED was performed to examine the surface structure. All ED spots were identified as h-BN structure. No particular surface phase was recognized. This result accords with that of lattice image observation.

3.3. Measurement by XPS

Fig. 9 shows XPS spectra from P1, P2 and P3 powders. Photoelectron peaks from B-1s, N-1s and C-1s are clearly recognized in all powders. The intensities of these peaks do not differ greatly among the powders. In contrast, the peak intensity from O-1s is different among the powders. It is the highest in P1 powder and is the lowest in P3 powder. Since the escaping depth of photoelectron is less than 2 nm, the spectra show that C exists on the surface of all powders, while O exists only on that of P1 and P2 powders.

4. Discussion

4.1. The minimum surface energy

The morphology and the crystal direction of h-BN powder have been obtained by SEM and TEM observations, which are schematically shown in Fig. 10. All particles are scale-shaped and the flat surfaces are

(001) of HCP structure as mentioned in Section 3.2. The following facts are well understood: (1) in general the surface energy decreases with the increase of atomic density in one plane or the lattice spacing; (2) the lattice spacings of (001), (100), (110) and (210) of h-BN are 0.3328 nm, 0.2169 nm, 0.1252 nm and 0.08197 nm, respectively; (3) since the bonding between (001) planes is of Van der Waals, while that between higher order planes is covalent in h-BN [15], the bonding between the former plane is relatively weak. It means that the surface energy of (001)

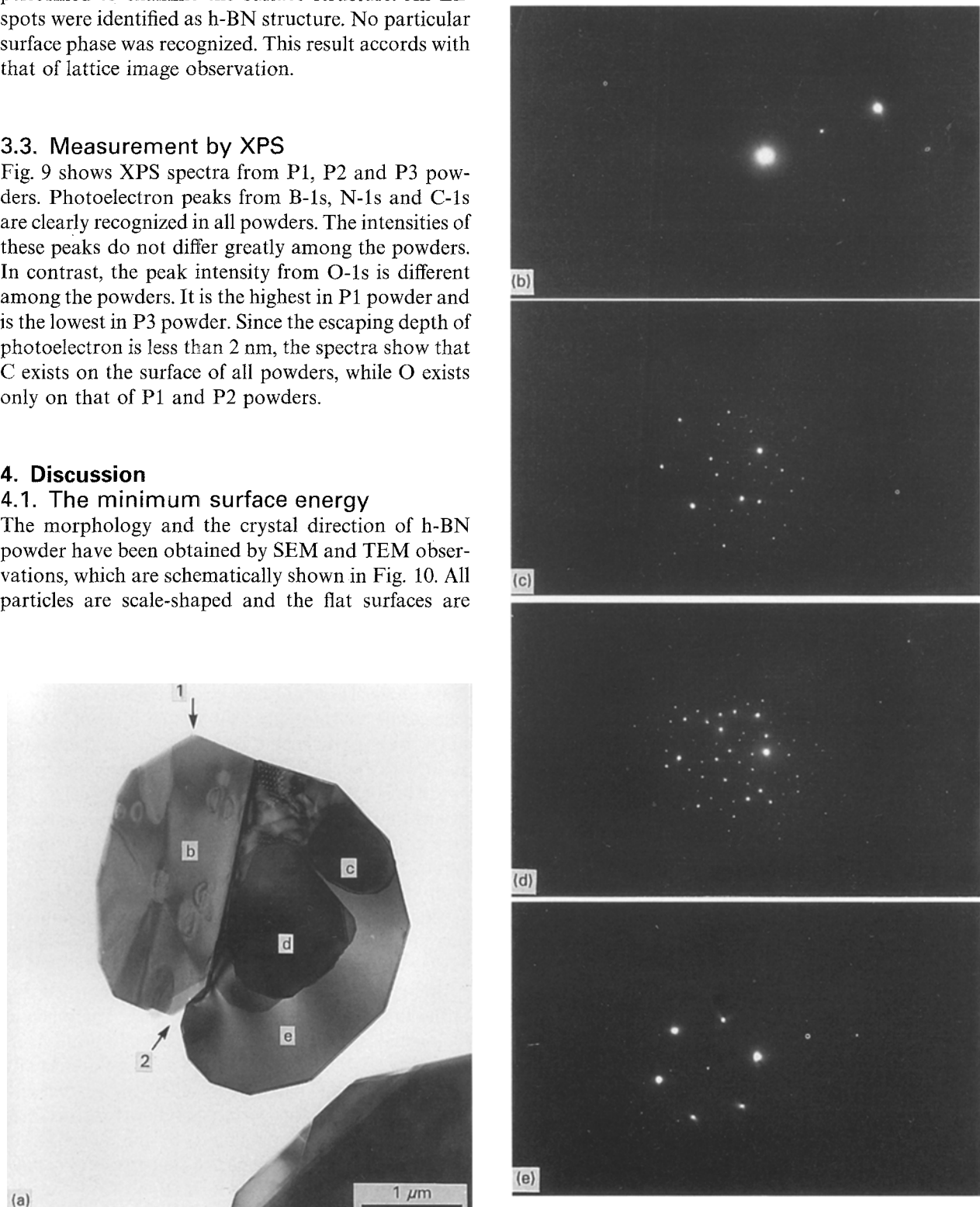


Figure 7 TEM image of combined grains in a P3 particle and ED patterns from the area indicated by (b), (c), (d) and (e) in (a).

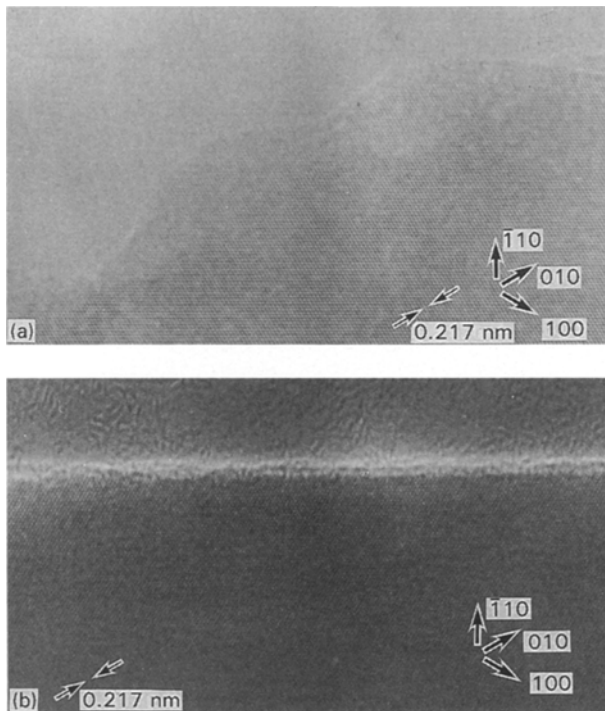


Figure 8 Lattice images in the vicinity of side surfaces of (a) P2 and (b) P3 particles.

plane is the lowest. It is understandable, therefore, that the flat surfaces of scale-shaped powder have (001) planes in order to minimize the surface energy.

4.2. The growth process

The growth of h-BN powder from first baking to second baking is illustrated in Fig. 10. In many one-stage baked particles especially in P1 particles, two or more grains overlap each other in contact with (001) flat surfaces, forming multi-grain particles. The overlapped grains have a common [001] axis forming a twist boundary and their relative rotation angle around the [001] axis ranges from 5 to 27°. Many of the overlapped grains have a coincidence lattice relation with respect to (001) grain boundary as shown in Fig. 6. The boundary energy is, therefore, low. The boundary does not migrate significantly. As a result, single grain particles hardly form during ordinary one-stage baking at 2073 K.

As is shown by XPS measurement, one-stage baked powder (P1 and P2) still has surface segregation of C and O, although they are subjected to the first baking (purifying) and rinse. It indicates that the crude BN powder before the first baking contained more impurities. Since the lattice image observation, as well as reflection ED, shows that there is no surface crystalline layer, it is expected that C and O are adsorbed in the surface. It is well known that impurities which are apt to segregate onto the surface are also apt to segregate to grain boundaries. During one-stage baking of crude BN powder impurities segregate onto the surface and the grain boundary inside a particle. It is reported that addition of C prevents grain growth [11]. Therefore it is expected that the grain boundary in a multi-grain particle cannot migrate and a single grain particle hardly forms.

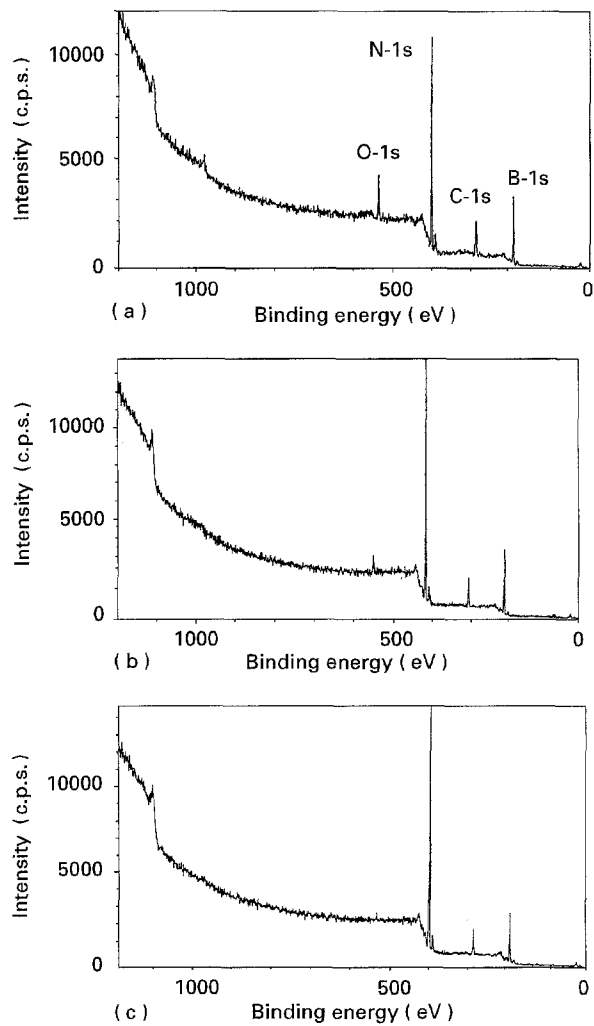


Figure 9 XPS spectrum from (a) P1, (b) P2 and (c) P3 powders.

In grain-overlapped particles the surface energy is minimized by lattice coincidence relation, which prevents the grain boundary migration or grain coalescence. Therefore each grain in grain-overlapped particles is substantially thin and as a result a thick single grain particle does not form during the baking at 2073 K. Fig. 4(c) shows a grain in which the thick part has a habit surface and the thin part has not. It means that being thick at the side surface is a necessary condition for a formation of the side surface habit. In a thin particle, the area of side surface is so small that total energy minimization by the formation of side surface habit is not expected. Consequently side surface habit does not form during one-stage bakings at 2073 K (P1).

In contrast, P3 powder is thoroughly purified due to the first baking (purifying) and rinse. Therefore, at the second baking, the grain boundary in grain-overlapped particles migrates, grains coalesce and finally thick single grain particles form. In the grains with thick side part, the side surface habit easily forms since the surface energy is minimized by the formation of side surface habit. It is expected that the total surface energy is minimized by the formation of side surface habits as well as flat surface habits. For these reasons, the side surface habit forms after two-stage baking.

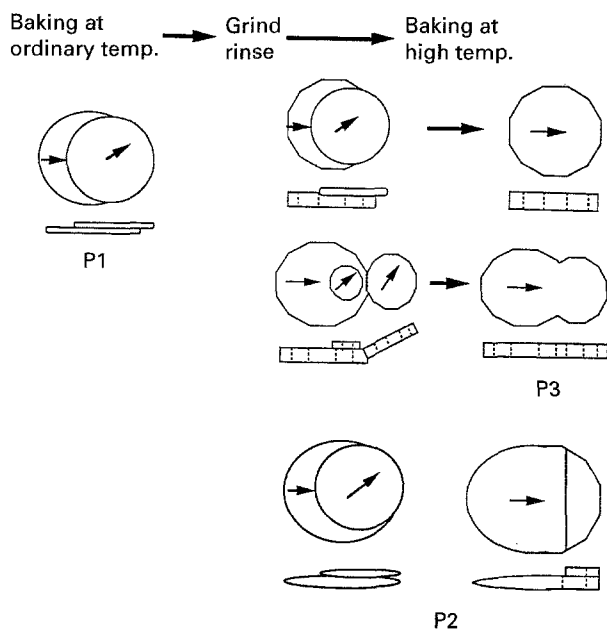


Figure 10 Growth model of h-BN powder. Top view and side view are shown. Arrows in the figure show one of $[100]$ directions.

In some cases, two grains are attached with each other in contact with the side surface and relative angle between flat surface normals is relatively large (more than 30°), as indicated in Section 3.2. Fig. 7 shows that the boundary between grains (b) and (e) has a neck as is indicated by the arrow 2 and another grain (d) starts to grow from the boundary between grains (b) and (e) over the top surface of grain (e). This indicates an atom stream from grain (b) to grain (d); excess atoms having formed at the boundary enlarges the grain (d), keeping the coincidence lattice relation. This may be one of the swelling processes of a particle. In other words, the particle having a neck, as shown in Fig. 7, may be the intermediate state of the present growing process.

4.3. Stability of h-BN powder

In general non-oxide ceramics are apt to be oxidized in high temperature oxygen atmosphere. Some non-oxide ceramics, however, can be used in high temperature air, since stable oxide film covers the surface and protects the interior from oxidation. As discussed by Yoshimura *et al.* [7–8], measured values of oxidation rate and of the activation energy scatter significantly. It means that not only the composition but also the surface state determines the surface oxidation rate. In the case of aspirin, for example, the elution rate in digestive organs is lowered by the presence of surface habit [9–10]. That means that the medical effect depends on the surface shape of powder. Similarly, since two-stage baked h-BN powder has side surface habits as well as flat surface habits, its surface energy is relatively low. The powder is expected to be stable against an attack by O or other environments owing to this characteristic shape. This means that two-

stage baked powder has remarkable properties for use in various environments or as a use of sintering materials.

5. Conclusion

The morphology and crystal properties of h-BN powder produced by one-stage baking processes at ordinary temperature and high temperature and two-stage baking process were investigated by SEM and TEM. The following results were obtained.

1. The particles are scale-shaped and the flat surface habits are (001) .
2. The side surfaces of one-stage baking particles are thin and round, while those of two-stage baking particles are thick and have side surface habits of (100) , (110) and their variants.
3. In one-stage baked powder, many particles are composed of overlapped grains contacting each other at the flat (001) twist boundary. The grains are in coincidence lattice relation and hardly migrate during the first baking.
4. During the second baking in two-stage baking, grain boundaries in grain-overlapped particles migrate to form a thicker single grain particle. In thick particles, side surface habits as well as flat surface habits are formed to minimize the total surface energy.
5. Since the particle of two-stage baking process has flat and side surface habits, the particle will be stable against O owing to its characteristic shape.

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