Growth of single crystals of aluminum nitride

TOSHIHICO ISHII, TADAO SATO and MINORU IWATA

National Institute for Researches in Inorganic Materials,
Kurakake, Sakura-mura, Niihari-gun, Ibaraki 300-31

Abstract

The growth mechanism and the growth condition of single crystals of aluminum nitride (AlN) prepared by the sublimation method are studied in relation with their morphology. The whiskers of AlN, whose growth directions are perpendicular to the (10\(\bar{1}0\)) plane (a-type whiskers), the (10\(\bar{1}1\)) plane (b-type whiskers) and the (0001) plane (c-type whiskers) grow through the VLS mechanism, iron acting as liquid-forming agent in the mechanism. The growth directions of whiskers depend on the growth temperature; the c-type whiskers grow above 1550°C, the a-type above 1700°C and the b-type above 1850°C. Blade-shaped crystals with large (0001) faces (a-type crystals) grow from lateral surfaces of the a-type whiskers.

Prismatic crystals with large prismatic (10\(\bar{1}0\)) faces (P-type crystals) and tabular crystals with large (0001) faces (T-type crystals) grow above 1900°C in the atmosphere free from iron. The P-type crystals grow in the circumstance of high purity. The T-type crystals grow in the atmosphere comprising carbon mono-oxide.

Growth spirals are observed on the (0001) face of the T-type crystals. The growth steps parallel to the c-axis and a-axis observed on the (10\(\bar{1}0\)) face of the P-type crystals.

Introduction

Aluminum nitride (AlN) has not been found in nature and its crystal structure is of the wurtzite type. Since it does not melt easily, the preparation of the single crystals of this material is mostly carried out by the sublimation method. Other methods such as chemical transport (Vepřek et al., 1971) and thermal decomposition of \(\text{AlCl}_3 \cdot \text{NH}_3\) (Renner, 1965) have also been reported.
The morphology of single crystals of AlN prepared by the sublimation method has been described by Drum (1965) and Witzke (1965). Drum grouped the crystals into five types: (1) platelets with (0001) habit plane, (2) thin blade-shaped whiskers with large surfaces (0001), (3) plates with (10\overline{1}0) habit plane, (4) thin blade-shaped filaments with large surfaces (10\overline{1}0), and (5) needles with hexagonal cross section and $\langle001\rangle$ growth direction. Witzke classified the morphology into five types: (I) whiskers with $\langle001\rangle$ as growth direction, (II) prisms or needle crystals with $\langle001\rangle$ as growth direction, (III) prisms distorted along $\langle0\overline{1}1\rangle$, (IV) tabular crystals with (0001), and (V) platelike crystals with (0001) and elongated in $\langle100\rangle$. Besides these descriptions, Pastřňák and Roskovcová (1964) classified the crystals of AlN into three types; type A, needle crystals elongated parallel to the $c$-axis; type B, platelike crystals parallel to the $c$-axis; type C, thin platelike crystals parallel to the (0001).

<table>
<thead>
<tr>
<th>Type</th>
<th>Authors</th>
<th>Witzke</th>
<th>Pastřňák &amp; Roskovcová</th>
<th>Present authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tabular crystal (0001)</td>
<td>Drum</td>
<td>(I)</td>
<td>type C</td>
<td>T-type</td>
</tr>
<tr>
<td></td>
<td>Witzke</td>
<td>(IV)</td>
<td>type C</td>
<td></td>
</tr>
<tr>
<td>Blade-shaped crystal (001)</td>
<td>(2)</td>
<td>(V)</td>
<td>type C</td>
<td></td>
</tr>
<tr>
<td>Blade-shaped filament with (10\overline{1}0)</td>
<td>(3)</td>
<td>(III)?</td>
<td>type B</td>
<td></td>
</tr>
<tr>
<td>Platý crystal with (10\overline{1}0)</td>
<td>(4)</td>
<td></td>
<td>P-type &amp; platelike crystal</td>
<td></td>
</tr>
<tr>
<td>Whisker &amp; needle normal to (0001)</td>
<td>(5)</td>
<td></td>
<td>b-type</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Comparison of classification on the morphology of AlN crystals by several authors.
Comparison of the classifications of the morphology of AlN crystals by several authors is shown in Table 1.

Drum reported that axial dislocations always found in the crystals of type (4) play an essential role in the growth, but he neither explained the growth mechanism of the crystals of other types, nor gave any detailed account of the growth conditions of the single crystals of AlN.

Witzke related the variety of the morphology of the single crystals with growth temperature, but he also did not go into the detailed investigation of the growth mechanism.

Pastrnák and Roskovich studied the relation between the morphology and the degree of supersaturation, and observed that the crystals of type A grow under a high degree of supersaturation and found that most of the crystals formed at lower degrees of supersaturation in their graphite-resistance tube-furnace are of type C, frequently associated with crystals of type B. Further, they suggested that traces of O, CO and C might affect the morphology of the crystals.

The present authors reported previously on the effects of impurities upon the morphology of AlN crystals. It was ascertained that the whiskers and needle crystals (prisms) of AlN grow through the so-called VLS mechanism (Ishii et al., 1971). We have further extended the study, and have found several new features relating to the morphology of AlN grown through the VLS mechanism and the effects of CO on the morphology of tabular crystals with large (0001) basal faces, which will be described in this paper in some details.

Experimental

Starting materials and furnaces used

Two kinds of AlN powder were used as the starting materials.
Growth of single crystals of aluminum nitride

One is called "pure powder" and the other is called "commercial powder" in this paper. Their properties and preparation methods were described in the previous paper (Ishii et al., 1971).

Both a graphite-resistance tube-furnace and a high-frequency induction-furnace were used for growing the crystals. The features were described in the previous paper (Ishii et al., 1971). These furnaces were used horizontally. The graphite crucible employed is shown in Fig. 1. The crucible has the following merits: (1) most part of vapor sublimed from the starting materials is kept within the crucible, and (2) suitable temperature gradient for the growth of single crystals can be realized by changing the length of the junction between the crucible and a water-cooled holder. This crucible will be specified as "closed crucible" in this paper. Another type of graphite crucible without a water-cooled holder and a lid was also used in this experiment. This crucible will be called "open crucible".

Two kinds of induction coil for the high-frequency induction-furnace were employed to change the temperature gradient. One type consists of a long coil, 160 mm in length, and a graphite susceptor, 160 mm in length. The moulded sample of the starting material was

![Fig. 1. Cross section of the "closed crucible" made of graphite.](image)

B: charged powder of AlN.  F: outlet for N₂ gas.
C: space for crystal growth.  G: inlet for N₂ gas.
placed in the middle of the susceptor which was closed at both ends in order to enclose the vapor sublimed from the starting material and to make the temperature gradient gentle. The furnace thus set up will be called "L-type furnace". The other type consists of a whirlpool-type induction coil, 6 mm in width, and a graphite susceptor, 70 mm in length. This setup will be called "W-type furnace". The susceptor of both types were made of reactor-grade graphite and with wall thickness of 2 mm and inside diameter of 16 mm. Both furnaces were used horizontally as shown in Figs. 2 and 3.

Temperature was measured by the optical pyrometer.

Experimental results

Preparation of blade-shaped crystals and whiskers—At first, the preparation of single crystals was carried out in the graphite-resistance tube-furnace, where the commercial powder of AlN was used as the starting material. The commercial powder put in the closed crucible was placed in a region of the highest temperature in the furnace and kept at 2150°C for 5 hours in a nitrogen atmosphere.

![Diagram of furnace](image)

Fig. 2. Cross section of the "L-type furnace" used for high-frequency induction-heating.

A: moulded sample of AlN.
B: graphite susceptor.
C: alumina tube.
D: carbon felt.
E: induction coil.
F: graphite disk for thermal shield.
Growth of single crystals of aluminum nitride

Fig. 3. Cross section of the "W-type furnace" used for high-frequency induction-heating.
A: moulded sample of AlN.  D: carbon felt.
B: graphite susceptor.  E: induction coil.
C: alumina tube.

Many single crystals, each crowned with a black globe on the top, grew between 1700°C and 2000°C on the inside and the outside of the wall of the closed crucible and sometimes on the inside wall of the furnace. The crystals thus formed were confirmed to be single crystals by optical and X-ray means. The black globe on the top of the crystal was identified to be iron with electron probe microanalyser (EPMA) and from its magnetism. The morphology of the single crystals thus obtained were classified into the following three types from X-ray diffraction experiments with a precession camera and observation under the polarizing microscope with a universal stage.

(1) Crystals with large (0001) faces elongated perpendicular to
Crystals falling in this category will be called "a-type crystal". A typical example is shown in Fig. 4. The central axis lies in the (0001) plane, and a black globe is observed on the top of the central axis. EPMA analyses revealed that a considerable amount of iron is distributed along the central axis (Figs. 5a and 5b). This selective distribution of iron along the central axis was also detected under the reflection microscope. The black iron globe at the tip is often

Fig. 4. Blade-shaped crystal (a-type crystal) with large (0001) face and elongated perpendicular to (1010).

Fig. 5a. Electron micrograph of an a-type crystal.

Fig. 5b. X-ray image produced by iron radiation from a globe on the top and the central axis of an a-type crystal (Fig. 5a).
missing in some larger crystals which had probably grown at higher temperature (Fig. 6a). However, the iron content is always high along the central axis even for the crystals, suggesting that the iron globe disappeared after the growth (Fig. 6b). The a-type crystals correspond to Drum’s type (2), Witzke’s (V) and Pastrňák and Roskovcová’s type C (Table 1).

The a-type crystals occurred most frequently and developed larger in size in this run. They, in fact, seem to be observed widely in other laboratories. They are colorless, but often look black or gray on account of iron, carbon etc. deposited on the surfaces. EPMA analyses revealed that iron is the main component of the globes, and small amount of chromium and manganese are also contained in these globes.

(2) Whiskers with the growth direction making an angle of 5° with the normal to (1011). Crystals of this type will be called “b-type whisker” in this paper. The typical one is shown in Fig. 7. The crystals are always needle-shaped and have a black globe on the top. EPMA analyses revealed that the globes of the b-type whiskers have the same components as those of the a-type crystals. However, in contrast with the a-type crystals, no iron content was detected.

Fig. 6a. Blade-shaped crystal (a-type crystal) without an iron globe on the top.

Fig. 6b. X-ray image produced by iron radiation from the central axis of an a-type crystal (Fig. 6a).
along the axes of the b-type whiskers.

The X-ray diffraction experiment with the precession camera proved that the growth direction of the crystals is inclined at about

![Whisker (b-type whisker)](image)

**Fig. 7.** Whisker (b-type whisker). The growth direction makes an angle of about 5° with the normal to (10\(\overline{1}1\)).

![Precession photograph](image)

**Fig. 8.** Precession photograph of a b-type whisker.
5° with the normal to (10\overline{1}1) and that the four well developed faces have comparatively high face indices such as (1\overline{5}45) in a close approximation (Figs. 8 and 9), though the surfaces of the b-type whiskers are generally too rugged to allow accurate determination of the face indices. The angle between the c-axis and the growth direction measured under the polarizing microscope is in accordance with the results of the X-ray diffraction. Twins about the growth direction were observed only in a few cases.

The b-type whiskers cannot be related with any one of the type in Drum’s, Witzke’s, and Pastrnáč and Roskocová’s classifications, and accordingly seem to be a new type. Crystals of this type were not found so frequently in this experiment as the a-type crystals.

(3) Whiskers and needle crystals with the growth direction along the c-axis. Crystals of this type will be called “c-type whisker” in

Fig. 9. Stereogram of the b-type whisker.
this paper. The growth mechanism and condition of crystals of this type were described in the previous paper (Ishii et al., 1971). The c-type whisker is identified as Drum’s type (5), Witzke’s (I) and (II) types and Pastrňák and Roskovcová’s type A (Table 1).

The temperature at which each of these types of AlN crystals begins to grow was measured in the open crucible: the c-type whiskers begin to grow at 1550°C, the a-type crystals above 1700°C and the b-type whiskers above 1850°C.

The crystals of these three types can also be prepared in the high-frequency induction-furnace. Therefore, in order to confirm the effects of iron impurity on the crystal growth of AlN, experiments were carried out in the L-type furnace. Firstly, a moulded sample of the commercial powder was heated at 2100°C for 5 hours in nitrogen atmosphere. Crystals of the three types grew at 1700°C and 2000°C. Secondly, a moulded sample of pure powder was heated in the same way. Then, tabular crystals with large (0001) basal faces and prismatic crystals with large (10\(\bar{1}0\)) prismatic faces were found to grow. If impurities were removed from the commercial powder by heat-treatments at 1900°C for 3 hours in nitrogen atmosphere, these tabular and prismatic crystals did grow. When iron powder of a few percents was added to the pure powder, crystals of the three types were confirmed to occur.

Preparation of tabular and prismatic crystals—As stated above, tabular crystals with large (0001) basal faces (Fig. 10) and prismatic crystals with large (10\(\bar{1}0\)) prismatic faces and (0001) faces (Fig. 11) grow above 1700°C from the starting materials free from iron. The tabular crystals with large (0001) faces will be called “T-type crystal” and those with large (10\(\bar{1}0\)) faces and (0001) faces will be called “P-type crystal” in this paper. Both crystals correspond to the types proposed by Drum, Witzke, and Pastrňák and Roskovcová as shown in Table 1.

We were aware from our preliminary experiments that T-type
crystals grow well in the graphite-resistance tube-furnace, and P-type crystals grow frequently in the high-frequency induction-furnace. Therefore, it was surmised that the difference in the growth condition for both crystals depends on either the degree of supersaturation (temperature gradient) or the CO content in the atmosphere. The graphite-resistance tube-furnace show generally a gentle temperature gradient and a high content of CO than the high-frequency induction-furnace.

In order to investigate the effects of the temperature gradient and CO, the following experiments were carried out. Firstly, a moulded sample of pure powder is heated at the highest temperature of 2100°C in a nitrogen atmosphere for 5 hours in W-type furnace.
Brown P-type crystals grew predominantly, and on their (10\overline{1}0) faces growth steps parallel to the c-axis and the a-axis were observed. Next, a moulded sample of pure powder is heated in the same furnace and under the same condition as in the above experiments except that the nitrogen atmosphere comprised 5% of CO. Then, the T-type crystals grew predominantly. In an experiment carried out in a nitrogen atmosphere comprising H₂O, CO produced by the reaction of H₂O with graphite was found to be suited for growing the T-type crystals. In this experiment, almost all the crystals grown were of the T-type. The T-type crystals prepared in this method looked often green and exhibited hexagonal (0001) and (00\overline{1}1) faces, on which several growth steps (Fig. 10) and growth spirals (Fig. 12) were observed.

The T-type crystals prepared in this method were also examined by means of EPMA, X-ray diffraction and infrared spectroscopic analysis in order to compare the T-type crystals with the crystal of Al₂CO which is isomorphous with AlN. The EPMA analysis showed that the main components of the T-type crystals are aluminum and nitrogen, and carbon and oxygen are comprised only in small quantities. The lattice constant along the c-axis of the crystals is in accordance with that of the standard crystals of AlN, both ob-

![Fig. 12. Growth spiral on the (0001) face of a T-type crystal.](image)
tained from X-ray oscillation photographs. The infrared spectroscopic analysis showed that the absorption spectrum of the T-type crystals coincides with that of pure AlN and differs from Al₅CO.

Thirdly, a moulded sample of pure powder was heated in the L-type furnace under the same condition as in the first experiment. P-type crystals grew. Consequently, the difference of the growth conditions between the T-type and the P-type crystals is due to the CO content in the atmosphere, not to the temperature gradient. The T-type crystals grow more frequently in an atmosphere with a higher content of CO than the P-type crystals.

Discussion

_Growth directions of AlN whiskers grown through the VLS mechanism_

Whiskers of Si, GaAs and GaP grow through the VLS mechanism and have been studied morphologically. A part of these whiskers has a twin plane parallel to the growth direction (Table 2), while the whiskers of AlN are not twinned in general. It is not always known

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>GaAs</th>
<th>GaP</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D-H</td>
<td>B-F</td>
<td>D-H</td>
<td>B-F</td>
</tr>
<tr>
<td>111</td>
<td>110*</td>
<td>111</td>
<td>100</td>
<td>111</td>
</tr>
<tr>
<td>220(110)*</td>
<td>111</td>
<td>200(100)</td>
<td>111</td>
<td>200(100)</td>
</tr>
<tr>
<td>311</td>
<td>112*</td>
<td>220(110)</td>
<td>112*</td>
<td>220(110)</td>
</tr>
<tr>
<td>400(100)</td>
<td></td>
<td>311</td>
<td>311</td>
<td></td>
</tr>
<tr>
<td>331</td>
<td></td>
<td>331</td>
<td></td>
<td></td>
</tr>
<tr>
<td>422(112)*</td>
<td></td>
<td>422(112)*</td>
<td>420(120)</td>
<td></td>
</tr>
</tbody>
</table>

D-H Donnay-Harker's rule
B-F Bravais-Friedel's rule
—— Plane perpendicular to the growth direction of whiskers
* Twinned whiskers
which factors decide the growth directions of whiskers grown through the VLS mechanism. Wagner and Ellis (1965) suggested that the growth directions of Si whiskers depend on the kinds of impurities, but he did not show the reason. The range of the temperature for the growth of AlN whiskers is wider than those of Si, GaAs and GaP. It is noticeable that the AlN whiskers elongated to the directions perpendicular to (0001), (10\overline{1}0) and (10\overline{1}1) planes grow from lower to higher temperature respectively in this sequence. This sequence corresponds to the order of the morphological importance not by Donnay-Harker's rule, but by Bravais-Friedel's rule (Table 2).

The growth rate normal to the (10\overline{1}1) is higher than that normal to the (10\overline{1}0) and the (0001) planes from Donnay-Harker's point of view. However, this is incompatible with the experimental results. The b-type whiskers occur less frequently than the c-type and the a-type whiskers.

In the crystal structure of AlN (wurtzite structure) (Fig. 13), there are two shortest bonds a and b, where a is a bond between (0, 0, 0) and (2/3, 1/3, \overline{1}/8), and b between (0, 0, 0) and (0, 0, 3/8). According to the Hartman's theory (1955), the bonds a and b constitute the following three periodic bond chain vectors (PBC vectors).

\[ A: [10.0], [01.0], [11.0]; \text{bonding 2a} \]
\[ B: [00.1]; \text{bonding 2(a+b)} \]
\[ C: [10.0], [01.1], [11.1]; \text{bonding 2(a+b)} \]

In the crystals of AlN, there are three F faces (0001), (10\overline{1}0) and (10\overline{1}1) which contain more than two PBC vectors.

The bond length of a is 1.855 Å, and that of b is 1.917 Å (Jeffrey et al., 1956). Therefore, the a bond is stronger than the b bond. The (0001) face contains the vectors 2a and 2a. Both the (10\overline{1}0) face and the (10\overline{1}1) face contain vectors 2a+2b and 2a. Therefore, the (0001) is morphologically more important face than the (10\overline{1}0) and the (10\overline{1}1). Let us next take the attachment energy into consideration. A slice d_{0002} is attached with the bond b per mol to the
Fig. 13. Crystal structure of AlN.

a is a bond between \((0, 0, 0)\) and \(\left(\frac{2}{3}, \frac{1}{3}, \frac{1}{8}\right)\), and 1.885 Å.

b is a bond between \((0, 0, 0)\) and \(\left(0, 0, \frac{3}{8}\right)\), and 1.917 Å.

surface of the (0001). A slice \(d_{10\overline{1}0}\) is attached with the bond \(b\) per mol to the surface of the (10\(\overline{1}\)0). A slice \(d_{10\overline{1}1}\) is attached with one or two bonds \(a\) per mol to the surface of the (10\(\overline{1}\)1). Therefore, the attachment energy on the faces of AlN crystal decreases in the order of (10\(\overline{1}\)1), (10\(\overline{1}\)0) and (0001). The (0001) is, therefore, morphologically the most important face of the three faces. The (10\(\overline{1}\)0) comes next, the (10\(\overline{1}\)1) face the least of them.

From these analyses, the growth process may be described as follows. At first, a crystallite with a large (0001) face is formed in the drop of liquid iron, whose size determines the size of the crystallite. The Fe drop on the (0001) face of the crystallite drives the crystals to grow in the form of the whisker in the direction perpendicular to the (0001) (c-type whisker). Under high temperature conditions, the second and the third important faces may appear on
the crystallite in Fe drop, which will result in the growth of the whiskers in the direction perpendicular to the (10\overline{1}0) and the (10\overline{1}1) respectively (a-type and b-type whiskers).

**Crystals grown in the pure system**

P-type and T-type crystals grow in the environments containing no iron as impurities. Since \{10\overline{1}1\} is the least important face among the three F-faces \{0001\}, \{10\overline{1}0\}, and \{10\overline{1}1\}, crystals grown under the near equilibrium conditions are expected to be bounded by \{0001\} and \{10\overline{1}0\} and \{10\overline{1}1\} is absent. One of such crystals has been shown in Fig. 11 and called "prismatic crystal" or "P-type crystal" in this paper. The P-type crystal is the ideal morphology of AlN crystal. However, AlN crystal is deformed from the P-type crystal by growth condition and often becomes into the platelike crystal, a pair of \{10\overline{1}0\} faces of which are larger than the other \{10\overline{1}0\} faces. This crystal is called "platelike crystal" in this paper and shown in Fig. 14. The platelike crystal seems to be one of the habits of AlN crystals. The growth of the T-type crystals will be discussed later on.

![Platelike crystal with a large (10\overline{1}0) face.](image)
Effect of CO

If a small amount of CO is added to the nitrogen gas flowing into the furnace where P-type and platelike crystals are growing, the morphology of the growing crystals changes drastically and both P-type and platelike crystals become no longer predominant. The T-type crystals grow predominantly.

If a part of N atoms in the AlN crystals grown in the atmosphere containing CO is substituted by C and O atoms, Al$_2$CO structure may be partly formed in the crystal structure of AlN. Al$_2$CO is isomorphic with AlN. In the structure of Al$_2$CO, on the average, a half of Al atoms occupies the normal interstices and the remaining half occupies the inverse interstices of hexagonal close packed arrangements formed by anions (Amma and Jeffrey, 1961).

The morphological importance of the (0001) faces of AlN crystals containing CO does not decrease as compared with that of AlN crystals containing no CO, because the (0001) faces of both crystals contain PBC vectors of 2a and 2a only. On the contrary, the bond length of b changes according to the Al positions in the normal and the inverse interstices, and the new bond b', which is longer than b, is generated in the ⟨001⟩ direction of AlN crystals containing CO. Therefore, the PBC vectors of 2a+2b must be replaced by 2a+2b(b') in the AlN crystals grown in the atmosphere containing CO. The (1010) face containing 2a+2b(b') in its PBC vectors decreases remarkably in the morphological importance. This is why the T-type crystals grow predominantly in the atmosphere containing CO.

Blade-shaped crystals (a-type crystals)

Though crystals of the a-type and the c-type have been prepared by several authors, their growth mechanism and conditions have scarcely been clarified. The b-type whisker has never been reported so far. The a-type crystals was briefly investigated by Drum et al. (1964), who reported that although many of these crystals are free
from dislocations, some contain axial dislocations running through the entire length of the crystals. They said that it is difficult to draw a definite conclusion whether or not these crystals grow by the means of the screw dislocation mechanism.

The present authors propose the following mechanism for the growth of the a-type crystals. At first, whiskers in the direction perpendicular to the (10\(\overline{1}0\)) plane (a-type whisker), to the (10\(\overline{1}1\)) plane (b-type whisker) and to the (0001) plane (c-type whisker) grow through the VLS mechanism, where iron is liquid-forming agent. The growth direction of the a-type whisker is \(\langle 210 \rangle\), and the indices of their lateral faces, which have the zone axis of \(\langle 210 \rangle\), are \(\langle hh2hl \rangle\), in which (0001) and (000\(\overline{1}\)) are involved. According to Hartman's theory, the (0001) and (000\(\overline{1}\)) faces of AlN crystals are F-faces and the other faces belonging to the zone \(\langle 210 \rangle\) are K-faces or S-faces. As the reticular density of the (0001) plane is larger than that of the other planes, the (0001) and the (000\(\overline{1}\)) are the most important faces among the faces belonging to the zone of \(\langle 210 \rangle\) from Donnay-Harker's point of view. Consequently, on the subsequent growth on the lateral surfaces of an a-type whisker after leader growth, the growth rate normal to the (12\(\overline{1}0\)) plane is larger than that normal to the (0001) plane and thus the blade-shaped crystals (a-type crystals) is derived. Fig. 4 shows a good example of the relation between a whisker with an iron globe and its subsequent development.

Contrary to the a-type whisker, the b-type and the c-type whiskers have some sets of equivalent lateral faces respectively, and the subsequent growth rate after the leader growth is perhaps equal on these lateral faces. Consequently, both b-type and a-type whiskers do not develop into blade-shaped crystals.

The hitherto known examples of blade-shaped crystals grown through the VLS mechanism are GaAs, GaP and Se (Barns and Ellis, 1965; Ellis et al., 1968; Keezer and Wood, 1966). In order to discuss
the morphology of AlN crystals, compound crystals such as GaAs and GaP should also be taken into account from the view point of reaction and stoichiometry. The growth direction of the blade-shaped crystals of both GaAs and GaP is $\langle 001 \rangle$ of the sphalerite-type structure. GaP has also the $\langle 112 \rangle$ growth direction with (111) as twinning plane. Since the whiskers of GaAs and GaP with $\langle 001 \rangle$ growth direction have four equivalent lateral faces, it is difficult to know the reason why the subsequent growth rate on a pair of opposite faces is larger than that on the other pair of faces. The other blade-shaped crystal of GaP with $\langle 112 \rangle$ growth direction has always (111) as twinning plane parallel to the extensive (111) face. It seems to be probable that the blade-shaped crystals of this type grow through the twinning growth mechanism. Se grows also through the VLS mechanism into the blade-shaped crystals which have $\langle 100 \rangle$ as growth direction and $\{1210\}$ lateral faces. However, Se forms a molecular crystals which consists of spiral chain, and it will not be appropriate to compare it with AlN. The central axis of the whiskers which grow through the VLS mechanism cannot be observed. Perhaps, the blade-shaped crystals of Se seem to grow in the same way as the a-type crystals of AlN.

The blade-shaped crystals with the large (0001) faces of AlN (a-type crystals) are resulted in the graphite-resistance tube-furnace. In the above experiments, it was found that AlN crystallizes into the tabular crystal with (0001) and (000$\bar{1}$) faces (T-type crystal) in a CO-rich atmosphere. It seems probable that the growth of the a-type crystals has a close relation with that of the T-type crystals. Both crystals grow easily in the graphite-resistance tube-furnace, in which large amount of CO is produced at high temperature. The growth in the direction of the $c$-axis is reduced and the (0001) and the (000$\bar{1}$) faces seem to be developed into the blade-shaped crystals, due to the absorption of CO. In the L-type furnace with a low CO content, whiskers grew in the direction perpendicular to (10$\bar{1}$0) with-
out blade-shaping (Fig. 15). The crystals of this type are called "a-type whisker" in this paper.

**Conclusion**

(1) The whiskers of AlN grow through the VLS mechanism in the directions perpendicular to the (0001) plane (c-type whiskers), the (10\overline{1}0) plane (a-type whiskers), and the (10\overline{1}1) plane (b-type whiskers).

(2) The growth directions of AlN whiskers depend on the growth temperature. The c-type whiskers grow above 1550°C, and the a-type whiskers above 1700°C and the b-type whiskers above 1850°C. This sequence accords with the order of the morphological importance deduced from the Hartman's theory.

(3) Iron is the liquid-forming agent for the VLS mechanism of AlN whiskers.

(4) The subsequent crystal growth progresses under the CO-rich atmosphere on the lateral surfaces such as (1\overline{2}10) of the a-type whiskers after the leader growth has been completed.

(5) Tabular crystals with large (0001) faces (T-type crystals) and prismatic crystals with large (10\overline{1}0) and (0001) faces (P-type
crystals) grow in the atmosphere free from iron. The more frequently the former appears, the richer is the content of CO in the atmosphere.

(6) P-type crystals grow near the equilibrium conditions, and are the ideal morphology of AlN crystals. Platelike crystals with larger (10$ar{1}$0) than (0001) faces grow often in almost the same surroundings. They are the crystals deformed from the P-type crystals.

(7) The relation between the morphology and impurities and growth temperature is given in Table 3 and Fig. 16.

Table 3. The relation between morphology, impurities and growth temperature.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1550°C&lt;</td>
</tr>
<tr>
<td>iron</td>
<td>c-type whiskers</td>
</tr>
<tr>
<td>iron, CO in atmosphere</td>
<td></td>
</tr>
<tr>
<td>CO rich in atmosphere</td>
<td></td>
</tr>
<tr>
<td>a small amount</td>
<td></td>
</tr>
</tbody>
</table>

*Acknowledgements*—The authors wish to express their sincere thanks to Dr. Yoshio Suzuki, Dr. Hiromoto Nakazawa, Dr. Motohiko Ishii and the fourth group (1967–1973) of this institute for their kind and valuable advice and criticisms. Their thanks are also due to the Japan Electron Optics Laboratory Co. Ltd. for its help in carrying out the EPMA experiments. The authors are indebted to Prof. Ryoichi Sadanaga of the Mineralogical Institute, University of Tokyo for critically reading the manuscript.
Fig. 16. Morphology of single crystals of AlN.

REFERENCES

Growth of single crystals of aluminum nitride


Received February 20, 1975; revised June 6, 1975.