研　究　速　報

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INTERFACIAL DEFECTS IN HOT PRESSED ALUMINIUM NITRIDE CERAMICS

ホットプレス窒化アルミニウム中の界面欠陥

Serge HAGEGE*, Yoichi ISHIDA* and Shyunichiro TANAKA*
セージュ　アジェジュ・石　田　洋　一・田　中　俊一郎

1. INTRODUCTION

The purpose of this preliminary study has been to analyze, mainly by transmission electron microscopy, the microstructure of a commercially produced pure Aluminium nitride containing nevertheless a small quantity of non-metallic (Oxygen...) as well as metallic (Fe, Si...) impurities. It will be suggested hereafter that the main characteristics of the microstructure and the nature of the structural defects are simply related to the presence of these impurity atoms inserted in the wurtzite structure of AlN 2H. Different configurations of polytypoids will be presented. The original feature of this material is a very particular configuration of a sequence of stacking faults lying alternatively on the basal plane and on a curved three-dimensional surface, the two parts being connected by a dislocation. It is believed that these often complicated arrangements are part of the growth process of a very simple defect. This defect is made of a dislocation loop containing a stacking fault in the basal plane and surmounted by a dome.

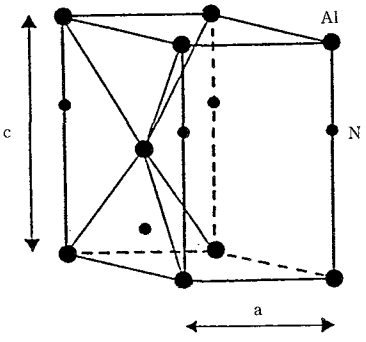
2. STRUCTURE OF AlN

2.1 The wurtzite structure

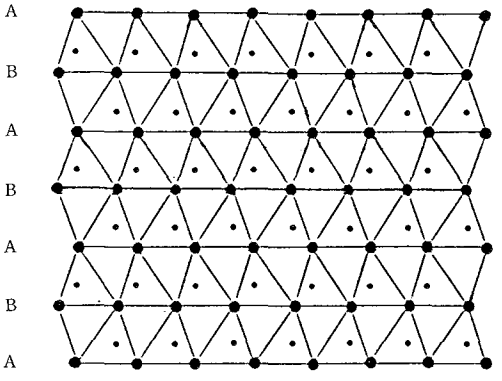
Aluminium nitride can be represented as in figure 1a by a hexagonal close packed arrangement of aluminium atoms defining tetrahedral sites half filled by nitrogen atoms (wurtzite structure). It is traditionally the custom to represent the structure of wurtzite type materials by a projection on the $(11\bar{2}0)$ plane as in Fig. 1b to characterize the hcp stacking of the basal planes.

2.2 Influence of the impurities

Aluminium nitride based ceramic materials are often found in combination with oxide type materials such as Al_2O_3, SiO_2, Y_2O_3[1]. In the case of alumina, solid solutions between AlN and Al_2O_3 are very special in the sense they have aluminium as a



a) unit cell with tetrahedral sites



b) (1120) projection

Figure 1　ALN wurzite structure

*Dept. of Industrial Chemistry and Metallurgy, Institute of Industrial Science, University of Tokyo

common element and it is well accepted that the addition of oxygen to AlN would create impossibly short distances between atoms which can be eliminated by changing the coordination of aluminium from six (as in AlN) to four (as in Al_2O_3). Therefore, in the presence of a smal quantity of oxygen impurities, AlN materials will contain, in addition to the wurtzite AlN 2H, a large variety of modulated structure called compositional polytypes or polytypoids.

The structure of these polytypoids has a well accepted model[2~6] based on an adequate stacking of layers with various combinations of the coordination of the metallic atom: coordination four as in AlN, coordination six as in Al_2O_3 and once per unit blocks, one or two metallic layers are shared by two or three adjacent tetrahedral sites to compensate the excess of non-metallic atoms. The coordination six is associated with a single stacking fault on the metallic layers.

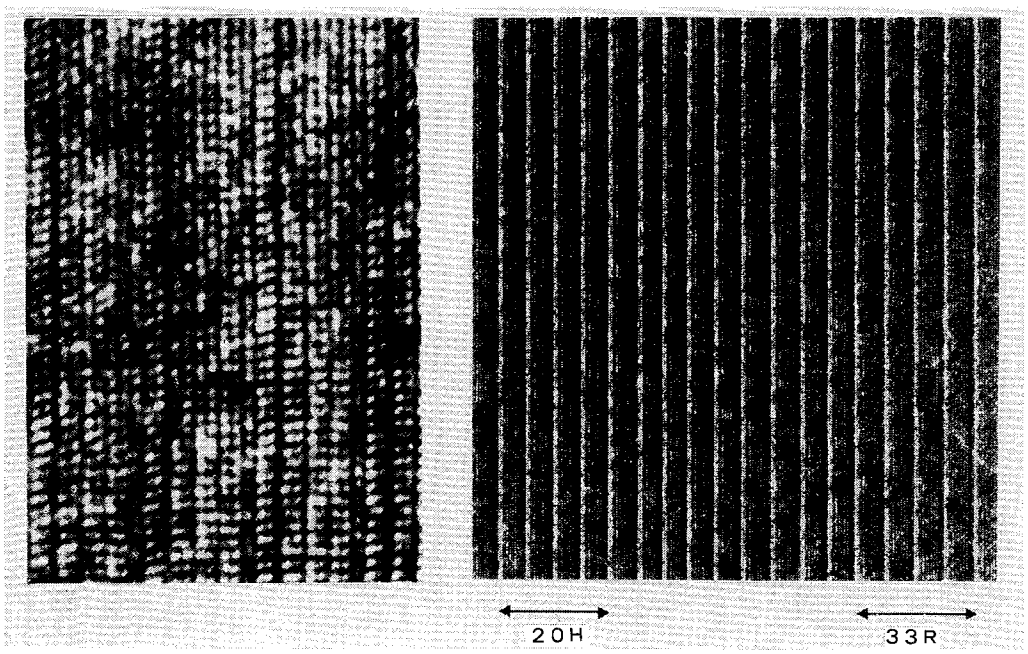
3. EXPERIMENTAL PROCEDURE

The specimen analyzed for this study came from a Aluminium Nitride wafer produced by Toshiba Corporation. Chemical composition determination and X ray analysis where performed on the same sample. The TEM specimen, 2.3 mm discs, were mechanically cut and thinned to approximatively 50 μm. Final electron transparency was obtained by ion beam thinning at 4.5 Kv. JEOL JEM1250 high voltage and 200CX high resolution microscopes were used for the observation.

4. RESULTS

4.1 Microstructure

AlN 2H grains are roughly equiaxed with an average size of a few microns. The polytypoids are always present in elongated grains with the basal plane parallel to the longest direction. Inclusions of small θ Al_2O_3 grains were often found inside the AlN 2H grains. Exceptionally larger θ Al_2O_3 grains were also found between AlN 2H grains at grain boundary junctions. The $FeAl_2O_4$ spinel phase also appeared but in the shape of very small precipitates attached to one side of a polytypoid grain. θ Al_2O_3 inclusions never show any preferential orientation with the AlN 2H matrix or neighboring grains. On the contrary the $FeAl_2O_4$ phase is on perfect epitaxy with the



a) 27R polytypoid grain　b) Compositional modulation of the polytypoid structure in a grain

Figure 2 HREM of polytypoids

polytypoid grain and show the following orientation:

$(11\bar{2}0)$ // (110) and [0001] // [111]

with an interface (0001) // [111]

4.2 Polytypoids

The chemical analysis of our sample has shown that oxygen was the main metallic impurity. Its total concentration was 1.43 wt%. Therefore only polytypoids with the highest n value are expected to be present. As predicted by the X-ray analysis, the 27R polytypoid was found the most frequently as a whole in one grain (Fig. 2a) but some other polytypoid grains where often composed of a mixture of various unit blocks. In Fig. 2b the structure is composed by unit blocks of 9, 10 or 11 layers (n=9, 10, 11). In order to form one unit cell of a particular polytypoid two (n even) or three (n odd) unit blocks are necessary. Then in Fig. 2b, at least some unit cells of the polytypoids 33R (3 unit blocks minimum) and 20H (2 unit blocks minimum) are present but in the middle part of the picture the mixture of unit blocks do not correspond to any particular complete polytypoid structure but appears as a compositional modulation. This modulated structure may have appeared as the phase 8 AlN - Al_2O_3 (n=10) in the X-ray analysis.

4.3 The dome-like defects

When the concentration of impurities is low enough in one grain, only few stacking faults are present and then, they show a very particular configuration (Fig. 3). They are formed by two types of surfaces (one flat lying in the basal plane and one curved), two different surfaces being connected by a dislocation. In the most simple cases the configuration is like a "dome" which is made of a dislocation loop containing a stacking fault and surmounted by an rather spherical faulted surface. Most of the time these configurtions are more complicated but are always composed by a continuous sequence of one basal fault, one dislocation, a curved faulted surface, one dislocation, a basal fault and so on. Another very peculiar particularity of this configuration is the fact that these sequences of faults closes by themselves dividing the space inside and outside the configuration.

The HREM image in Fig. 4 is the $(11\bar{2}0)$ projection of the structure showing the atomic arrangement for the two surfaces with a stacking fault for the planar part and a shift of the basal planes for the curved part. This image shows also clearly the extra basal plane defining partly the core of the dislocation limiting the two faults. The difference of contrast between every second basal plane is believed to be due to a slight misorientation of the specimen that enhances the shift in the curved part.

The various displacement and Burgers vectors of these configurations have been determined by

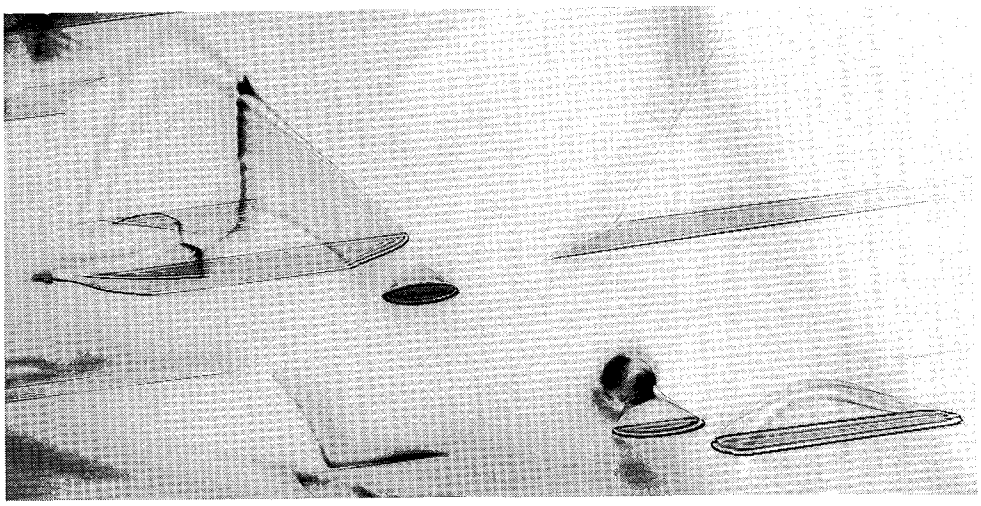


Figure 3 Several "dome" configurations within a ALN 2H grain

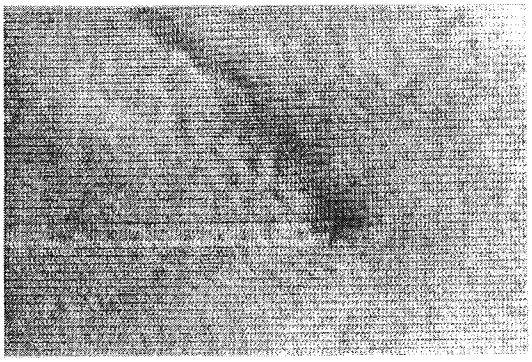


Figure 4 HREM of a part of a simple dome

conventional TEM contrast experiments. There is for the basal plane a displacement of 1/6 [0001] in addition to the traditional stacking fault 1/3 [$1\bar{1}00$] (Fig. 5a). The curved surface is characterized by a 1/2 [0001] shift which is believed to give to the interface a very low energy configuration (Fig. 5b). The shape of the curved surface and its sometimes wavy aspect was a fair indication of a low energy configuration.

It is believed that the presence of oxygen impurities is the key point of the nucleation and growth of the dome configuration. A small number of non-metallic atoms filling the empty tetrahedral sites of the wurtzite structure induces the formation of a faulted dislocation loop. Inside the loop the structure is now energetically unstable and a shrinkage of the basal planes occurs in order to give the structure the opportunity to change its coordination from four to six. The actual difference of shift of the basal planes between this six atom coordinated structure inside the loop and the dislocation core of the same loop induces the nucleation of the dome surmounting the defect. The size of dome will increase by absorbing more oxygen atoms in the dislocation core of the loop. More complicated configurations are the result of the interaction of a growing dome with matrix dislocations or another defect within one grain.

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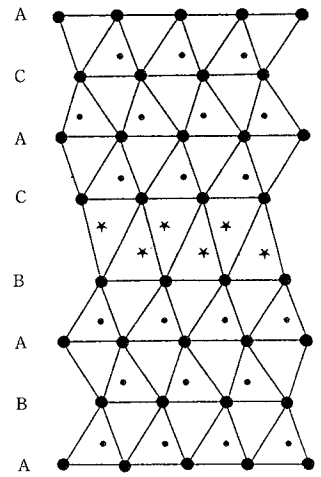
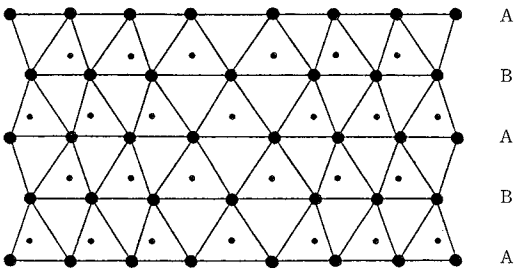


a) Basal part with an excess number of non-metal atoms



b) Curved part showing a low energy configuration

Figure 5 Geometric description of the interfaces defining the dome

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