Microstructural studies of polytype formation in oxygen-containing aluminium nitride

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Oxygen-doped AlN polycrystals were investigated by transmission electron microscope, and different stages of multilayered polytype formation during pressureless sintering were fixed. The decomposition of polytypes was found to take place during quasihydrostatic compression of samples at high temperatures. A model of multilayered polytypes appearing is proposed. The process of polytype formation is represented as isostructural delamination of the AlN–0 solid solution at the expense of oxygen extraction on stacking faults, causing the oxygen-rich interlayer formation.

1. Introduction

Diamond-like crystals show a tendency to form multilayered polytypes (MPs) under various conditions, in particular with heating (with or without external loading) and under the effect of impurities dissolved in a crystal lattice. The most typical representatives of such crystals – SiC and ZnS – possess polytypism under all these conditions [1–4]. In the dense phases of carbon (diamond and lonsdaleite) and boron nitride (wurtzite and sphalerite modifications) MPs can be formed under high pressure and at high temperature [5, 6]. In AlN (wurtzite 2H modification), polytypes are formed only in the presence of dissolved impurities. Also, MPs have been observed in AlN containing oxygen impurities [7, 8]. Now, more than 15 doping substances are known to promote polytype formation in AlN [9]. Such polytypes have also been observed in AlN-based compounds [10]. However, the nature of polytypism in AlN, unlike its structural analogues, has not yet been discussed in the literature.

Polytype formation causes the hardening of AlN polycrystal materials [11]. Thus the study of this process is not only of scientific but also of practical interest.

This paper deals with experimental investigations of real structure formation during sintering in oxygen containing AlN samples. Structural features of MP formation and disintegration are considered, and the probable mechanism of this process is discussed.

2. Experimental procedures

AlN polycrystalline samples were prepared by pressureless sintering at $T = 1600$ to 1900°C in a nitrogen atmosphere. The initial fine-grained powder ($d = 0.1$ to $0.7\,\mu$m) contained 2 wt % of adsorbed oxygen [12, 13].

Structural investigations were carried out by transmission electron microscopy (TEM) on the thin foils prepared by the ion-milling technique.

3. Results

Sintering at $T = 1600^\circ$C led to formation of near equiaxial grains of 1.0 to 1.5 μm. Electron diffraction patterns did not show the presence of oxygen-based phases, suggesting that initially adsorbed oxygen is dissolved in the AlN lattice during sintering.

The increase in sintering temperature up to 1700° C resulted in grain growth up to 3 to 7 μm. At the same time, basal stacking faults (SF) appeared in the planes (0 0 1) of the grains, often crossing the whole grain. Besides the basal SFs, two-dimensional defects were observed having no definite lay-out plane (Fig. 1a–c).

At sintering temperatures of 1800 to 1900° C, grain size increased up to 10 μm, the concentration of the basal SF increased also, and plates of MPs appeared. SFs were not distributed randomly in the bulk of a grain, but were usually united in stacks. These SF stacks nucleate the growth of the MP plates which are restricted by the basal planes (0 0 1) (Fig. 2). At the initial stage of growth, the MP plates are conjugated coherently with the matrix along the basal planes, with the orientation relationship $(0\,0\,1)_{\mathrm{matr}} \parallel (0\,0\,1)_{\mathrm{MP}}$. A net of misfit dislocations is formed on the conjugation boundary with an MP-plate thickness of 1 to 2 μm. Durable isothermic exposure at T = 1800 to 1900° C led to the anomalous growth of grains containing MPs (Fig. 2b). Grain growth takes place along the $\langle h\,k\,0\rangle$ direction of the MP plate, plate thickness not being essentially increased.

The MP-plate substructure is characterized by a high concentration of plane defects and Shockley partial dislocations (Fig. 2a, b). Selected area electron diffraction (SAD) of MP plates showed that they are the 2H–AlN phase in a specific structural state, shown by the shape of the diffraction reflections: these are radial diffused spots rather than point reflections typical of SAD of the grain matrix (Fig. 3a). As MP formation is going on, the diffuse *hol* reflections ($l = 2n$) become weak and then vanish. The *hol* reflections with $2n$ elongated in the a-axis direction and weak diffuse streaks appear between them along the $\langle 1\,0\,1\rangle$ direction (Fig. 3b).

In contrast to the 'classical' polytypism in SiC and ZnS, the $h\,k\,l$ reflections, in series parallel to $\langle 0\,0\,1\rangle^*$

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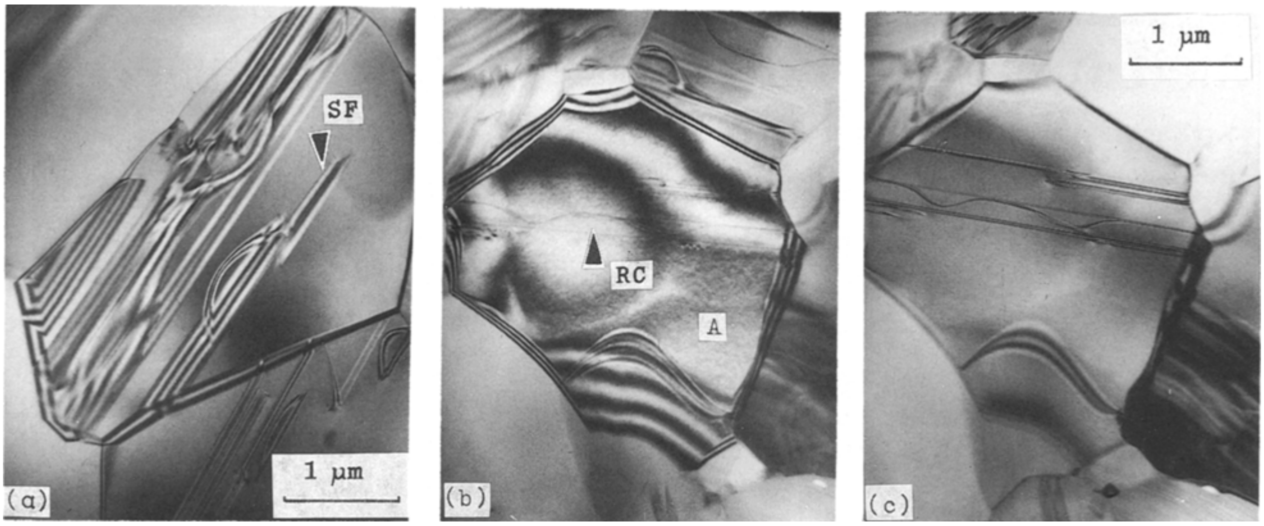

Figure 1 (a–c) Bright-field transmission electron micrographs of defects in AlN polycrystals sintered at 1700° C. Diffractional conditions for A-grain: (b) $g = 0\,0\,2$; (c) $g = 0\,\bar{1}\,2$. Residual contrast on SF is shown by arrows (RC).

on the SAD patterns of AlN containing MP are split. This is associated with the difference in 'a' period values of MPs and the 2H–AlN matrix. In SiC and ZnS, the distance between $1\,0\,l$ and $1\,0\,(l + 2)$ reflections (of the 2H phase) is divided by MP spots into N equal parts (N is the number of layers in a hexagonal polytype lattice cell). In the case of AlN, the distance between 2H-reflections and MP-reflections are incommensurate. This is expressed particularly clearly in the $0\,0\,l$ series. It should be noted here that reflections with $l \neq Nn$ and h–k = 0, 3, 6 . . . are forbidden for classical polytypes and are observed only in the case of double diffraction [14], but in AlN these reflections are always rather intense. The incommensurability of the above-mentioned distances indicates the appreciable difference in the interlayer distance values in 2H and MP phases.

Direct resolution (of polytype period) images (obtained under 2- and 4-beam conditions in reflections of $0\,0\,l$ and $1\,0\,l$ series) suggest that there are two types of MP which differ as to their structure. MP-1 is characterized by strict periodicity of the basal layer packing, while MP-2 demonstrates the irregular modulation of distances between interference maxima. (Fig. 4a, b). MP-1 usually contains hexagonal polytypes 9H, 10H and others, and MP-2 consists of rhombohedral polytypes 27R, 33R and others. Rhombohedral symmetry is revealed by the shift of reflections in $h\,k\,l$-series with h–k $\neq 3n$ with reference to $0\,0\,l$ series.

Some samples sintered at T = 1800 to 1900° C and containing a large number of MP plates were subjected to an additional treatment: the quasihydrostatic compression at P = 8 to 10 GPa and T = 2000° C. MP plate disintegration was found out to take place during such treatment. This process always starts from the boundary between a plate and a neighbouring grain, and the structural elements formed during disintegration are in the plate-like form (Fig. 5). SAD investigation showed two phases are formed as a result of disintegration: hexagonal 2H of AlN, and cubic aluminium oxynitride described in [15].

4. Discussion

The experimental results may be interpreted as follows. Structural transformation in AlN starts from oxygen dissolution initially adsorbed on the particle surface. A substitutional solid solution is known to be formed in this case [16]. The dissolved oxygen causes a decrease in the SF energy in AlN. According to [17]

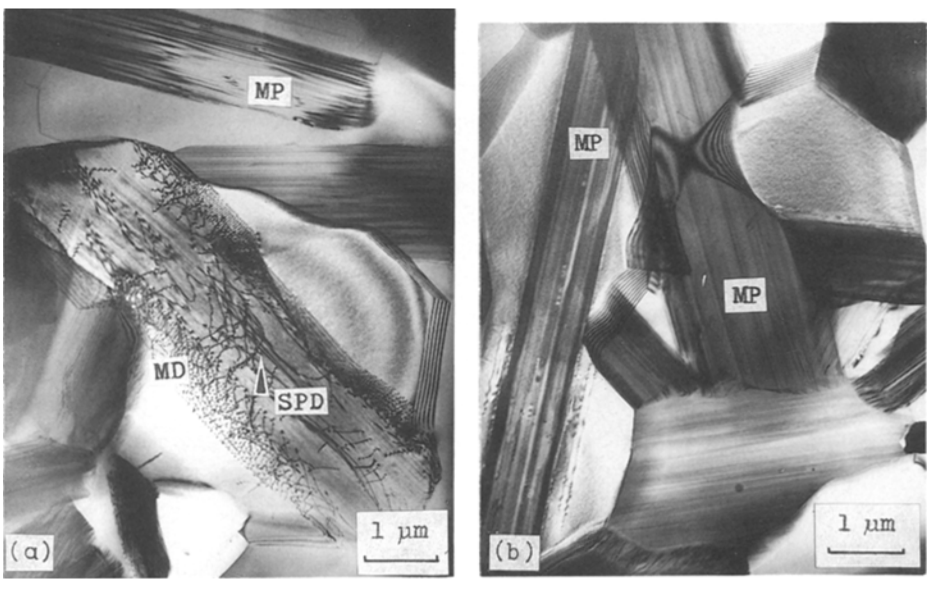

Figure 2 Real structure of AlN polycrystals sintered at (a) 1800° C and (b) 1900° C MP, plates of multilayered polytypes; MD, misfit dislocations; SPD, Shockley partial dislocations.

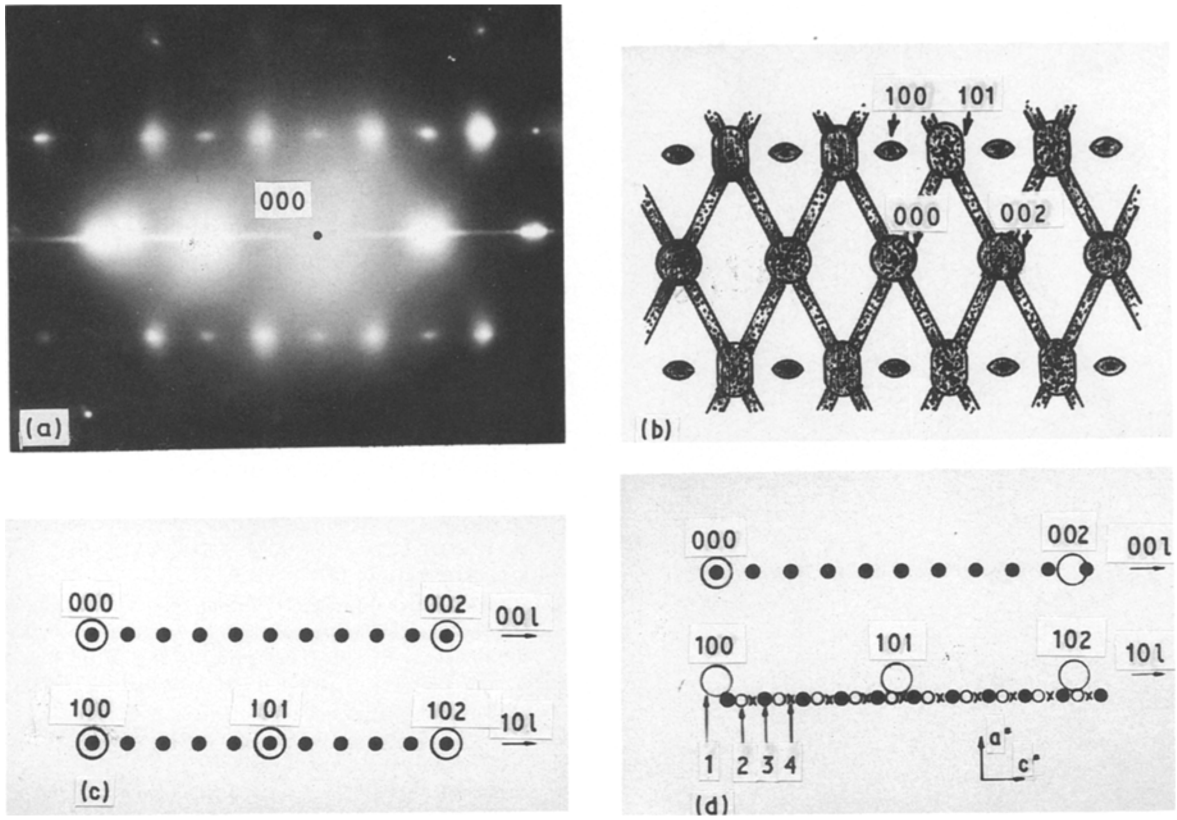

Figure 3 Diffraction effects from MP-plates. (a) Selected-area diffraction pattern from MP plate showing diffuse spots; (b) scheme of diffuse streaks on SAD pattern; (c) scheme of jointed SADs from classical 2H and I0H polytypes; (d) scheme of jointed SADs from 2H phase and MP-2 of AlN. ○ 2H spots; ● MP spots; o twin spots; x extra spots.

the SF energy in AlN is $4\,\mathrm{mJ\,cm^{-2}}$ which corresponds to the dislocation splitting width of less than 100 nm. Data on the impurity presence are not given in this paper. In the AlN samples under study, the dislocation splitting width is considerably greater up to the unlimited splitting when SF expands throughout the bulk of grain. This confirms the suggestion made above that oxygen dissolved in AlN causes a decrease in SF energy. Such a process can be explained by impurity segregation on SFs (Suzuki mechanism) analogous to solid solutions in metallic systems [18]. Indirect evidence of the impurity atmosphere formation on defects may be found in the residual contrast observed on SFs in AlN under contrast disappearance conditions (Fig. 1b).

It is known [18] that this segregation process is accompanied by an increase in the dissolved element concentration, not only in the SF lay-out planes, but also in the nearest parallel ones. This may activate new SF nucleation and promote the mechanism of SFs generating on SFs, that is autocatalytic formation of SF stacks. According to [19], such a mechanism can act under nonequilibrium conditions involving solid solution decomposition. We suggest that this mechanism is responsible for the oxygen-rich plate-like region formed in AlN grains: isostructural delamination of AlN-O solid solution takes place. The oxygen-rich plate formation is confirmed both by SAD pattern geometry from these plates (see Fig. 3a) and their disintegration with the 2H phase and aluminium oxynitride formation (Fig. 5).

The formation of SFs with the impurity atmosphere must result in local changes of lattice parameters, and hence in the elastic distortions in the 2H phase. Such

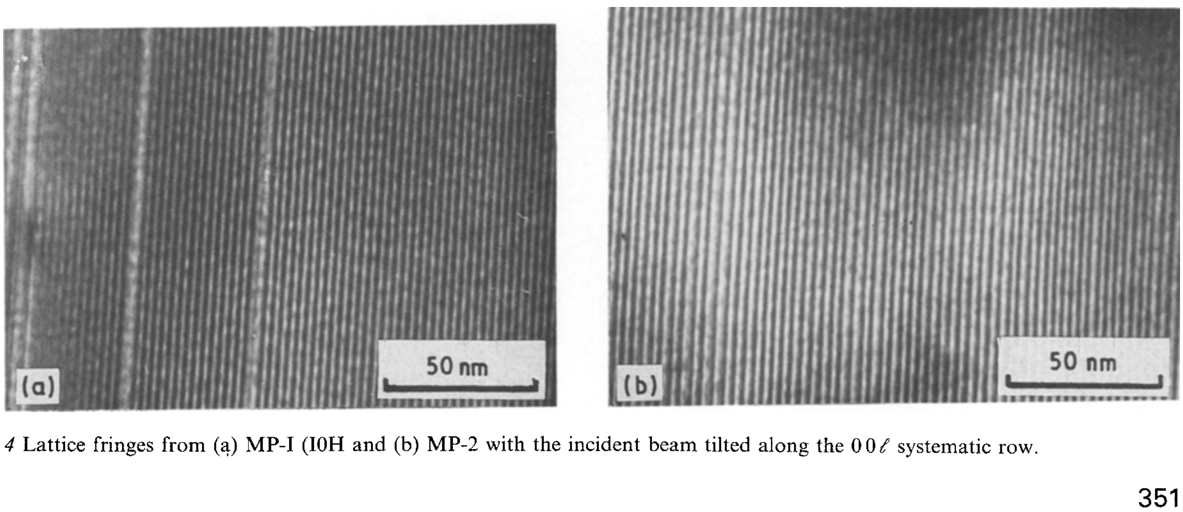

Figure 4 Lattice fringes from (a) MP-I (I0H and (b) MP-2 with the incident beam tilted along the 00ℓ systematic row.

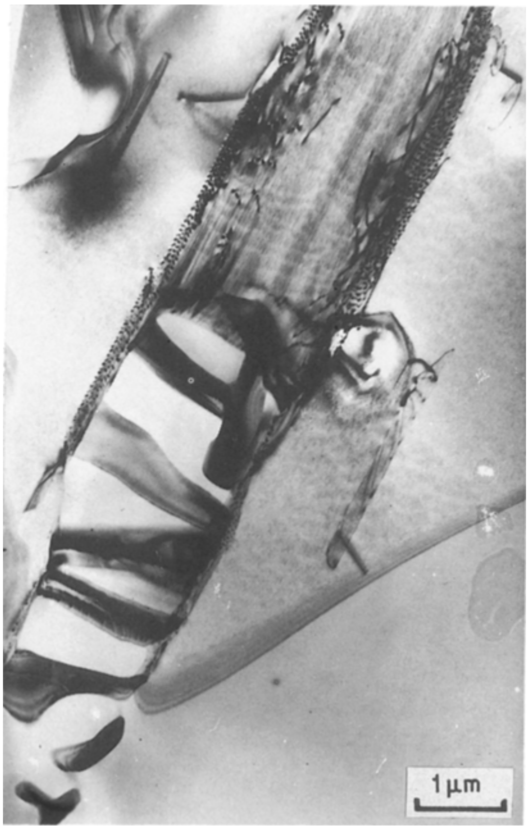

Figure 5 The disintegration of MP in AlN.

distortions are shown by diffuse scattering effects on SAD patterns from MP plates. The observed shape of diffuse scattering may be connected with the short-range order structure formed in AlN-O solid solution, according to the concept developed for metals [20]. The subsequent changes of diffuse scattering shape is evidence for the rearrangement of the short-range order, which may be considered as a transient state before MP formation. The latter is shown by the appearance of superlattice reflections on the diffuse scattering background.

The probable mechanism of this transient structure relaxation may be basal SF formation. This SF ordering leads to a change in the stacking sequences of basal planes and to wurtzite-based MP formation. The AlN-O solid solution delamination with SF participation is connected with the appearance of the concentration inhomogeneity in the oxygen-rich region due to kinetic factors. This may explain the co-existence of the polytypes with a different number of layers in microvolumes and irregular modulating in MP-2.

5. Conclusions

The experimental data and their analysis make it possible to represent MP formation in oxygen-containing AlN as the following steps of elemental structural rearrangements.

1. Formation of substitutional solid solution of adsorbed oxygen in AlN lattice.
2. Formation of the basal SFs and impurity condensation on SFs resulting in a sharp decrease of their energy.
3. Autocatalytic formation of SF stacks.
4. Isostructural delamination of AlN–O solid solution and oxygen-rich plate formation.
5. Short-range ordering in oxygen-rich plate and its rearrangement.
6. Polytype formation.

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