Core-Shell structure of nanocrystalline AlN in real and reciprocal spaces

E. Grzanka[1,*], S. Stelmakh[1], B. Palosz[1], S. Gierlotka[1], Th. Proffen[2], M. Drygas[3], J. F. Janik[3]

[1] Institute of High Pressure Physics, Polish Academy of Sciences, Warsaw, Poland
[2] Los Alamos National Laboratory, LANSCE, Lujan Center, Los Alamos, NM, USA
[3] AGH University of Science and Technology, Faculty of Fuels and Energy, Krakow, Poland
[*] Contact author; e-mail: elesk@unipress.waw.pl

Abstract. Investigation of the atomic structure of nanocrystalline AlN approximated by a core-shell model was performed based on neutron diffraction data obtained at NPDF/LANL diffractometer and collected up to about Q=40 Å^{-1}. The measurements were done at room temperature and at 823^{0}C. Both PDF function (real space) and *apparent lattice parameters, alp,* based on analysis of Bragg scattering (reciprocal space) were examined. PDF analysis shows that all inter-atomic distances *r* for nanocrystalline powder are smaller than those measured for microcrystalline material, what conforms with *alp*-Q analysis. The *alp*-s calculated for *c* and *a* lattice parameters change differently with Q and, therefore, also *(c/a)* ratio is Q-dependent. This is interpreted as that there is an anisotropic strain in the surface shell. At elevated temperatures, due to difference in thermal expansion between surface shell and grain core there is an increasing strain in the surface shell.

1. Introduction

Aluminum Nitride is of a paramount importance in ceramics and electronics (as an insulator with advantageous heat conductivity) and is known to be sintered with an addition of sintering additives which are causing property deterioration [1]. Other studies have indicated that under extreme temperatures (in the 1700-1900°C range) certain AlN nanopowders can be sintered without additives [2]. Using anaerobic synthesis method (conversion of aluminum amide-imide by nitridation) low oxygen content powders of hexagonal AlN with crystallite sizes ranging from several to several tens of nanometers were prepared [3]. The ultimate goal of our studies is to investigate the process of sintering of pure AlN nanopowders without additives. The purpose of present paper is application of a core-shell model to structural analysis of AlN samples and determination of their thermal expansion coefficients, discerning between the core and shell components. Data analysis in terms of core-shell models allows to derive information about interatomic distances of the interior and surface of nanograins [4]. A difference between bond length in the grain core and that in a relaxed lattice of a single crystal may be interpreted as a result of a presence of internal pressure (hydrostatic type pressure) which corresponds to either compression or expansion of the lattice.

2. Data analysis

2.1 Reciprocal space analysis

Microcrystalline and 9 nm powders of hexagonal AlN were measured at room temperature and at 823°C at NPDF at the Lujan Center at Los Alamos Neutron Science Center. Analysis of Bragg scattering showed that nanocrystalline AlN grains have a core-shell structure with interatomic distances smaller at the shell than those in the grain core; there is compressive strain in the shell [5,6]. We found that relative changes of *apparent lattice parameter*, *alp*, along *c* axis are about two times larger than those of in-plane *a* lattice parameter, figure 1. Although an overall character ("shape") of *alp*-Q is same for *a* and *c* parameters, there is much more pronounced increase of *c* parameter (*alp*) measured at small Qs. Since this effect is related to small size [5], we deduce that dimension of crystalline domains of AlN in the direction normal to the layer plane (c-axis) is smaller than their in-plane dimensions, in *a*-direction. This effect might be connected with presence of stacking faults and coexistence of hexagonal with cubic structure domains in one grain (see below). We have found that for nanocrystalline samples *(c/a)* ratio shows a dependence on the Q-vector, c.f. figure 2, similar to that of *alp* values, figure 1. The measured dependence of *(c/a)* on diffraction vector Q is a consequence of different changes of *alp*-Q dependencies for *a* and *c* parameters. Although variation of *(c/a)* with Q obviously reflects the presence of strain in the surface shell, we do not apply a specific meaning to the calculated values.
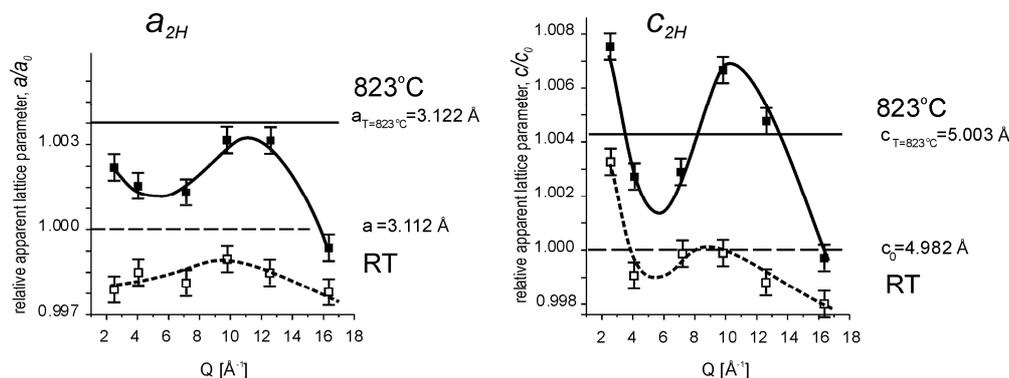
Figure 1. Changes of relative values of alp's measured experimentally for 9 nm AlN powder for a and c parameters of the hexagonal (2H) unit cell. Solid and broken horizontal lines indicate respective values measured for the microcrystalline sample; a_0 and c_0 taken for calculation of relative alp's are those measured for microcrystalline sample.

With an increase of temperature all *alp* values calculated for *c* and *a* increase, but at the same time the difference between the smallest and largest *alp* values becomes larger, figure 1. This is an indication of increasing surface strain what results from an increase of difference between lengths of corresponding inter-atomic distances in the core and in the shell. The reason for that behavior is that amplitudes of thermal vibrations and thermal expansion coefficients of the surface shell and the grain core increase with temperature, but this increase is stronger in the surface shell [7]. With increasing temperature the *(c/a)* ratio, which is equal

to 1.610 for 2H, increases slightly which may be interpreted as the symmetry evolution from hexagonal (trigonal in presence of stacking faults) towards cubic with *(c/a)* $\cong$ 1.633 for 3C, c.f. figure 2.
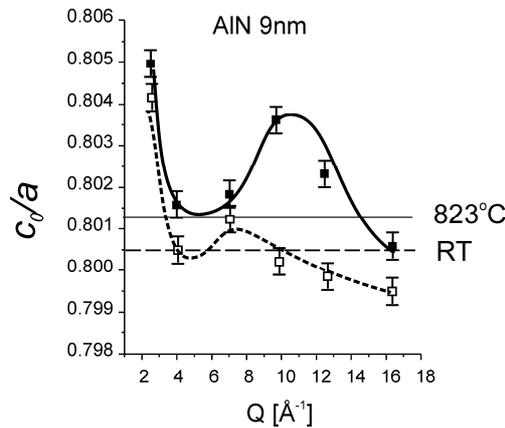
Figure 2. The c/a ratio vs the Q-vector measured experimentally for 9 nm AlN powder at room temperature and at 823°C. Solid and broken horizontal lines indicate respective values measured for the microcrystalline sample.

A direct consequence of the specific (core and shell) structure of nanograins is that thermal expansion coefficient becomes Q dependent, figure 3. (Note that *a* and *c* taken for calculation of thermal expansion are the *alp* values measured for given Q values at RT and at 823°C, figure 1.). The thermal expansion coefficients, α_T, plotted in figure 3 for different Q's have no specific meaning because they result from combination of different expansions of core and shell and from different dependence of *alp* values on Q at different temperatures. One has to notice that an overall thermal expansion of nanocrystalline AlN (average over large Q interval) is approximately that of crystalline material.
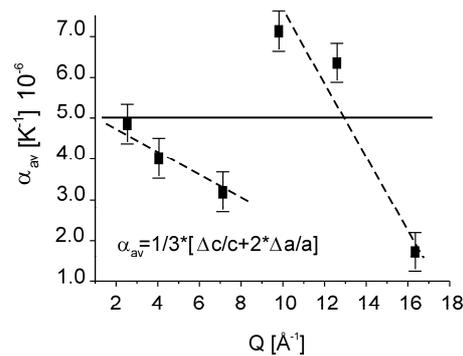
Figure 3. Average values of thermal expansion coefficient α determined experimentally for different Q values for 9nm AlN.

2.2 Real space analysis

On diffraction patterns of both micro- and nanocrystalline AlN there are all Bragg reflections of 2H modification. However, on PDF of nanocrystalline sample there is a clear indication of presence of cubic-type stacking in nanocrystalline AlN. In figure 4 there are plotted two peaks at experimental PDF corresponding to r_5 and r_6 interatomic distances of hexagonal 2H structure.
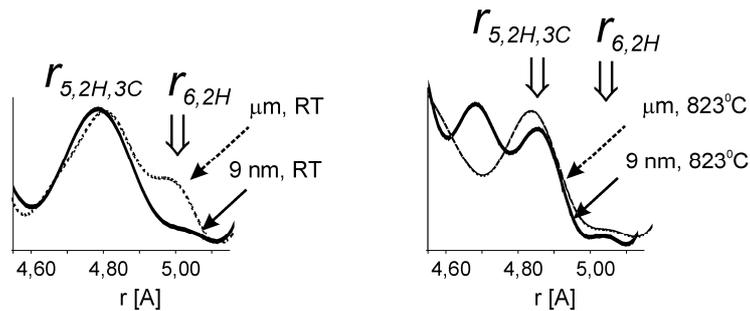
Figure 4. Peaks of r_5 and r_6 interatomic distances on experimental PDF of micro- and 9 nmn nano-crystalline AlN measured at room temperature and at 823°C.

Figure 4 shows that on PDF of 9 nm sample there is a very weak peak r_6 ; this distance occurs in 2H structure but it is absent on PDF of cubic structure 3C. This is indication of presence of cubic-type domains in 9nm AlN. At 823°C, r_5 distance remains unchanged for microcrystalline, but it splits in two distances for nanocrystalline sample. The r_6 distance disappears for microcrystalline sample, what is not a result of transformation of 2H into 3C, but due to a positional disorder induced at high temperature; r_6 distance appears back at PDF after cooling down the sample from 823°C to room temperature.

PDF analysis of the AlN powders measured at room temperature shows that all inter-atomic distances r for nanocrystalline powders are somewhat smaller than those for microcrystalline samples, e.g. r_1, figure 5 and r_5, figure 4. This conforms with our *alp* studies, where individual *alp* values calculated for all Q's are smaller than those measured for the microcrystalline material.
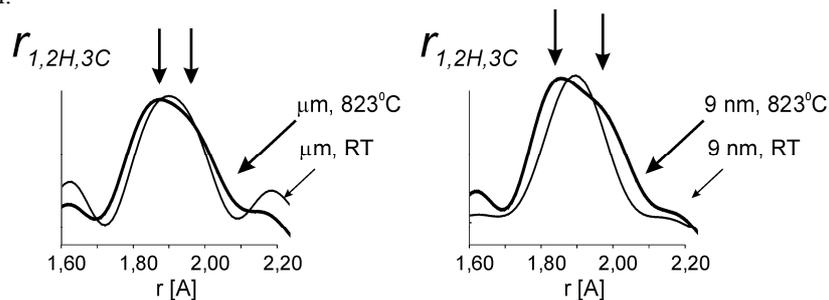
Figure 5. Peaks of r_1 on experimental PDF of micro- and 9 nm nanocrystalline AlN measured at RT and at 823°C.

Width of r_1 peak of nanocrystalline sample is smaller than that measured for microcrystalline material, figure 5, which may be an indication that there is some deviation from ideal 2H

structure in microcrystalline sample. In a close packed cubic structure, 3C, the ratio of inter-planar spacing c_0 to the shortest interatomic in-plane distance a, (c_0/a), is strictly defined and equals 0.8165. Two sublattices (here: Al and N) are identical and in cubic structure they are shifted in c-direction relative to each by a distance $u = 0.75c_0$. In this case the inner atom in a tetrahedron (AlN$_4$ or NAl$_4$) is located in its center and all shortest Al-N bonds r_1 within indi-vidual tetrahedrons are equal. In hexagonal 2H structure of AlN, for which $(c_0/a) = 0.8005$ all interatomic distances r_1 are equal when the relative shift of Al and N sublattices u is 0.76c_0. Appearance of broadening of r_1 distance of microcrystalline sample on PDF plot, what is seen in figure 5, means that there is either a deviation of (c_0/a) from 0.8005 while u remains 0.76, or (c_0/a) remains unchanged but u deviates from 0.76. One also has to consid-er that "uncorrelated" changes of both (c_0/a) and u appear at the same time. In nanocrystal-line material which is predominantly cubic all r_1 distances are same. We need to stress that this happens, although individual grains exhibit a complex core-shell structure.*(Note: the above analysis is valid only with reference to real space, PDF. A change in u is not reflected by positions of Bragg reflections, since it has no effect on the dimensions of the unit cell [8]).*
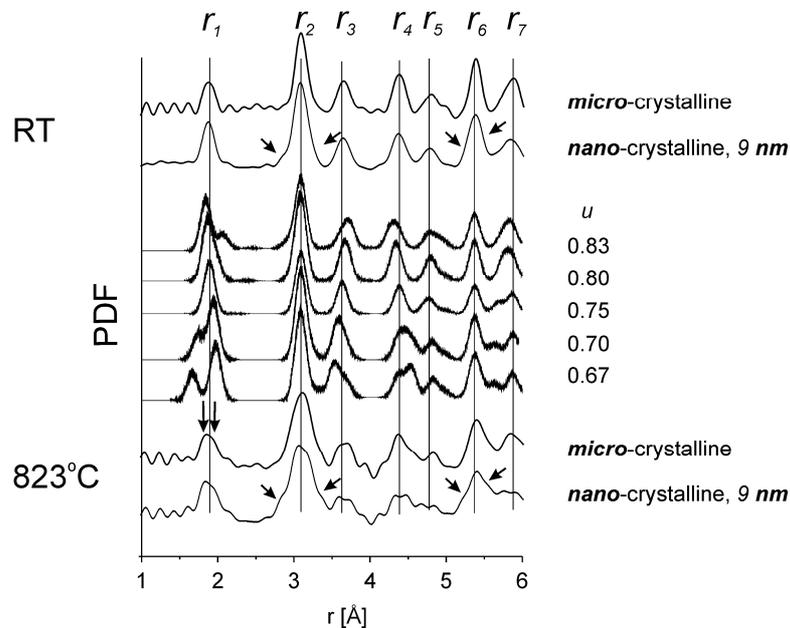
Figure 6. PDF plots of micro- and 9 nm AlN powders determined experimentally at RT and 823°C, compared to theoretical PDFs calculated for 2H AlN lattice with (c₀/a) = 0.8005 and different u values [6].

The AlN samples measured at 823°C clearly show split of many individual interatomic dis-tances about the respective average r-values for both micro- and nanocrystalline samples; figure 5 shows split of r_1 distances for micro- and nanocrystalline samples, split of some other PDF peaks is marked by arrows in figures 6. One has to notice that it is much stronger for nano- than for micro-crystalline powder, figure 5. We suppose that this is due to differ-ent thermal expansion of core and shell structures.

Figure 6 also presents theoretical PDF plots calculated for models of 2H structure with (c_0/a)=0.8005 and different u parameters. These plots are compared with those measured experimentally at room temperature and 823°C. Figure 6 shows that if the reason for split would be a change of u then, ratio of intensities of the two components of r_1 should be about 1:3. For microcrystalline sample asymmetric broadening of r_1 might be explained by aniso-tropic expansion in a and c-directions what results in an increase of (c_0/a) above 0.8005, c.f. figure 2, and u value remaining about 0.76. In nanocrystalline sample there is a strong split of r_1 peak into two values of similar intensities. We interpret this as that the split is mostly due to different thermal expansion of grain cores and shells. This conforms with strong split of other r-distances on PDF of nanocrystalline AlN, c.f. split of r_5, figure 4.

3. Summary

In this work we presented preliminary results of structural analysis of nanocrystalline AlN with use of real and reciprocal space approaches. Further elaboration of the core-shell model with use of *alp* concept and through examination of distribution of inter-atomic distances on PDF plots is currently under way. It requires analysis of various models accounting for dif-ferent combinations of u values and *(c/a)* ratios in the core and shell, and also anisotropy of relaxation of the surface shell in a and c-directions. We expect that the model will serve for determination of thermal expansion coefficients separately for the core and shell of AlN nanograins.

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